

The Importance of Reaction Mechanisms in Interpreting the Arsenic Reactive Transport of FeS-coated Sand Column

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ABSTRACT

FeS, as a natural reduced iron mineral, has been recognized to be a viable reactive material for As(III) sequestration in natural and engineered systems. In this study, FeS-coated sand packed columns were tested to evaluate the As(III) removal capacities under anaerobic conditions at pH 5, 7 and 9. The column obtained As(III) removal capacity was then compared with the capacity result obtained from batch reactors. In the comparison, two different approaches were used. The first approach was used the total As(III) removal capacity which method was proved to be useful for interpreting pH 5 system. The second approach was used to consider sorption non-linearity and proved to be useful for interpreting the pH 9. The results demonstrated that a mechanistic understanding of the different removal processes at different pH conditions is important to interpret the column experimental results. At pH 5, where the precipitation of arsenic sulfide plays the major role in the removal of arsenic, the column shows a greater removal efficiency than the batch system due to the continuous dissolution of sulfide and precipitation of arsenic sulfide. At pH 9, where adsorption mainly governs the arsenic removal, the sorption nonlinearity should be considered in the estimation of the column capacity. This study highlighted the importance of understanding reaction mechanism to predict column performance using batch-obtained experimental results.

Key words : FeS-coated sand, reactive transport, precipitation/adsorption mechanism, column and batch comparison

1. Introduction

Reactive transport in a column is more complex than a reaction in a batch reactor because it is controlled by multiple reaction phenomena, for example the interaction between physical transport such as advective and/or diffusive flow and immobilization reactions such as adsorption and/or precipitation (Gabriel *et al.*, 1998). The removal of contaminants may be controlled by the flow rate if the reaction does not reach equilibrium quickly. Furthermore, batch systems have much lower solid/solution ratios (SSR). Batch experiments can provide useful information about the removal of contaminants by sorbents such as adsorption isotherm, kinetic adsorption characteristics, etc. However, in many cases batch experimental results do not represent the reactive transport behavior in column because batch experimental conditions are fundamentally different from those in column systems (Maraqa, 2000).

The prediction of column performance using an analogous batch system generally works well if the system under consideration is physically and chemically simple: linear sorption with fast kinetics and without any co-existing ligand or competing elements. However, the FeS-coated sand and As(III) system showed highly non-linear sorption characteristics and As(III) removal involves multiple mechanisms - adsorption of As(III) on FeS-coated sand, precipitation of arsenic sulfide, the existence of oxidized phases, and transformation of FeS to more oxidized phases (Han *et al.*, 2011a). Therefore, differences between batch and column removal efficiencies are expected. Moreover, the As(III) uptake is highly pH-dependent with a precipitation-dominant reaction at pH 5 and the adsorption-dominant reaction at pH 9. This difference may result in different behavior in each reactor system (Han *et al.*, 2011b). Therefore, the more research on interpreting how to utilize batch obtained result to predict column or field system in a complex system is

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necessary. In this study, column experiments were performed at various values of pH using FeS-coated sand and the obtained column capacities for arsenic removal was compared to the arsenic removal capacity obtained in batch reactors. As well, the reasons of discrepancies in the results from two different reactors were profound. The result of this study may suggest a method how to analyze column-obtained results when different reaction processes govern a system.

2 Methods

2.1. Column experiments

The methods of synthesizing FeS and FeS-coated sand can be found in elsewhere (Han et al., 2001a). FeS-coated sand was packed in a glass column (internal diameter = 4.8 cm; length = 15 cm or 4.8 cm) by successively depositing approximately 1.5 cm layers and compacting evenly with a ceramic pestle. The columns were set up vertically in an anaerobic chamber. The experimental conditions and physical parameters of column experiments are presented in Table 1. Acid extraction of the FeS-coated sand used in the column tests yielded 1.42×10^{-5} mol FeS/g sand, the same as the amount obtained in the batch experiments. Thus, the total amount of FeS contained in a column was calculated to be 6.75 mmol (539 mg) FeS for a 15-cm column packed with approximately 475 g sand. An influent concentration of 1 mg/L As(III) was prepared with deionized and de-aerated Milli-Q water to simulate groundwater under reducing conditions and buffered at pH 5, 7 and 9. The system was buffered using 0.1 M acetate buffer at pH 5, 0.1 M MOPs for pH 7 and 0.1 M CHEs for pH 9. The columns were con-

