

## Using surface complexation modeling to assess the role of silica in arsenate adsorption onto metal oxides

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### ABSTRACT

A surface complexation model was developed to predict arsenate removal by ferric hydroxides in the presence of silica and natural organic matter. Modeling of arsenate removal in the presence of silica is improved somewhat by explicit consideration of both monomeric and dimeric silica species. Consistent with previous observations, the model simplifies to a linear isotherm under conditions present in many natural waters at  $\text{pH} \leq 7.8$  and if silica concentrations are relatively low. In waters at higher pHs with relatively high levels of silica, the model predicted that arsenate removal would be relatively insensitive to coagulant dose, but decreasing coagulation pH would produce very significant improvements to arsenate removal, as has been confirmed in practice.

**Key words** | activated alumina, adsorption, arsenic, coagulation, silica, surface complexation model

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### NOTATION

$\equiv$	surface species
{ }	activity
[ ]	molar concentration (mol/L or M)
$A_s$	specific surface area ( $\text{m}^2/\text{g}$ )
$F$	Faraday constant ( $= 96\,490\text{ C/mol}$ )
$f_s$	surface site density (mol sites/mol Fe)
$\text{H}_2\text{A}^{n-}$	natural organic matter
$K^{\text{app}}$	apparent equilibrium constant
$K^{\text{int}}$	intrinsic equilibrium constant
$n$	valence of natural organic matter
$R$	molar gas constant ( $= 8.314\text{ J mol}^{-1}\text{ K}^{-1}$ )
$T$	absolute temperature (K)
$\Psi$	surface potential (V)

### INTRODUCTION

Due to the adverse health effect of arsenic, the United States Environmental Protection Agency (USEPA) established a Maximum Contaminant Level (MCL) of 0.01 mg/L for total arsenic in drinking water (USEPA 2001). USEPA also

identified modified coagulation–filtration and activated alumina as two of the best available technologies for arsenate ( $\text{As(V)}$ ) removal. Currently, water utilities and engineers use jar testing to identify appropriate coagulation conditions and pilot testing to test adsorption column performance. This trial-and-error practice is inefficient, especially when multiple water quality goals are to be achieved. A desirable alternative is to develop an ability to predict performance with a model. Because both adsorption and subsequent particle removal are necessary for arsenic removal by coagulation, and the particle surface potential plays a major role in determining whether particles will agglomerate, an ideal model would predict both adsorption and surface potential.

Several studies have utilized models to fit  $\text{As(V)}$  adsorption or coagulation data (Edwards 1994; Hering *et al.* 1996; McNeill & Edwards 1997; Swedlund & Webster 1999; Meng *et al.* 2000; Holm 2002). Some of them found that a linear isotherm could characterize  $\text{As(V)}$  removal (Hering *et al.* 1996; McNeill & Edwards 1997). Although this

isotherm was very useful in a wide range of water systems, its potential drawbacks include a limited proven pH range of application and an inability to directly account for competition from other anions or to predict surface charge.

Dzombak & Morel (1990) used the diffuse layer surface complexation model to describe specific adsorption of solutes onto oxide surfaces. Following Dzombak and Morel's approach, Hering *et al.* (1996) evaluated the applicability of the surface complexation model (SCM) to predicting As(V) removal by adsorption to ferric hydroxides (formed by dosing  $\text{FeCl}_3$ ) via adsorption and coagulation in the presence of calcium, sulfate and phosphate. They concluded that adsorption processes were significant in governing As(V) removal during coagulation, and that the application of the SCM to natural water was limited partly due to the interference of natural organic matter (NOM). No attempt was made to account for surface charge effects in the Hering study or to model NOM interference, although the diffuse layer model is among the simplest available with this capability.

