

Arsenic in Aquifers: Bicarbonate Ions and the Adsorption of Inorganic Arsenic by Iron Oxide Minerals

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ABSTRACT

Aquifer Storage and Recovery (ASR) has been implemented in many regions of the world to supplement groundwater storage for withdrawal in times of need. However, high levels of dissolved arsenic (As) detected at some ASR locations have stalled its implementation. Mechanics of As release and persistence are not well understood. It has been hypothesized that bicarbonate ions introduced into ASR wells via recharge water inhibited iron oxide minerals present in aquifers to act as As adsorbents; however, knowledge about the effects of bicarbonate is limited and needs to be investigated systematically. My study aimed to characterize As adsorption by iron oxide minerals in the presence of bicarbonate and determine whether bicarbonate affects As adsorption by iron oxide minerals. Kinetic studies and batch experiments were conducted on As(III) and As(V) (4 μ M), bicarbonate (atmospheric-5mM) and iron oxide coated sands (1-10g/L). Results from kinetic studies indicate that As(III) and As(V) adsorption equilibrate in 24 hours and follow a 2nd-order rate law in the difference of $[As]_{t-t}$ and $[As]_{eq}$. Furthermore, bicarbonate lowered the adsorption of As(V) on iron oxide mineral but had no effect on As(III) in batch studies. This was demonstrated by higher adsorption maximum values for As(V) in comparison to As(III) at all bicarbonate levels and decreasing affinity parameters with increasing bicarbonate concentrations for As(V) compared to unaffected affinity parameters for As(III). Overall, this study illustrates that bicarbonate is most likely one of several factors in lowering As adsorption on iron oxide minerals in aquifers.

KEYWORDS

aquifer storage and recovery, kinetics, batch experiments, isotherms, rate orders

INTRODUCTION

Groundwater contamination by dissolved arsenic (As) has become an alarming issue in the United States because of its potential to cause detrimental health impacts. Chronic exposure to the maximum contamination level of 10 μ g/L imposed by the United States Environmental Protection Agency poses cancer risks (Tsuji, Yost, Barraj, Scrafford & Mink, 2006). Thus, when high levels of As (up to 300 μ g/L) appeared in Aquifer Storage and Recovery (ASR) pilot wells, ASR implementations in numerous regions came to a stall (Bell, Liseman & Turner, 2009). Understanding the cause of As release and persistence in aquifers is pivotal to the successful reimplementation of ASR.

ASR has been implemented in many regions of the world to supplement groundwater storage for withdrawal in times of need (Brown, Hatfield & Newman, 2006). Its benefits are numerous, including the support of potable water supply, irrigation water supply and environmental water supply for restoration (Brown et al., 2006). ASR has been implemented in diverse environments so no two projects are alike; however, because arsenic is ubiquitous in nature, As release is a common issue for many ASR locations. For stalled projects to resume, modifications must be made to the ASR model to maintain As concentrations below the 10 μ g/L limit (Bell et al., 2009).

Arsenic occurs naturally in the environment and historically, human activities such as acid mining have induced the leaching of As in groundwater (Susaya, Kim & Jung, 2010). Inorganic arsenic released into water via the dissolution of As containing minerals in ASR follows this phenomenon. The prediction that artificial aquifer recharge caused the release of dissolved arsenic was supported by relating the mineralogy of aquifer core samples with the observed arsenic concentrations in the recharged groundwater (M. Nocon, pers. comm., 2009). At an ASR pilot well in Green Bay, Wisconsin, environmental consulting firm CH2M HILL obtained core samples and dissolved arsenic concentrations from three different depths in the aquifer. Analysis of both groundwater and core samples showed that high solids concentration of As for core samples taken near the middle depth was likely responsible for the correspondingly high As concentrations in the recharged groundwater (CH2M HILL, 2003). Framboidal pyrite, a FeS mineral commonly found in aquifer solids with trace levels of arsenic, is stable in water with low levels of dissolved oxygen. Groundwater naturally occurring in aquifers has virtually no

dissolved oxygen since it is not in contact with air; thus, pyrite minerals are usually stable in deep aquifer environments. However, when recharge water that is rich in dissolved oxygen is injected into an aquifer, the equilibrium is disturbed and framboidal pyrite dissolves into soluble sulfur, arsenic, and ferrous iron (Jones & Pichler, 2007).

Although CH2M HILL knew that there was a possibility that framboidal pyrite would dissolve and release As in the oxygenated recharge water, it was expected that an oxidation of ferrous iron to ferric iron and precipitation of iron oxide minerals would immediately follow to sequester the dissolved As (CH2M HILL, 2003). Due to their positively charged surface sites, iron oxide minerals have the ability to accumulate As molecules in solution by a process called adsorption (Sposito, 2008). By capturing soluble As, iron oxide minerals can lower the As concentration of the solution (Thirunavukkarasu, Viraraghavan & Subramanian, 2003). Thus, CH2M HILL expected that iron oxide minerals would re-adsorb As, naturally restoring the original low As concentration. However, the aquifer failed to restore low levels of As in the recharged groundwater on its own; high As concentrations persisted, suggesting that some other substance in solution had interrupted the adsorption process. The chemical analysis of the pilot well showed that as the well was recharged, alkalinity (which is equivalent to bicarbonate concentration at near-neutral pH) of the system dropped (CH2M HILL, 2003). This decrease in bicarbonate ions followed a corresponding increasing trend of As in the recharged groundwater, leading to the hypothesis that bicarbonate has a significant influence on the adsorption of As by iron oxide minerals. However, not enough sound empirical evidence has been produced to support or refute this hypothesis (M. Nocon, pers. comm., 2009).