ditioned with buffer solution in the absence of As(III) first until the iron concentration of the effluent stabilized. At that point, an aqueous solution containing 1 mg/L As(III) was injected at the same pore water velocity of the conditioning fluid. The solutions were pumped in an up-flow mode through the column at a constant flow rate with an HPLC pump (Varian Dynamax SD-200, Walnut Creek, CA). Then, effluent from the column was collected with an automated fraction collector (ISCO ISIS autosampler, Lincoln, NB), with about 1/10 of pore volume collected in each sampling tube. The injection of As(III) was terminated when the effluent As(III) concentration reached a plateau. Upon reaching the plateau, an As(III)-free buffer solution was pumped into the column until the effluent As(III) concentration approached 0 mg/L. The collected effluent samples were taken out of the anaerobic chamber after acidification with nitric acid and then analyzed for their As(III) and Fe(II) concentration as total concentrations of As and Fe using an ICP-MS. A bromide tracer was injected along with As(III) and the bromide concentration was measured for the first 2-3 pore volumes of effluent using an ion chromatograph (Dionex IonPac AS4A column, Perkin-Elmer 200 series LC pump, Perkin-Elmer 200 series autosampler). All column work presented in this study was performed in an anaerobic glove box with 5% H₂/95% N₂ atmosphere maintained near zero oxygen environment using palladium catalyst.

The physical parameters of column porous media such as pore water velocity and dispersion coefficient were inversely obtained using the CXTFIT program (Toride *et al.*, 1995) using a form of the advection-dispersion equation assuming that bromide acts conservatively. The dispersivity (α) was then calculated using a relationship of $D = v \alpha$. A

Table 1. Column experimental conditions

	pH	Column Length	Pore water velocity*	Dispersivity*	Porosity	Retention time	Bulk density
Col #	–	cm	cm/hr	cm	–	hr	g/cm ³
1	pH 5	15	4.42	0.09	0.35	3.37	1.70
2	pH 7	15	4.55	0.06	0.34	3.27	1.73
3	pH 9	15	4.55	0.08	0.34	3.31	1.72
4	pH 5	4.8	4.11	0.08	0.35	1.16	1.67
5	pH 9	4.8	4.55	0.08	0.35	1.16	1.67
6	pH 9	4.8	1.39	0.14	0.35	3.44	1.67

*Values were obtained using CXTFIT fitting results of bromide breakthrough curves.

retention time (R_T) of a column was calculated using the measured length of column (L) and applied flow rate (Q) using the relationship of $R_T = L \cdot A/Q$, where, A is a cross-sectional area of the column.

2.2. Comparison of batch and column derived solute removal capacities

2.2.1. Using total uptake capacity

In batch systems, the uptake capacity is generally obtained from isotherm data, especially when the data can be modeled with the Langmuir isotherm, which is characterized by a leveling-off and maximum uptake value with increasing solute concentration. In column experiments, uptake capacities can be calculated from the data in a variety of ways. For example, the capacity (or total amount retained) can be calculated by integrating the areas above the observed BTCs during adsorption phase (Barnett *et al.*, 2000). Sometimes the column breakthrough point is used to determine a contaminant removal capacity of a column. The breakthrough point can be selected as the point where the detectable concentration begin, the point at which C/C_0 achieves a specific number, such as $C/C_0 = 0.1$ (Wibulswas, 2004), or the point where the effluent concentration exceeds the maximum contaminant level. In this study, the break through point was determined as $C/C_0 = 0.01$ (10 ppb), which is the maximum contaminant level of arsenic in a drinking water.

2.2.2. Using the distribution coefficient

The column and batch results of an adsorbent are often compared using a distribution coefficient (K_d). In batch reactor, K_d is defined as the ratio of adsorbate concentrations between aqueous phase and solid phase and in column reactor, K_d is defined as an important component of a retardation factor ($R = 1 + \frac{\rho K_d}{\theta}$). Here, R is the retardation factor (unitless), ρ and θ are the bulk density (g/cm^3) and porosity (unitless), respectively, of a porous medium.

Finding R in a batch results

The Langmuir isotherm, which is derived by assuming a limited number of equivalent sorption sites, is described by the equation (Appelo and Postma, 2005):

$$q_e = \frac{q_m C_{eq}}{K_l + C_{eq}} \quad (1)$$

where C_{eq} ($\mu\text{g}/\text{g}$) is the equilibrium concentration of solute in solid, K_l ($\mu\text{g}/\text{L}$) is the Langmuir constant related to the binding energy of the sorption system and q_m ($\mu\text{g}/\text{g}$ solid) is the adsorption capacity. In the Langmuir isotherm model, if the solute concentration is small, if $C_{eq} \ll K_l$, the sorbed concentration increases linearly, but if the solute concentration is large, if $C_{eq} \gg K_l$, the surface becomes saturated and the adsorption levels off to q_m .