In addition to As(V), the SCM has also been used to estimate adsorption of NOM (Chen & Edwards 1999), silica (Swedlund & Webster 1999; Meng *et al.* 2000; Stumm *et al.* 1980; Sigg & Stumm 1981; Davis *et al.* 2002) and sulfate (Hering *et al.* 1996; Stumm *et al.* 1980; Sigg & Stumm 1981; Ali & Dzombak 1996a, b). Simple SCM models describing silica adsorption have been combined with those for As(V) adsorption to predict major interferences to As(V) removal observed for silica. For instance, Meng *et al.* (2000) noted that silica significantly reduced As(V) adsorption not only by competing for surface sites but also by reducing the surface potential. Swedlund & Webster (1999) developed an SCM accounting for silica interference to As(V) removal that provided good predictive abilities. However, it slightly underestimated the actual interference from silica at pH 6–8, quite possibly because their SCM did not consider any polymeric silica species which the authors believed to be present on the iron surface. Davis *et al.* (2002) have proposed a SCM model that includes dimeric silica which might better account for interference from silica.

This study first calibrates an SCM for As(V) using laboratory adsorption data and then applies it to predicting trends in As(V) removal in natural waters. Major goals of

the work are to explain the range of interference noted for silica in previous work, and to reconcile some observations regarding As(V) removal in natural waters that may seem contradictory at first glance.

## MATERIALS AND METHODS

### Experiments

Laboratory experiments were conducted to investigate the adsorption of As(V), silica and NOM onto the surface of preformed amorphous ferric hydroxide ( $\text{Fe}(\text{OH})_3(\text{am})$ ) under various conditions at 20°C: 10 mg/L Fe, 62 or 71  $\mu\text{g}/\text{L}$  As(V), 7.0 or 7.4 mg C/L NOM, 0–50 mg/L  $\text{SiO}_2$  at pH 5.00, 6.00, 7.25, 8.50 and 9.50. The ionic strength was in the range of  $1.9 \times 10^{-3}$ – $3.7 \times 10^{-3}$  mol/L. Plasticware was used to avoid the problem of silica leaching from glassware. Fresh  $\text{Fe}(\text{OH})_3(\text{am})$  was prepared by raising the pH of a ferric chloride stock to 6.0. An As(V) stock and a silica stock were prepared from  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}(\text{s})$  and  $\text{Na}_2\text{SiO}_3(\text{s})$ , respectively. The NOM used for this study was isolated from natural water bodies in Colorado, USA (Chen & Edwards 1999). After  $\text{Fe}(\text{OH})_3(\text{am})$  was aged for 12–16 h, it was added to As(V), silica and/or NOM solutions. The pH was immediately adjusted to the target values and maintained within  $\pm 0.15$  pH units during a reaction period of 1.5 h. Subsequently, an aliquot of each solution was passed through a 0.45  $\mu\text{m}$ -pore-size nitrocellulose or nylon filter. The adsorption sample solutions and the filtrates were analyzed for Fe, Si and As with a JY 2000 Inductively Coupled Plasma–Emission Spectrometer (ICP–ES) and for total organic carbon (TOC) with a TOC analyzer. The detection limits are approximately 1  $\mu\text{g}/\text{L}$  for both As and Si. The zeta potential of solids in silica adsorption samples was also measured. Details of material preparation and experimental procedures were described elsewhere by Davis *et al.* (2002).

### Surface complexation model calibration

The SCM used for model calibration was based on the Gouy–Chapman diffuse double layer theory (Stumm 1992) and consisted of surface complexation reactions for As(V)

modified from the work of Dzombak & Morel (1990), for silica described by Davis *et al.* (2002) and for NOM by Chen & Edwards (1999) (Table 1). Natural organic matter, denoted by “ $H_2A^{n-}$ ”, was assumed to be comprised of organic acids with discrete acidity constants and a total charge of  $n$  (Figure 1). The authors understood that this approach was inconsistent with many aspects of acidity in actual NOM (Edwards *et al.* 1996), but it is likely that interferences to As(V) adsorption could be quantitatively captured by defining “average” characteristics of heterogeneous NOM. Both monomeric and dimeric silica species in the aqueous phase as well as on the surface were included in the model. The detailed modeling procedure was presented elsewhere (Chen 2001).