To further our understanding on the effect of bicarbonate on As adsorption by iron oxide, empirical evidence was produced systematically. The first goal of this research was to characterize the kinetics of As adsorption reactions onto iron oxide minerals in the presence of bicarbonate. I determined the time required for As/iron oxide adsorption reaction to reach equilibrium with bicarbonate in solution. I hypothesized that the reaction would stabilize within 24 hours. The second goal of this study was to determine how As/iron oxide adsorption differs at various bicarbonate levels. Thus, I determined whether bicarbonate acts as a competitor for adsorption sites. I hypothesized that bicarbonate would indeed act as a competitor, thus experiments with the highest bicarbonate concentration would most likely have the highest concentration of As remaining in solution.

METHODS

Data collection

Kinetic experiments

Kinetic experiments were conducted to characterize the adsorption of As by iron oxide coated sands (IOCS) over time with bicarbonate in solution. I used the following variables in my duplicated experiments: As(III)/As(V) (two chemical forms of As), IOCS content and bicarbonate concentrations. In the failed Green Bay ASR pilot well, the As concentration was around 4 μ M; thus to simulate real conditions in the field, the initial As concentration was set at 4 μ M (CH2M HILL, 2003). I used one concentration of bicarbonate (5mM) and 1, 5 and 10g/L of IOCS, and the two As chemical forms (As(III)/As(V)). The solution pH was adjusted to 7.5 by the addition of small volumes of acid (HCl) and base (NaOH) and the ionic strength was set at 0.01M with the addition of NaCl. In order to closely represent an aquifer, I wrapped the solution bottles in aluminum foil to eliminate UV exposure and consequent As redox reactions (Tufano et al, 2008). Once the bottles were prepared, they were attached on a rotator to insure continuous mixing during the 24 hours of reaction time. To minimize air exchange in the course of sampling, I attached a two-way stopper to the bottle caps. I attached a 1mL syringe needle to the stopper to draw out the solution, which was then injected through a syringe filter into 4mL test tubes. I collected samples at times 0, 10, 20, 60, 360, 480 and 1440 minutes and recorded the final pH.

Batch experiments

Batch experiments were conducted to determine whether As adsorption by IOCS differs at various bicarbonate levels. I applied the reaction equilibrium time determined by the kinetics experiment as the duration of my batch experiments. I had four bicarbonate concentrations (atmospheric, 1.25mM, 2.5mM and 5mM), which defined the range of alkalinity found in ASR wells high in dissolved As (CH2M HILL, 2003). I used 10 concentrations of IOCS (1-10g/L)

plus a batch with no sand as a control. Experimental conditions were the same as those in the kinetic study. I collected samples at reaction equilibrium and recorded the final pH.

Analytical methods

I analyzed the samples collected from the kinetic study and the batch experiments under a Perkin Elmer HG-ICP-OES (inductively coupled plasma spectroscopy) to measure the concentration of As remaining in solution. The hydride generation (HG) setting was used since it provides the highest detection limit for As (M. Nocon, pers. comm., 2009). Prior to analysis under the ICP, I stored the samples in a potassium iodide reductant solution (4M HCl, 0.08 M KI, 0.015M Ascorbic Acid) which reduced all As to As(III). This step was necessary because the hydride generation can only detect As in its reduced form of As(III) (Planer-Friedrich & Wallschalger, 2009). For each sample, I obtained an As concentration by averaging readings of As measured at 4 wavelengths which are sensitive to As (188, 193, 197 and 228nm).

Data analysis

Kinetic experiments

I analyzed the kinetics data by fitting the data to various reaction rate orders, which could potentially describe the kinetics of As adsorption by IOCS in the presence of bicarbonate. First, for each of the 6 runs (3 IOCS (1g/L, 5g/L, 10g/L) concentrations x 2 chemical forms of As) I created zero-order plots of As remaining in solution vs. time. Where the plots flattened out indicated the time at which the reaction equilibrated. To determine the reaction model which best described the kinetics, I transformed the data according to each model (Table 1). The transformation that produced the highest R^2 value and the tightest 95% confidence intervals for the slope parameters was considered the best reaction model.

Table 1. Rate orders and their corresponding data transformations and rate determinants.