When the equilibrium concentration of a solute is low enough, the curve is essentially linear and the distribution coefficient, K_d can be estimated simply as

$$K_d = q/C_{eq} = q_m/K_l \quad (2)$$

When the surface approaches saturation, the distribution coefficient becomes a function of equilibrium solute concentration, C_{eq} , and can be expressed by the following equation (Gabriel *et al.* 1998):

$$K_d = \frac{q_m K_l}{(1 + K_l C_{eq})^2} \quad (3)$$

Using the fitted Langmuir isotherm, the determined q_m and K_l predicts K_d for the varying equilibrium concentrations of As(III) in solution. Therefore, in Langmuir type sorption, a retardation factor $R = 1 + \frac{\rho}{\theta} K_d$ can be expressed using equation (3) as following,

$$R = 1 + \frac{\rho}{\theta} \frac{q_m K_l}{(1 + K_l C_{eq})^2} \quad (4)$$

Finding R in a column results

The transport of solute in a porous media is generally characterized by the system response to an injected solute which is typically presented by breakthrough curve (BTC). The most commonly used techniques of BTC analysis are based on moment analysis or advective-dispersion-reactive transport model analysis. MOM can provide robust and comparable parameters independent of the physical chemical characteristic of the system. One of the main drawbacks of MOM, is that MOM implicitly assumes reversible sorption, and that 100% mass recovery will be obtained. In column experiments where long tailing results and incomplete mass desorption occurs over the time frame of the measurements, inaccuracies in the model parameters can result.

Even so, MOM has been shown to be useful in cases of irreversible sorption, with the analysis showing good agreement with retardation values estimated using analytical solutions (Limousin *et al.*, 2007).

The MOM can be described by the following equations, where the solute breakthrough curve (BTC) may be viewed as a probability distribution function. The n th absolute moments and normalized absolute moments for a pulse input may be defined as

$$\mu_n = \int_0^{\infty} t^n C(L, t) dt \quad (5)$$

$$\mu_n^* = \frac{\mu_n}{\mu_0} \quad (6)$$

where $C(L, t)$ is the flux-averaged concentration at the exit boundary ($x = L$) at time t . The zeroth moment of a BTC is a measure of the solute mass recovered from the system; the first moment is a measure of the travel time and the second moment is a measure of the mixing and/or the travel time distribution of the system. For a pulse input of solute of duration t_0 , the analytical expressions for the moments of the BTC is (Leij and Dane, 1991)

$$\mu_1^* = \frac{\mu_1}{\mu_0} = \frac{RL}{v} + \frac{t_0^2}{2} \quad (7)$$

Here, R can be back-calculated using the used experimental conditions L , v and t_0 .

3. Results and discussion

3.1. As(III) transport in FeS-coated sand

Fig. 1-Fig. 3 show the breakthrough curves of FeS-coated sand columns with a retention time of about 3.3 h at pH 5, 7, and 9 (Columns #1-#3, Table 2). The column that shows the highest As(III) removal is the one at pH = 5, with an observed breakthrough point occurring at 213 pore volumes. The As(III) removal occurring up to the breakthrough point was 100%, so that the effluent concentration was below detection up to this point. After breakthrough, the As(III) effluent concentration increased gradually until it reached 0.2 mg/L (i.e., 20% of the initial injected As(III)) and showed a more gradual increase up to 0.4 mg/L over the next 85 pore

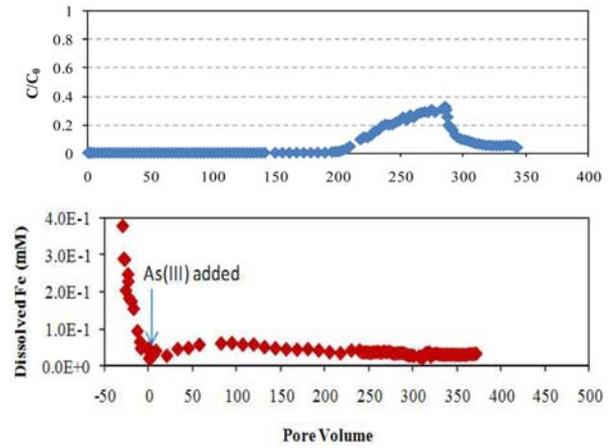


Fig. 1. Column breakthrough curve at pH 5 (top) of FeS-coated sand column (Col #1) and concentration of dissolved Fe measured in effluent (bottom). (Influent: 0.1 M buffered solution with 0.013 mM (1 mg/L) As(III) and 10 mM bromide with an average pore water velocity of 4.42 cm/hr).