Model parameters were optimized using Microsoft Excel<sup>®</sup>. Results of laboratory adsorption experiments were entered onto a worksheet to calibrate the model. Model inputs included pH, electrolyte concentrations, total concentrations of Fe, As(V), organic carbon and silica. The mass law and mass balance equations and the electrostatic terms were then solved for the concentration of each species with functions written in Microsoft Visual Basic<sup>®</sup> by the authors based on the bisection method (Chapra & Canale 1988). Characteristic parameters of  $Fe(OH)_3(am)$  and NOM as well as the intrinsic adsorption constants were optimized with the Microsoft Excel Solver<sup>®</sup> for a maximal coefficient of determination ( $r^2$ ) to fit the adsorption data.

All adsorption constants were optimized to fit the adsorption experiment results under various pH conditions. The silica adsorption constants were first optimized to fit the adsorption data from experiments where silica was the only adsorbate. Subsequently, the As(V) adsorption constants optimized to fit the Si–As(V) dual-adsorbate data were obtained. Finally, the results of the As(V)–NOM dual-adsorbate experiments were used to optimize the NOM adsorption constants.

## RESULTS AND DISCUSSION

After describing the calibration of the model using experimental data, its usefulness was examined by testing its

ability to explain perplexing aspects of As(V) removal that have been reported in the literature.

### Model calibration and comparison to previous work

The SCM with the optimal values of the model parameters (Table 2) fit adsorption data for As(V), silica and NOM (Figure 2). As noted elsewhere (Davis *et al.* 2002), the “best fit” surface area of the  $Fe(OH)_3$  is about 10 times higher than was expected based on previous estimates, perhaps due to simplifications inherent in diffuse layer models in describing electrostatic interactions between adsorbed species such as silica. The model still fit the data well if more common estimates of surface area (e.g.  $600\text{ m}^2/\text{g}$ ) are entered into the model (Table 2), but since the accepted surface area measurements for hydrous ferric hydroxide (Dzombak & Morel 1990) vary over a wide range, a decision was made to use the “best fit” value. Because surface potential cannot be measured directly, zeta potential measurements were used to evaluate the relative accuracy of surface potential predictions. Surface potential and zeta potential should share the same sign, and the magnitude of the zeta potential should be less than that of the surface potential. The surface potential predicted by the SCM satisfied these criteria for silica, as noted elsewhere (Davis *et al.* 2002).

Swedlund & Webster (1999) also calibrated an SCM model to describe As(V) and silica adsorption onto iron hydroxides. Although the authors provided evidence that polymers of silica were forming on the iron hydroxide surface, a model considering only monomeric silica species was surprisingly accurate in predicting As(V) removal in a system that contained 1.8 mM of silica ( $108\text{ mg/L}$  as  $SiO_2$ ) (Figure 3(a)). It was of interest to determine whether the SCM described by Davis *et al.* (2002), which considered adsorption of the dimers, was an improvement over the existing model.

With respect to the calibration data for silica, both approaches provided a good fit at silica adsorption densities below 0.1 M Si/M Fe (Figure 3(b)), but the model in Swedlund and Webster led to substantial underprediction of adsorption density at higher levels, whereas the model considering dimers provided reasonable accuracy to levels as high as 0.3 M Si/M Fe. At and above these adsorption