Rate Order	1 st -order	2 nd -order	Pseudo 1 st -order	General rate law
Data Transformation	$\ln[\text{As}]$ vs. time	$1/[\text{As}]$ vs. time	$\ln([\text{As}]_t - [\text{As}]_{\text{eq}})$ vs. time	$1/([\text{As}]_t - [\text{As}]_{\text{eq}})$ vs. time
Rate Determinants	[As]	[As], available surface sites on IOCS	[As], surface sites in excess	[As], available surface sites on IOCS

1st and 2nd-order rate laws are based on the assumption that As kinetics only consists of an adsorption phase. If the As kinetics consisted of both adsorption and desorption, these rate laws did not characterize the entirety of the kinetic study and did not follow the actual data when superimposed on zero-order plots. In this case, the kinetics were tested for pseudo 1st-order and the general rate law. Pseudo-1st order reaction means that a 2nd order reaction acts as a 1st order reaction since one of the reactants is in excess. In these experiments, there was a possibility that surface sites on IOCS were in “excess”, pointing to a situation where a significant number of sites with no As bounded to them were present even when all initial As had adsorbed. If Pseudo-1st order plots did not produce a significant linear regression at the 95% confidence level, the general rate law was tested. Kinetics described by a general rate law has a reaction rate that is dependent on the concentration of As in solution and the surface site density of IOCS.

Batch experiments

I analyzed the batch experiments data by calculating adsorption parameters for each tested bicarbonate concentration and plotted adsorption isotherms to visualize whether bicarbonate had an effect on the adsorption of As by IOCS. First, for each data point, I calculated a surface excess value (n), or the amount of As that adsorbed on the IOCS surface by the equation (Sposito, 2008),

$$n = ([As]_{initial} - [As]_{equilibrium}) / [IOCS].$$

I calculated the corresponding distribution coefficient (K_d) for the reaction by the equation $K_d = n / [As]_{equilibrium}$ (Sposito, 2008). If the plots of K_d versus n produced statistically significant linear regressions, I determined that the adsorption followed a Langmuir isotherm (Sposito, 2008). Prior to analyzing the K_d versus n plots, I eliminated outliers from the data by first calculating 95% prediction bands using Data Desk XL (DDXL) (Triola, 2006). I then imposed the calculated upper and lower 95% prediction bands on the K_d versus n plots and labeled any data points that fell outside of the bands as outliers. The x-intercept of the linear regression of K_d versus n plots is the value of adsorption maximum (b) and the slope of the linear regression is the value of affinity parameter (K). Adsorption maximum is the maximum possible amount of As that can be adsorbed by the IOCS surface and the affinity parameter is the ratio of $k_{adsorption}$ to $k_{desorption}$. By comparing these adsorption parameters produced at each bicarbonate concentration,

I determined whether bicarbonate had an influence on the adsorption of As(III) and As(V) on IOCS.

Furthermore, in order to determine the relationship between affinity parameter and maximum adsorption in As/IOCS/bicarbonate adsorption reactions, I set a fixed maximum adsorption value (b) in my analysis. I selected maximum adsorption values found by Pierce & Moore (1982) and Dixit & Hering (2003) because their adsorption experiments were conducted at similar solid to solution ratio and pH as my study. From their published results, I estimated that the average value for the maximum adsorption for both As(III) and As(V) by iron oxide coated sand is $3.859 \pm 0.767 \mu\text{mol As/g IOCS}$. This average value was used to create graphs of K_d versus $b-n$ for each batch run. By comparing K_d versus n graphs to K_d versus $b-n$ graphs, I determined the relationship between affinity parameter and maximum adsorption.

Finally, I converted the data for each bicarbonate concentration and As chemical form to Langmuir isotherms. Surface excess value specific to a Langmuir isotherm (n_L) was calculated by the equation,

$$n_L = \frac{bK}{1 + K[As]}$$

where K is the affinity parameter and b is the adsorption maximum. I plotted n_L versus $[As]$ to determine the effects of adsorptive concentration on the surface excess (Sposito, 2008).

RESULTS

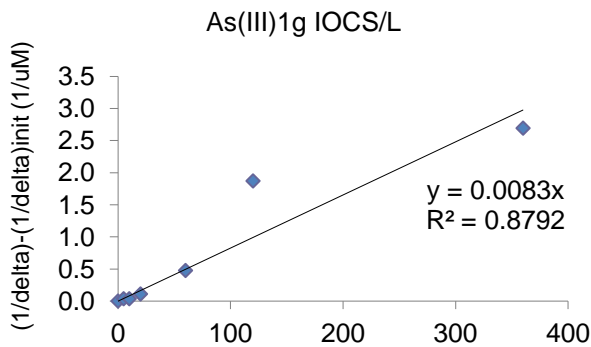
Kinetic experiments

From the kinetic experiments, I discovered that both As(III) and As(V) equilibrated in 24 hours. The reaction equilibration time could be estimated well from the zero-order ($[As]$ vs time) plots. I was able to support this estimation by superimposing 1st-order and 2nd-order rate order models to the zero-order plots and illustrating that these rate models diverge from the actual data at later times (360-1440min) for both As(III) and As(V). These rate orders assume that only an adsorption reaction is occurring, therefore their failure to model the entirety of kinetics indicated that my experiments went under both adsorption and desorption.