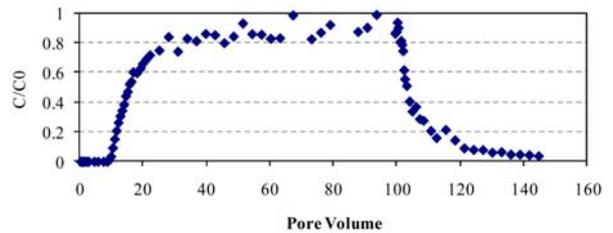


Fig. 2. Column breakthrough curve at pH 7 of FeS-coated sand column (Col #2). (Influent: 0.1 M buffered solution with 0.013 mM (1 mg/L) As(III) and 10 mM bromide with an average pore water velocity of 4.55 cm/hr).

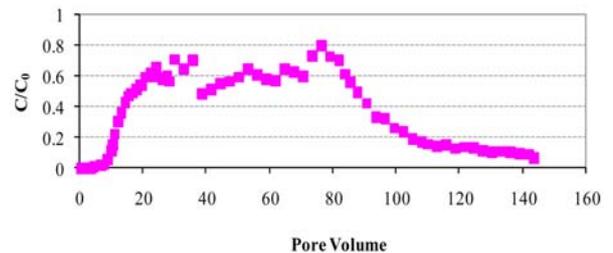


Fig. 3. Column breakthrough curve at pH 9 of FeS-coated sand column (Col #3). (Influent: 0.1 M buffered solution with 0.013 mM (1 mg/L) As(III) and 10 mM bromide with an average pore water velocity of 4.55 cm/hr).

volumes. This continuous high removal of As(III) at a pH 5 solution is hypothesized to be due to the continuous dissolution of FeS, providing sulfide ions for the formation of the arsenic sulfide (As_2S_3). The dissolved Fe concentration, measured as an indicator of dissolved sulfide, showed that the

Table 2. Comparison of As(III) removal capacity between column and batch reactor results

Index	Calculated result of As(III) removal (unit: $\mu\text{g As(III)/g FeS-coated sand}$)				Estimated parameters using Langmuir isotherm model				Using MOM
	a	b	c	d	e	f	g	h	i
	*BT capacity (BT point, % batch result)	Total removed (Injected PV)	Maximum capacity (% batch)	Percent desorption	q_m (g As/g sand)	K_l (L/g As)	R^2	R_B at $C_{eq}=1 \text{ mg/L}$	R_C with MOM $C_{eq}=1 \text{ mg/L}$ (\pm error)
Col #1 (pH 5)	43.3 (215 PV, 82.2 %)	56.6 (298 PV)	55.6 (105.6%)	1.8	5.20×10^{-5}	1388.15	0.99	61.3	> 300 (> +389%)
Col #4 (pH 5)	12.1 (60 PV, 23.2%)	17.4 (422PV)	14.3 (27.5%)	17.9					52.2 (-15%)
Col #2 (pH 7)	1.9 (10 PV, 13.9 %)	5.6 (100 PV)	3.8 (27.7 %)	34.6	1.34×10^{-5}	781.74	0.95	16.7	14.1 (-16%)
Col #3 (pH 9)	1.3 (6.4 PV, 8.9 %)	7.4 (80PV)	2.8 (20.1%)	61.3					24.9 (+26%)
Col #5 (pH 9)	1.7 (7.4 PV, 10.5 %)	4.8 (62PV)	2.7 (16.8%)	56.7	1.58×10^{-5}	1076.13	0.96	19.7	13.8 (-30%)
Col #6 (pH 9)	4.7 (18.5 PV, 29.5%)	15.1 (83 PV)	11.9 (75.4 %)	21.1					23.6 (+20%)

- BT capacity = As(III) removal capacity of packed column until the effluent As(III) concentration meets the regulated As(III) concentration for drinking water (10 ppb)

- % batch result = mass of As(III) removed in column as percent of that removed in batch.

- PV = pore volume.

- Total removed (b) = total adsorption – total desorption.

- Maximum capacity (c) = mass removed in batch system at the given pH.

- Percent desorption (d) = mass of total As(III) removed that elutes upon injection with As(III)-free solution expressed as percent of total mass removed.

- R_B (h) = retardation factor defined by batch experiments (Eqn (4)).

- R_C (i) = retardation factor obtained from column experiments (Eqns (5)-(7)).

- q_m and K_l were defined in Eqn (2-8).

concentration of continuously dissolved sulfide is 0.03 mM, considerably greater than the injected concentration of 0.013 mM of As(III). This measured dissolved sulfide concentration stoichiometrically exceeds the needed sulfide concentration, but thermodynamic calculations performed by Li (2009) concluded that this amount is not enough to precipitate orpiment. Therefore, to identify whether the As(III) removal process is caused by precipitation or adsorption, further spectroscopic research using samples collected after column work should be conducted.