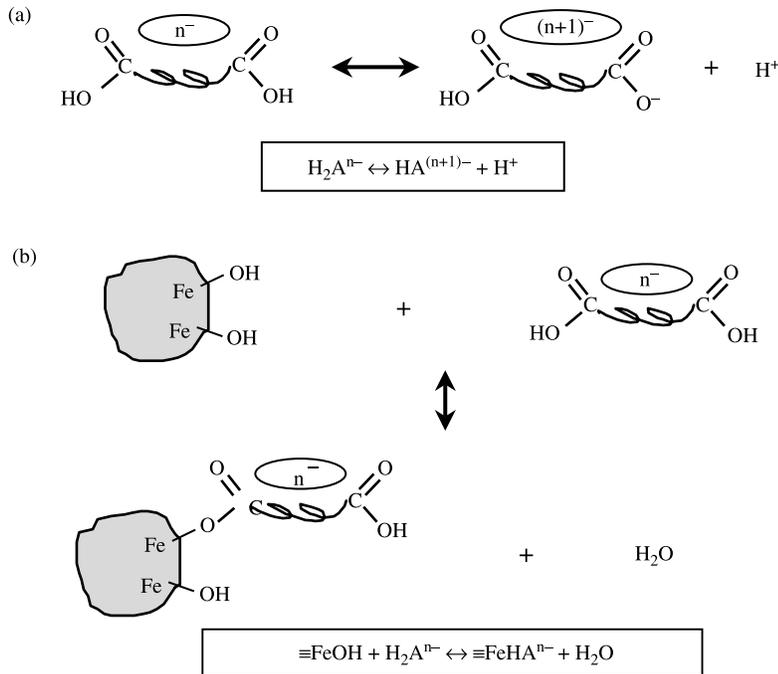
**Table 1** | Equilibrium expressions for solution reactions and surface complexation reactions used for model calibration

Solution acid–base reactions	
$\{\text{OH}^-\} = K_w \{\text{H}^+\}^{-1}$	$K_w = 6.18 \times 10^{-15}$ at 20°C (Stumm & Morgan, 1996)
$\{\text{HAsO}_4^{2-}\} = K_{a2\_As5} \{\text{H}_2\text{AsO}_4^-\} \{\text{H}^+\}^{-1}$	$K_{a2\_As5} = 10^{-6.96}$ (Dzombak & Morel, 1990)
$\{\text{AsO}_4^{3-}\} = K_{a2\_As5} K_{a3\_As5} \{\text{H}_2\text{AsO}_4^-\} \{\text{H}^+\}^{-2}$	$K_{a3\_As5} = 10^{-11.50}$ (Dzombak & Morel, 1990)
$\{\text{SiO}(\text{OH})_3^-\} = K_{a1\_Si} \{\text{Si}(\text{OH})_4\} \{\text{H}^+\}^{-1}$	$K_{a1\_Si} = 10^{-9.5}$ (Stumm & Morgan, 1996)
$\{\text{HA}^{(n+1)-}\} = K_{a1\_NOM} \{\text{H}_2\text{A}^{n-}\} \{\text{H}^+\}^{-1}$	
Silica polymerization	
$\{\text{Si}_2\text{O}_2(\text{OH})_5^-\} = K_{\text{poly\_Si}} \{\text{Si}(\text{OH})_4\}^2 \{\text{H}^+\}^{-1}$	$K_{\text{poly\_Si}} = 10^{-5}$ (Svensson <i>et al.</i> , 1986)
Surface acid–base reactions	
$[\equiv \text{FeOH}_2^+] = (K_{sa1}^{\text{app}})^{-1} [\equiv \text{FeOH}] \{\text{H}^+\}$	$K_{sa1}^{\text{app}} = K_{sa1}^{\text{int}} E_{-1}^*$
$[\equiv \text{FeO}^-] = (K_{sa2}^{\text{app}}) [\equiv \text{FeOH}] \{\text{H}^+\}^{-1}$	$K_{sa2}^{\text{app}} = K_{sa2}^{\text{int}} E_{-1}$
Arsenate adsorption	
$[\equiv \text{FeH}_2\text{AsO}_4] = K_{sL1\_As5}^{\text{app}} [\equiv \text{FeOH}] \{\text{H}_2\text{AsO}_4^-\} \{\text{H}^+\}$	$K_{sL1\_As5}^{\text{app}} = K_{sL1\_As5}^{\text{int}}$
$[\equiv \text{FeHAsO}_4^-] = K_{sL2\_As5}^{\text{app}} [\equiv \text{FeOH}] \{\text{H}_2\text{AsO}_4^-\}$	$K_{sL2\_As5}^{\text{app}} = K_{sL2\_As5}^{\text{int}} E_{-1}$
Silica adsorption	
$[\equiv \text{FeSiO}(\text{OH})_3] = K_{sL1\_1Si}^{\text{app}} [\equiv \text{FeOH}] \{\text{Si}(\text{OH})_4\}$	$K_{sL1\_1Si}^{\text{app}} = K_{sL1\_1Si}^{\text{int}}$
$[\equiv \text{FeSiO}_2(\text{OH})_2^-] = K_{sL2\_1Si}^{\text{app}} [\equiv \text{FeOH}] \{\text{Si}(\text{OH})_4\} \{\text{H}^+\}^{-1}$	$K_{sL2\_1Si}^{\text{app}} = K_{sL2\_1Si}^{\text{int}} E_{-1}$
$[\equiv \text{FeSi}_2\text{O}_2(\text{OH})_3] = K_{sL1\_2Si}^{\text{app}} K_{\text{poly\_Si}} [\equiv \text{FeOH}] \{\text{Si}(\text{OH})_4\}^2$	$K_{sL1\_2Si}^{\text{app}} = K_{sL1\_2Si}^{\text{int}}$
$[\equiv \text{FeSi}_2\text{O}_3(\text{OH})_4^-] = K_{sL2\_2Si}^{\text{app}} K_{\text{poly\_Si}} [\equiv \text{FeOH}] \{\text{Si}(\text{OH})_4\}^2 \{\text{H}^+\}^{-1}$	$K_{sL2\_2Si}^{\text{app}} = K_{sL2\_2Si}^{\text{int}} E_{-1}$
NOM adsorption	
$[\equiv \text{FeHA}^{n-}] = K_{sL1\_NOM}^{\text{app}} [\equiv \text{FeOH}] \{\text{H}_2\text{A}^{n-}\}$	$K_{sL1\_NOM}^{\text{app}} = K_{sL1\_NOM}^{\text{int}} E_{-n}$
$[\equiv \text{FeA}^{(n+1)-}] = K_{sL2\_NOM}^{\text{app}} [\equiv \text{FeOH}] \{\text{H}_2\text{A}^{n-}\} \{\text{H}^+\}^{-1}$	$K_{sL2\_NOM}^{\text{app}} = K_{sL2\_NOM}^{\text{int}} E_{-(n+1)}$