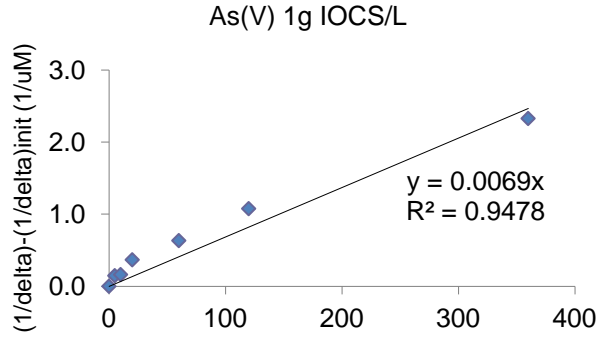
The discovery that the As adsorption on IOCS in the presence of bicarbonate is described by both adsorption and desorption led me to investigate whether the kinetics were a pseudo 1st - order reaction. However, data transformation of both As(III) and As(V) did not produce statistically significant linear regression, indicating that the surface sites are not in excess for both As(III) and As(V). Finally, the general rate order was tested on As(III) and As(V) kinetics.

Plots of $\frac{1}{[As]_{time=t} - [As]_{eq}}$ versus *time* produced statistically significant linear regressions at the 95% confidence level (Table 1), demonstrating that the general rate law is an appropriate characterization for As(III) and As(V) kinetics. Furthermore, plots of $\frac{1}{[As]_{time=t} - [As]_{eq}} - \left(\frac{1}{[As]_{time=t} - [As]_{eq}}\right)_{init}$ versus *time* (Fig. 1) gave a better estimate of the slope by removing the y-intercept, which was an acceptable action because the initial conditions are known values from experiments that do not need to be estimated by the model.

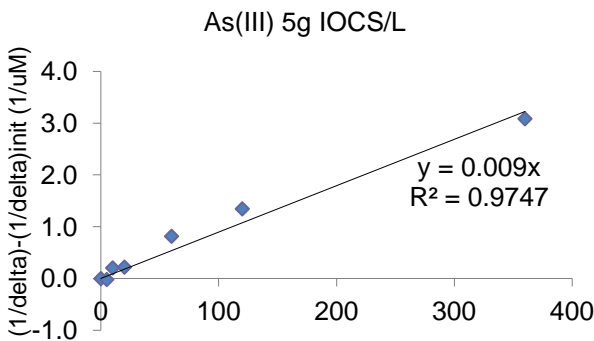
a.



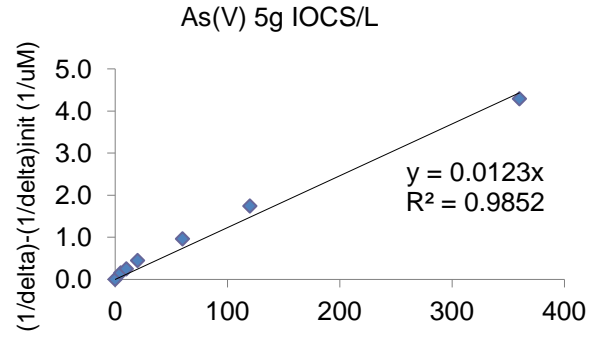
d.



b.



e.



c.

f.

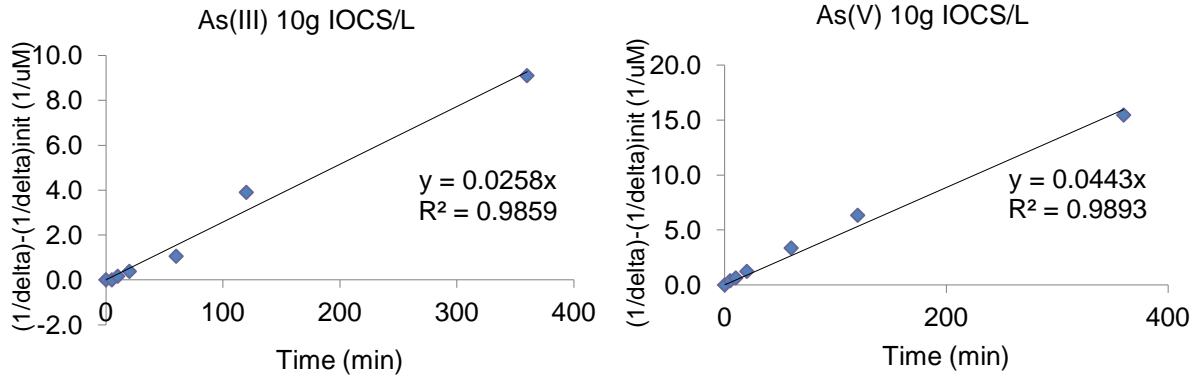


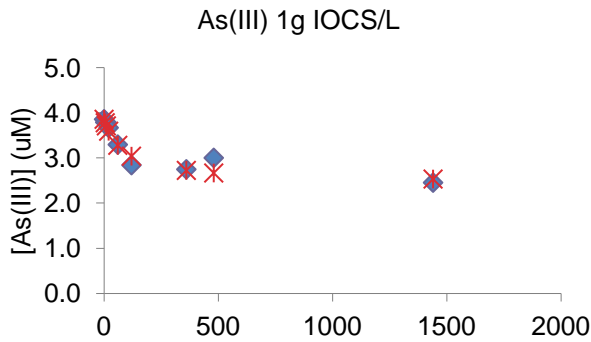
Figure 1. General Rate Laws for As(III) and As(V) at 1,5 and 10g/L IOCS. Delta is the As concentration measured at time t minus the equilibrium As concentration. a-c are As(III) kinetics, and d-f are As(V) kinetics.