The long column experiment performed at pH 7 (Col #2) (Fig. 2) resulted in the complete removal of As(III) over 10 pore volumes (effluent concentration was < 0.01 mg/L). In the pH 9 long column (Col #3) (Fig. 3), the effluent concentration of As(III) was below the detection level of 1 $\mu\text{g/L}$ until 2 pore volumes. Over the subsequent 4 pore volumes, more than 98% of initially injected As(III) (under

0.02 mg/L As(III)) was removed until the breakthrough point which occurred at 6.4 pore volumes. At pH 5, a considerable amount of Fe dissolved and was eluted from the column due to the high solubility of FeS at this low pH. However, the dissolved Fe concentration became stable as it was observed during the column tests. This was confirmed by the measured amount of FeS left in each column (Col #1, 2, and 3) after finishing the column experiments. The results of acid extraction (Fig. 4) showed that FeS-coated sand still contained 90-100% of FeS on its surface after running 100 and 80 pore volumes through pH 7 and 9 columns, respectively. In contrast, at pH 5, around 60% of FeS was dissolved and eluted from the column during the injection of ~300 pore volumes in Col #1. However, this loss of FeS results in sufficient sulfide concentration to remove arsenic through arsenic sulfide precipitation, if the mole quantify of sulfide can be assumed to be equivalent to the

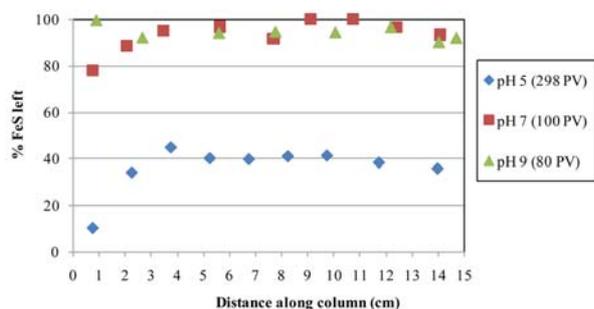


Fig. 4. Results of acid-extraction of FeS-coated sand from Col #1 (pH 5), Col #2 (pH 7), and Col #3 (pH 9).

measured Fe concentration. Based on a mass balance calculation and using the equilibrium concentration of the dissolved Fe at pH 5 (3.5×10^{-5} M Fe), the pH 5 long column can provide another 1700 more pore volumes of a similar concentration of sulfide ion assuming stoichiometric dissolution of FeS.

3.2. Comparison of column and batch results using capacity calculations

Table 2 summarizes the total immobilized As(III) per unit mass of FeS-coated sand in the batch reactor experiments based on the sorption isotherm analysis (column e, in Table 2), in the column reactor the amount up to the point of breakthrough (a), the total amount of As(III) uptake (b), and the total retained amount (c) by subtracting the amount desorbed (d) from the total. It shows that if the removals up to breakthrough are only considered, Cols #1- #3 removed 82.2%, 13.9% and 8.9% at pH 5, 7, and 9, respectively. However, if the total amount of As(III) retained at pH 5 in the long column with a retention time of 3.3 hour (Table 2, Column #1) after breakthrough is considered, the As(III) removal capacity of the column is greater than that obtained in the batch. The sorption isotherm results in Table 2 were adopted from Han *et al.* (2011a). In fact, the maximum capacity would be expected to be greater than the reported 105.6% since further arsenic removal would be expected as the concentration of iron (Fig. 1), indicative of the presence of sulfide, does not show signs of declining even at 350 pore volumes. However, the maximum computed capacities of the long columns at the higher values of pH, at pH 7 and pH 9, appear to be considerably less than their respective batch capacities. Yet this comparison may not be valid as

the As concentrations in the batch systems were considerably greater (20 mg/L) than those in the column systems (1 mg/L).

From the desorption part of each breakthrough curve, the relative potential for the remobilization of removed As(III) from FeS-coated sand columns may be evaluated. At pH 5, only 1.8% (Col #1) of the removed As(III) was eluted, indicating very effective retention of As(III) at this pH. In contrast, at pH 7 and pH 9, much higher amounts of As(III) were eluted during the desorption step, 34.6% (Col #2) and 61.3% (Col #3), respectively. At pH 9, the desorption curve was much less steep than that at pH 7. The pH 9 column curve also showed a longer tailing feature. The differences in the desorption behavior at the various values of pH suggest the possibility of differences in the removal mechanisms. The formation of orpiment is thought to be the primary removal mechanism at pH 5 and to a lesser extent at pH 7, resulting in more irreversible removal based on the spectroscopic study result (Han *et al.*, 2011c Water Research). The higher extent of desorption at pH 9 is thought to be caused by the slow reversibility of the adsorption.