\* $E_{-i} = \exp\left(\frac{e\Psi}{RT}\right)$ ;  $i = 1, n$  or  $n + 1$ ;  $\Psi$  = surface potential in volts.

densities it is quite likely that significant adsorption (or surface precipitation) of silica species larger than a dimer is occurring (Davis *et al.* 2002). Swedlund and Webster did not report data on either surface charge or zeta potential;

therefore, it was not possible to compare the two models in this regard, although a failure to properly account for trends in zeta potential provided the initial impetus for developing the SCM directly considering dimeric silica.



**Figure 1** | Conceptualization of modeling natural organic matter and its (a) deprotonation and (b) adsorption reactions.

To compare the ability of the models to predict interference, the SCM established in this work was modified for the wide-pH-range data in Swedlund & Webster (1999) (Table 3). Adsorption constants were optimized to fit single-adsorbate (either As(V) or silica) adsorption data in Swedlund and Webster (Table 4) and were used to predict As(V) removal in the presence of silica (Figure 3(a)). It was appropriate to recalibrate the adsorption constants due to differences in preparation of the iron hydroxide adsorbent in the two studies. The model considering dimeric silica reduced the average predictive error for As(V) to 10% from 16% over the pH range of 6.1–9.9. Interestingly, consideration of dimeric silica adsorption led to a consistent slight overprediction of silica interference (i.e. underprediction of As(V) removal). The model considering only monomeric silica consistently underpredicted silica interference to As(V) adsorption at pH below 8.5, which would be expected if dimeric silica interfered with As(V) adsorption due to increased electrostatic repulsion or site competition.