Table 2. p values of the slope of linear regression for the general rate law. p-values indicate that the general rate law is suitable model for all runs.

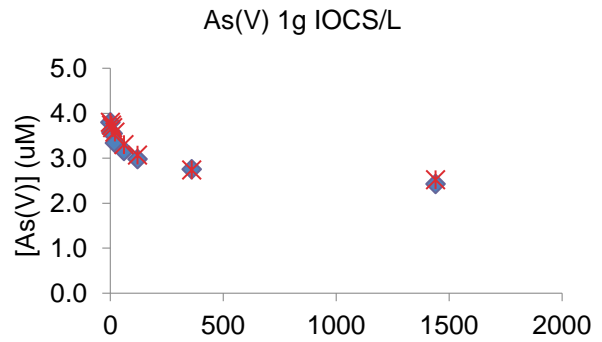
[IOCS] (g/L)	1	5	10
	p-values		
As(III)	0.0002	< 0.0001	< 0.0001
As(V)	< 0.0001	< 0.0001	< 0.0001

Furthermore, the general rate law superimposed on zero-order plots showed that this model characterizes the whole 24 hours of the kinetics.

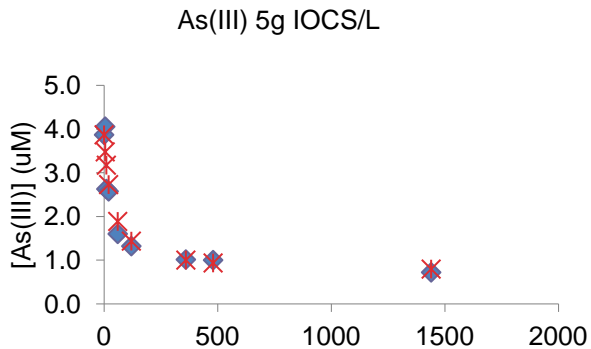
a.



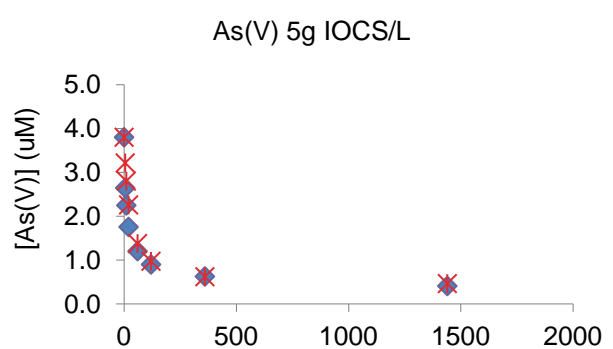
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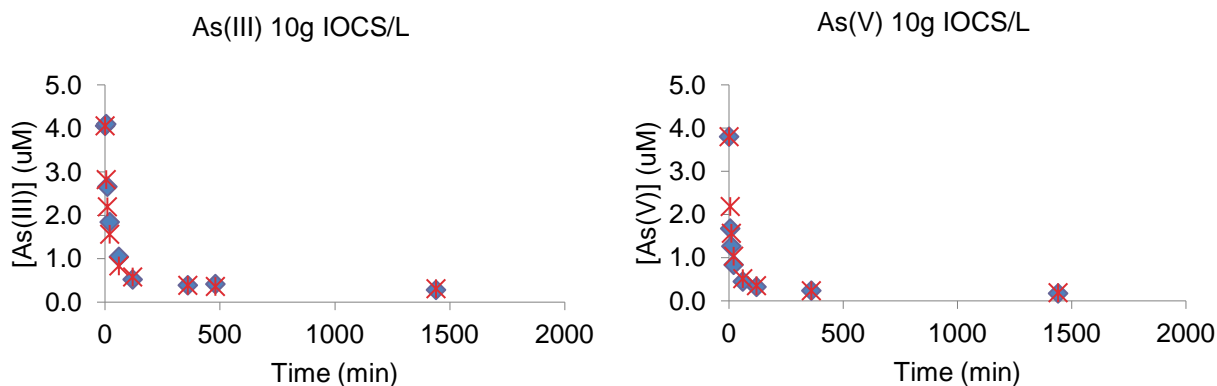


Figure 2. General rate law model superimposed on zero-order plots. The blue diamond represents the actual data and the red asterisk represents the general rate law model. a-c are general rate law models for As(III) and d-f are general rate law models for As(V).

Batch experiments

The statistically significant linear regression of the K_d versus n plots demonstrated that As adsorption on IOCS can be characterized by a Langmuir isotherm. By comparing the Langmuir adsorption parameters for As(III) and As(V), I observed several indicators which showed that bicarbonate ions affect As(V) adsorption more than As(III) adsorption on IOCS.

First, the adsorption maximum values are slightly larger for As(III) than As(V) at all tested bicarbonate levels (Table 3).

Table 3. Adsorption maximum values for As(III) and As(V) at the 4 bicarbonate concentrations.