The different desorption behavior at the various values of pH suggests a different removal mechanism under each pH condition. This incomplete reversibility at low pH is evidence that the removal mechanism responsible is likely associated with the formation of arsenic sulfide. In contrast, complete reversibility has often been assumed as evidence of a surface complexation reaction (Bostick *et al.*, 2003) rather than precipitation. The removal reaction occurring at high pH is therefore expected to be primarily reversible adsorption. This is consistent with the formation of orpiment as the primary removal mechanism at pH 5 and to a lesser extent at pH 7, resulting in more irreversible removal.

Based on the experimental results reported by Wibulswas (2004), the column capacity determined by estimating the adsorbed amount of solute up to the BTC point at $C/C_0 = 0.1$ for three different clay columns led to capacity values that were 78%, 19% and 18% of the batch capacity values determined by Langmuir isotherm analysis. In contrast, in a study of the total retained amount of heavy metals (As, Cd, Cr, Cu, Hg, Pb and Zn) by a natural sediment (Seo *et al.*, 2008), a higher maximum adsorption capacity was found in the column experiments compared to the capacity obtained

from batch reactor analysis. The authors suggested the reason for this difference was the precipitation of metal sulfide in the columns, a mechanism which did not occur in the batch reactors.

3.3. Comparison of column and batch results using retardation factors

A comparison of column and batch capacity data using the simple approach taken in the previous section may not be valid since the As(III) concentration in the batch and column experiments differ considerably, with the initial concentration in the batch equal to 20 mg/L (50 mg/L at pH 5) and the influent concentration in the column equal to 1 mg/L. Alternatively, retardation factors may be calculated. In Table 2, the batch obtained-retardation coefficients, R_B (calculated from Eqn (4)), and column-obtained retardation coefficients, R_C (calculated using Eqns (5)-(7)), are listed. The values of R_B and R_C are more similar at pH 7 and pH 9, when adsorption dominates the As(III) removal process. Since the sorption behavior of As(III) on FeS-coated sand shows a high degree of non-linearity as evidenced by the Langmuir-shaped sorption isotherms, the retardation factors should vary with the different equilibrium As(III) concentrations. In the same manner, the column retardation factor should vary with different concentrations of injected As(III). Thus, the retardation factors were recalculated using Eqn (4), for various equilibrium As(III) concentrations and are shown in Fig. 5. The retardation factor approaches $R = 1$ as the As(III) concentration increases, while the retardation factor increases abruptly when the equilibrium As(III) concentration decreases. Based on Eqn (4), R_B at an aqueous As(III) concentration equal to 1 mg/L was estimated to be 61.3, 16.7 and 19.7 at pH 5, 7, and 9, respectively. In contrast, the values of R_C calculated using the method of moments (MOM) (Eqn (7)), are 14.9 (88% of R_B) and 24.9 (126% of R_B) at pH 7 and pH 9, respectively for the long columns at a retention time of 3.3 hr. At pH 5, the MOM cannot truly be applied to Col #1 since the effluent concentration never reaches a value greater than $0.5C_0$, due to the continuous removal of As(III) by precipitation. However, the data presented suggest that the value of R_C for this column would be greater than 300 PV, or greater than 400% of the value of R_B . Therefore, it can be concluded that the FeS-

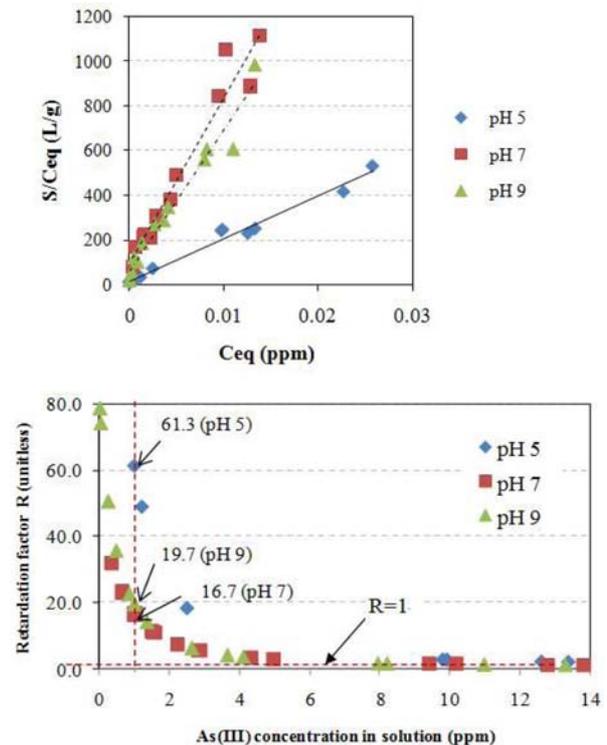


Fig. 5. Linearized Langmuir sorption isotherm results at pH 5, 7, and 9 (top) and estimated retardation factors (bottom) with varying equilibrium arsenic concentration in solution at pH 5, 7, and 9. The vertical dotted line marks the As(III) concentration = 1 mg/L and the horizontal dotted line shows that R approaches 1 as the As(III) concentration increases.

coated sand shows reasonable performance for PRB application based on the coating stability shown in Fig. 4 and performance under all range of pH conditions considered in this study.