In summary, while our result confirms the conclusion of Swedlund & Webster (1999) that most of the interference could be accounted for by a model that considers only

monomeric silica, inclusion of dimeric species provided much better predictive ability for silica data alone. The silica portion of the model in this work is also conceptually consistent with the Swedlund and Webster observation that silica adsorption beyond a monomer was occurring. In addition, inclusion of dimeric silica provided somewhat better predictive ability for As(V) adsorption in the presence of high levels of silica, although it is not clear whether this is due to an additional fitting parameter or due to better description of the underlying reactions actually involved.

### Practical evaluation of the model in relation to existing data

Usefulness of the SCM in explaining a few practical observations regarding As(V) removal by adsorption to metal hydroxides was evaluated. One important issue is attempting to reconcile the relative importance of coagulant dose versus coagulation pH in facilitating As(V) removal. The first case study illustrates a scenario where As(V) removal was controlled by coagulant dose. In contrast, in the second case study of As(V) removal by coagulation in a

**Table 2** | Values of surface complexation model constants optimal for experimental data

<b>Fe(OH)<sub>3</sub>(am) parameters</b>					
$f_s$ (mol sites/mol Fe)	$A_s$ (m <sup>2</sup> /g)	$K_{sa1}^{int}$	$K_{sa2}^{int}$		
0.247	6924	$5.13 \times 10^{-8}$	$1.17 \times 10^{-9}$		
<b>NOM parameters</b>					
$n$	<b>HOCC (mg C/mol H<sub>2</sub>A<sup>n-</sup>)</b>			$K_{a1,NOM}$	
0.44	$9.70 \times 10^4$			$9.00 \times 10^{-3}$	
<b>Arsenate and NOM adsorption constants</b>					
	$K_{sL1}$	$K_{sL2}$	Number of points	$r^2$	
As(V)	$1.51 \times 10^{15}$	$1.30 \times 10^7$	12	0.942	
NOM	$1.53 \times 10^{10}$	$6.68 \times 10^3$	12	0.928	
<b>Silica adsorption constants</b>					
$K_{sL1,1Si}$	$K_{sL2,1Si}$	$K_{sL1,2Si}$	$K_{sL2,2Si}$	Number of points	$r^{2*}$
$< 1.90 \times 10^1$	$< 1.97 \times 10^{-7}$	$9.50 \times 10^{11}$	$3.90 \times 10^5$	12	0.883

\* $r^2 = 0.840$  when  $A_s = 600$  m<sup>2</sup>/g.

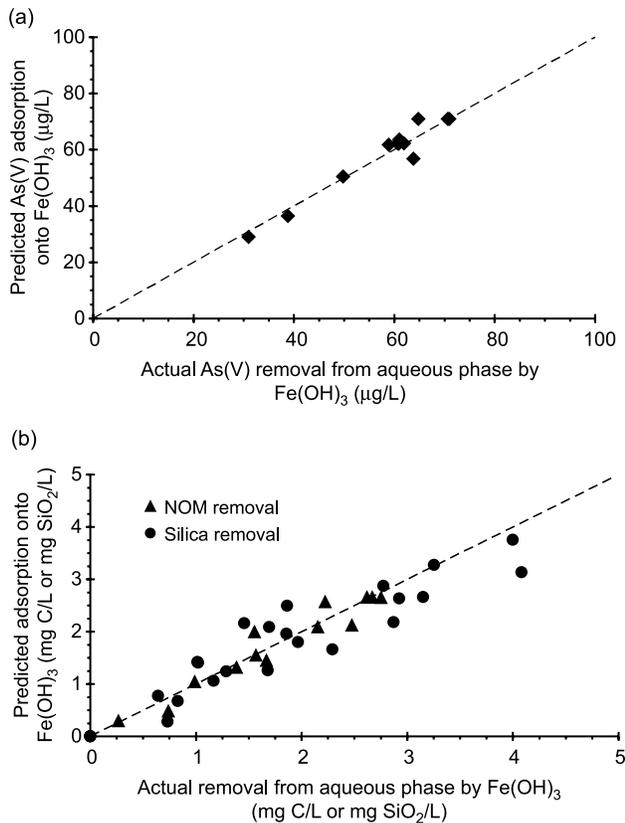
water with much higher silica, it was observed that coagulation pH exerted a much stronger control over As(V) removal. From the practical perspective of trying to achieve effective As(V) removal at minimum cost, understanding the interplay between coagulant dose and coagulation pH in a given water is important because this interplay controls the selection of an optimal combination of treatment chemicals (acids and coagulants). An effort was made to determine if the SCM could be used in this capacity to resolve the apparent discrepancies in observations between the different studies.