[HCO ₃ ⁻] (mM)	As(III)				As(V)			
	atm	1.25	2.5	5	atm	1.25	2.5	5
Ads. Max (μmol /g)	2.619	2.666	2.707	2.418	1.297	1.911	2.016	1.969
Std. dev (μmol /g)	0.364	0.348	0.356	0.376	0.188	0.546	0.691	0.615

Second, the affinity parameters for As(III) are statistically the same across the 4 bicarbonate levels ($p=0.7612$) whereas the affinity parameter values of As(V) clearly drop with increasing bicarbonate concentration (Table 4). The affinity parameters for As(III) stay fairly constant at the 4 bicarbonate concentrations whereas those for As(V) follow a decreasing logarithmic trend with increasing bicarbonate concentration (Figure 3).

Table 4. Affinity parameters for As(III) and As(V) at the 4 bicarbonate concentrations.

[HCO ₃ ⁻] (mM)	As(III)				As(V)			
	atm	1.25	2.5	5	atm	1.25	2.5	5
Affinity Parameter (L/μmol)	1.077	0.885	0.888	1.058	5.465	3.507	1.926	1.198
Std. dev	0.143	0.115	0.138	0.173	0.713	0.820	0.617	0.394

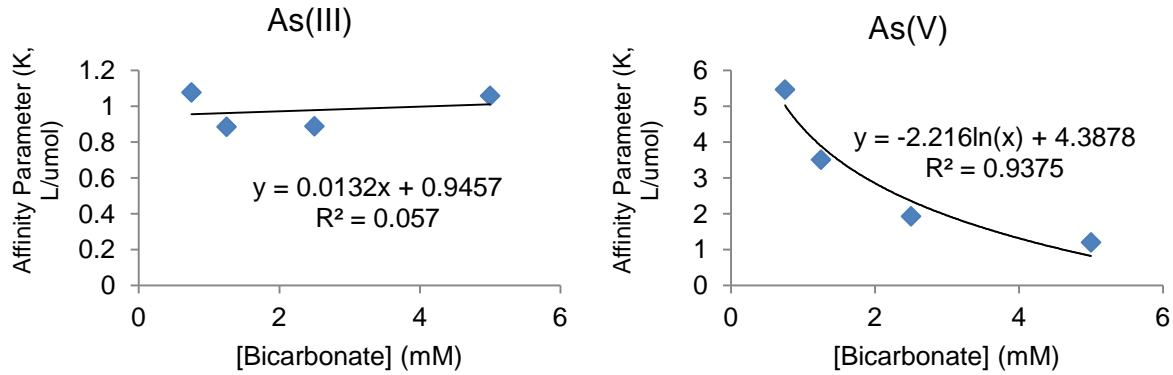
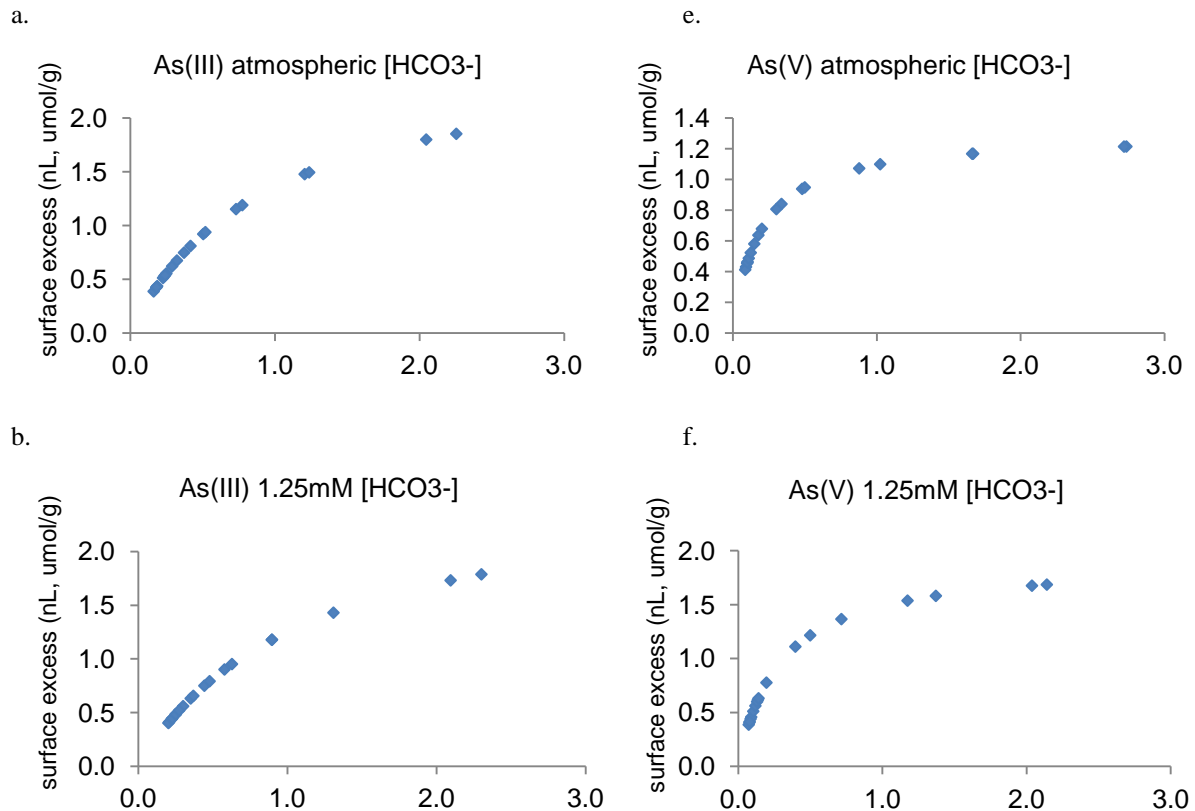


Figure 3. Affinity parameters versus bicarbonate concentrations. The p-value for the slope parameter for the linear regression of As(III) is 0.7612, indicating that there is no observable relationship between affinity parameter and bicarbonate concentration.