3.4. Speculation about discrepancies between batch and column results

Two different approaches were utilized to compare As(III) removal results obtained in the batch and column reactors. The first approach used a capacity calculation based on removed amounts of As(III). If the total amounts removed are compared, greater removals occurred in the column reactor at pH = 5 where the precipitation of arsenic sulfide predominates as the As(III) removal mechanism, and lesser removals at pH 7 and pH 9, where adsorption dominates. However, the results from MOM suggested far greater removals in the column at pH 5, slightly more at pH 9, and slightly less at pH 7.

These differences may be attributable to three factors: (1) the difference in the mechanism of uptake, (2) the difference in the solid solution ratio (SSR) effect at pH 5 versus pH 9, and (3) the kinetics of removal. At pH 5, As(III) removal occurs through the precipitation of arsenic sulfide solids (e.g., orpiment, As_2S_3). Since the flowing column system leads to a greater mass of sulfide being available for the formation of precipitates, the removals are greater in the column. At pH 7 and 9, uptake occurs mostly via a surface-limited sorption reaction (Gallegos *et al.*, 2007). Therefore, the distribution of As(III) between the solid and solution phases is more important; if the uptake in the batch and columns systems is evaluated at similar concentrations (e.g., $\text{As(III)} = 1 \text{ mg/L}$), the uptake is comparable, as shown from the calculation based on the approach using retardation factors.

3.5 Kinetic effects (retention time-dependent BTC behavior)

Often kinetic limitations play a role in the determination of the shape of column breakthrough curves (Darland and Inskeep, 1997; Limousin *et al.*, 2007). To examine the role of kinetics in these complex systems with different mechanisms of removal and opposite impacts of SSR, additional column experiments were carried with different retention times. This was achieved by varying the column length (Col #1 and Col #4 for pH 5, and Col #3 and Col #5 for pH 9) and by varying the flow rate (Col #5 and Col #6 for pH 9) (Table 7.2). Col #7 examined the effect of flow rates in a single column with flow rate changes.

The results are presented in Figs. 6. At pH 5, the relative effluent concentration eventually reaches 1.0 in the shorter column at about 150 pore volumes, whereas when the retention time is three times, as long in the longer column, the relative effluent concentration does not reach even 0.4 after over 250 pore volumes. At pH 5, the removal of As(III) is dominated by precipitation of arsenic sulfide (Gallegos *et al.*, 2007). Thus, the comparative lack of removal at a shorter retention time may be due to the kinetics of the formation and deposition of the precipitate. A similar phenomenon was reported in a study investigating the deposition of goethite colloids in a column in that eventual breakthrough occurred at longer time scales as the flow velocity decreased (Jia *et al.*, 2007). Furthermore, in a study of zerovalent iron

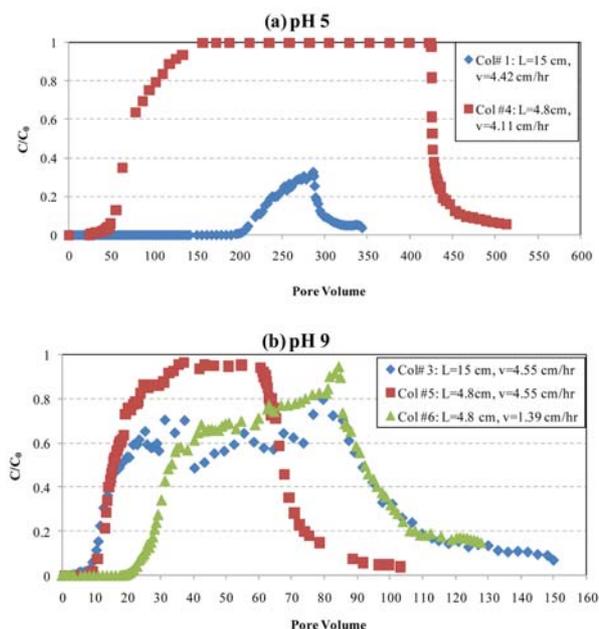


Fig. 6. As(III) breakthrough curves with different column experimental conditions for (a) pH 5 and (b) pH 9 column influent containing $1.3 \times 10^{-5} \text{ M}$ (1 mg/L) As(III). The solute retention (travel) time for each column is 3.37 hr (Col #1), 1.16 hr (Col #4), 3.31 hr (Col #3), 1.16 hr (Col #5) and 3.44 hr (Col #6).