Third, the initial portion of the Langmuir isotherm is much steeper for As(V) than As(III), which is also explained by the significantly larger affinity parameters for As(V) compared to those of As(III) (Figure 4).



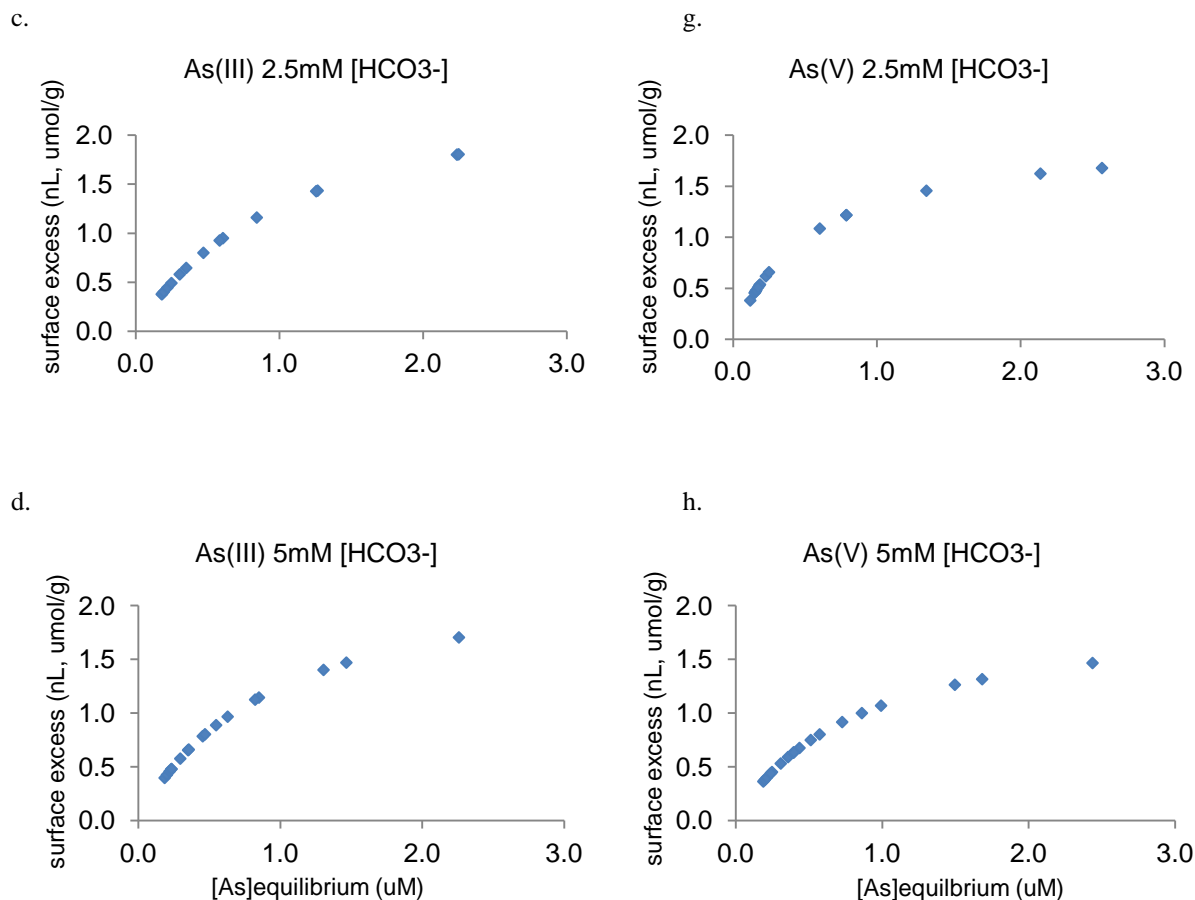


Figure 3. As(III) and As(V) Langmuir isotherms. a-d are As(III) isotherms and e-h are As(V) isotherms.

Furthermore, the Langmuir adsorption parameter analysis illustrated that K_d versus n graphs and K_d versus $b-n$ graphs yielded the same linear regression slope and R^2 . This observation demonstrates that adsorption maximum and affinity parameter are independent Langmuir parameters for the adsorption of As by IOCS.