nano-particle deposition, (He *et al.*, 2009) found that particle deposition efficiency was proportionally related to the travel distance or travel time of the particles through the porous media, resulting in the achievement of different relative concentration plateaus at different flow rates. Therefore, the different shapes of the breakthrough curve with different column lengths may be interpreted as a kinetic effect of particle-deposition due to a shorter travel time of the precipitated arsenic sulfide particles.

However, the shape of breakthrough curve of Col # 4 (short column at pH 5) is much likely to be a typical shape of a breakthrough curve which is controlled by an adsorption mechanism. Therefore, the possibility of a different removal mechanism operating in the shorter column from in the longer column cannot be ruled out. The shorter column provides only one third of contact time between FeS and the As(III)-containing influent, so that a less reduced condition may be achieved in the shorter column. Consequently much higher oxidation condition may have accelerated the change of the mineral phase in the FeS-coated sand column to a less soluble and more oxidized condition. As a result, the As(III) removal mechanism might be mainly controlled by

much more insoluble mineral phases such as greigite or Fe-oxides. This hypothesis is consistent with the 1-D transport modeling results using a equilibrium-kinetic two-site model combined with surface complexation models (SCMs) by Li (2009). The Col #4 breakthrough curve was successfully reproduced by the model without considering the precipitation of arsenic sulfide; instead, the rate-limited adsorption of As(III) on the FeS and Fe₃O₄ (magnetite) surface was used to describe the macroscopic behavior of the breakthrough curve. Even though the batch study results with high FeS and high As(III) concentration showed clear evidences of As(III)-removal mechanisms at pH 5 and pH 9 systems, no analytical or spectroscopic evidence could be collected in the column system due to the low As(III) concentration, so that the mechanism of As(III) removal in column system still remains as an open question. Further modeling and experiments need to be conducted to draw a more accurate picture of mechanisms how As(III) removal may change under different experimental conditions of pH, As(III) loading, or flow rate.

At pH 9, the short column with the higher velocity (retention time = 1.16 hr) (Col #5) broke through with the fewest pore volumes of throughput and plateau at a relative concentration of 1.0. The longer column at the same velocity (Col #3), but with a longer retention time (retention time = 3.31 hr), showed initial breakthrough occurring at the same number of pore volumes as in the shorter column with the same flow rate (Col #5). However the effluent concentration plateaued at a relative concentration of about 0.7 in the longer column, followed by a subsequent increase approaching 1.0. The difference in behavior based on residence time suggests a rate-limited process in the shorter column. The short column with the slower velocity (Col #6), with a similar retention time (retention time = 3.44 hr) to the longer column (Col #3), showed a later breakthrough, but similar behavior in that the relative concentration reached an initial plateau of about 0.6, followed by an increase over another 50 pore volumes or so. The columns with the longer retention times seem to show evidence for perhaps irreversible sorption, and/or multiple types of adsorption sites. (Kim *et al.*, 2006)) showed that, by incorporating irreversible sorption into the advection-dispersion equation, plateaus at relative concentrations of less than 1.0 could be simulated. In

addition, simulations with two-site models showed rising relative concentrations, following an initial plateau. Certainly, the desorption results suggest some irreversible desorption. Furthermore, the spectroscopic assessment of the FeS-coated sand surface suggests the existence of a variety of sorption sites, including FeS, the oxidized magnetite or greigite of the coating and the iron oxide uncoated surface of the natural sand as described in the surface characterization of the FeS-coated sand in Han *et al.* (2011a).

4. Conclusions

FeS-coated sand packed columns were tested to evaluate the As(III) removal capacity under anaerobic conditions at pH 5, 7 and 9. A mechanistic understanding of the different removal processes at different pH conditions is important to the interpretation of the column experiment results. Overall, the results of the column studies suggest that FeS-coated sand removes As(III) as efficiently in a column system as in a batch system, provided that an adequate retention time is provided. These results suggest that FeS-coated sand is a viable alternative for removing As(III), and is especially effective if the pH is maintained below 7. The results reported here do not consider the field complexities of, for example, spatially and temporally variable pH and pe regimes or background solutes. Further investigation should focus on developing optimum geochemical site criteria in order to maximize the efficiency of the FeS-coated sand reactive medium presented here.

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