DISCUSSION

Implications of kinetic study and batch experiments

The main purpose of this study was to determine whether bicarbonate ions affect the adsorption of inorganic arsenic by iron oxide minerals. Improving our understanding of the role of bicarbonate could potentially lead to isolating the cause of As release and persistence in ASR. From the kinetic study, I discovered that As(III) and As(V) equilibrate in 24 hours. Both

chemical forms follow a 2nd –order general rate law, indicating that within the 24 hours, both adsorption and desorption take place. The rate of adsorption is governed by the surface site density of IOCS and the difference between [As] at time t and the equilibrium [As]. In addition, the unsuitability of the pseudo 1st-order for both As(III) and As(V) demonstrates that surface sites on IOCS are not in excess. This means that there is potential for competition between bicarbonate and As for adsorption sites.

Batch experiments were conducted to illustrate the effect of bicarbonate on adsorption. Based on the results from the kinetic study, I ran the batch experiments for 24 hours to insure reaction equilibration. From the results, it is clear that As(III) and As(V) are affected differently by bicarbonate. For As(III), the adsorption maximum and affinity parameters do not statistically differ among the four bicarbonate concentrations whereas bicarbonate ions exhibit an obvious influence on the two reaction parameters for As(V). Thus, at the concentrations of As, IOCS and bicarbonate used in this study, bicarbonate acted as a competitor for adsorption sites for As(V) but not for As(III). In addition, since the kinetic study showed that the adsorption reaction for both As(III) and As(V) are second order reactions, where the rate of the reaction depends on both the concentration of As and surface sites on IOCS, repeating the experiments at lower surface site concentration (i.e., lower [IOCS]) may induce more competition and pronounce the bicarbonate effect (M. Nocon, pers. comm., November, 2010). Therefore, bicarbonate is most likely one of the influential components in lowering the efficiency of As adsorption on iron oxide minerals.

Outlier analysis

Outlier analysis was the initial step in data analysis since adsorption experiments are sensitive to uncontrolled variables (Limousin et al., 2007). No outliers were detected for the kinetic study, however batch experiments produced numerous outliers, which were removed from the data to accurately analyze the results. After careful study comparing initial and final conditions of samples, I discovered that outlier points corresponded to samples that leaked during the duration of the experiment. When the solution bottles leaked, CO₂ gas seeped into the bottle and lowered the pH (Benjamin, 2007). At lower pH, more As adsorbed to the IOCS surface which yielded higher distribution coefficients. Furthermore, overall, As(V) had more

outliers than As(III) because As(V) standard solution was stored in NaOH while As(III) was stored in HCl. I had more difficulty adjusting the pH of As(V) batch solutions than As(III) batch solutions because of this difference in standard solutions. Thus, in conjunction with similar studies published on As adsorption, the outlier analysis supported that pH fluctuations severely affect adsorption.

Limitations

In analyzing the results, it is important to keep in mind that the simple batch methodology employed in this study does not fully describe the complex geochemical phenomena occurring in ASR wells. Other numerous ions present in the well (e.g., calcium and phosphate) may be producing synergistic effects with bicarbonate to favor As persistence (Saalfied & Botsick, 2010). As the outlier analysis indicated, adsorption experiments are subjected to many limitations such as solid/solution ratio, ionic strength, and pressure of CO₂ in addition to pH. Empirical values produced at one pH and solid/solution ratio cannot be applied to a setting with different pH and solid/solution ratio (Limousin et al., 2007). Furthermore there are limitations imposed by the inherent gap between a natural environment and a controlled lab setting (M. Nocon, pers. comm., November, 2010). In addition to the numerous ions excluded from the study, the solid to solution ratio is very low compared to an actual ASR well (CH2M HILL, 2003). Thus, constants produced empirically from this study may not directly explain the geochemistry of an ASR aquifer alone. Other factors, such as those previously mentioned, should be considered in the calibration of predictive models for ASR geochemistry.

Future directions and broader implications

Empirical evidence I produced in this study may be applied to future laboratory and field studies that more closely model an ASR. For example, the general rate law found from the kinetic study can be used to derive an adsorption coefficient, which can then be applied to complex flow through media experiments (e.g., column experiments) (Limousin et al., 2007). These experiments could be used to develop a reactive transport model to describe how As adsorption varies in transport under the combined effects of geochemical phenomena and

hydrologic movement (Fendorf, Michael & van Green, 2010). Thus, this study's characterization of As/IOCS/bicarbonate adsorption reaction can enhance the limited existing literature on ASR geochemistry.

My analysis demonstrated that for As(V), bicarbonate acts as a competitor for adsorption sites even without the possible synergistic effects occurring in ASR to induce this competition (Stachowicz, Hiemstra & van Riemsdijk, 2008). Similarly, if other ions are included in the batch system, As(III) could be affected by bicarbonate ions as well. Therefore, bicarbonate may likely be the base factor in the release and persistence of As in ASR whose adverse affects are amplified by the complex chemistry of ASR aquifers. My research serves as a baseline for tracking the evolution of bicarbonate effects on As adsorption by iron oxides from which chemical variation can be compounded in future research. If future research could isolate the exact cause, necessary modifications could be made to predictive modeling of ASR geochemistry (CH2M HILL, 2003). Predictive modeling would be integrated into baseline risk assessment studies needed for ASR projects (NRC, 2008). Resuming ASR projects would mitigate water shortages found in California and the United States (Brown et al., 2006).

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