#### Simplified Langmuir isotherm: arsenic removal controlled by coagulant dose

McNeill & Edwards (1997) examined As(V) removal at water utilities in the United States practicing coagulation or Fe/Mn removal. At these utilities, which had up to 5 mg/L

of silica in their water and a coagulation pH of up to 7.8, percentage As(V) removal was a function only of the Fe(OH)<sub>3</sub> formed (Figure 4), consistent with expectations based on a linear isotherm. Although the SCM was calibrated for preformed ferric hydroxides and not for those formed *in situ* during coagulation, the SCM does predict the quantitative trend in the McNeill and Edwards data for a representative water quality (Fig. 4).

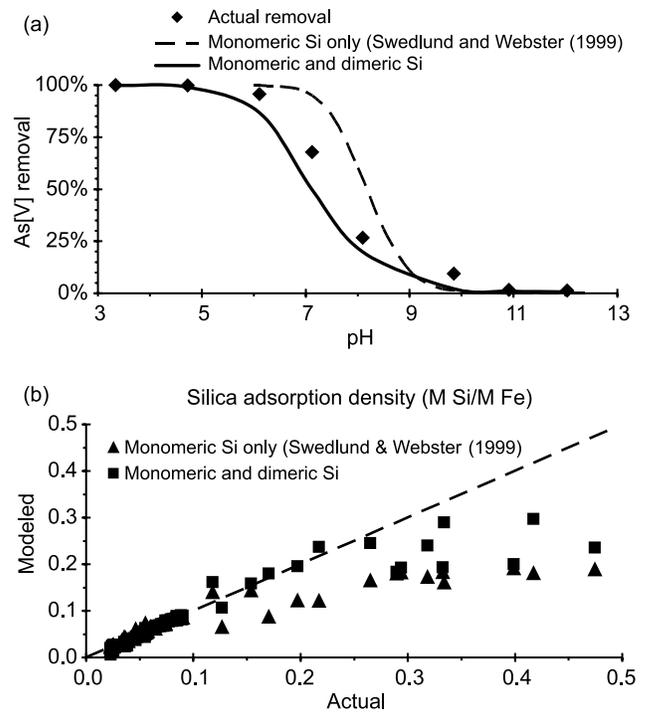
Applying the SCM to the range of pH, As(V) concentrations, silica, calcium and TOC levels in a given water described by McNeill & Edwards (1997) illustrated somewhat less quantitative agreement between the model and actual data, most likely because it was calibrated for preformed solids and actual removal by adsorption/co-precipitation mechanisms are more complex. However, model predictions of As(V) removal as a function of coagulant dose in a given water could always be closely approximated by a linear isotherm. The latter observation is consistent with the



**Figure 2** | Surface complexation modeling fitted to adsorption data for (a) As(V) and (b) NOM and silica onto ferric hydroxides. (Fe = 10 mg/L; pH = 6.00, 7.25, or 8.50; ionic strength =  $1.9 \times 10^{-3}$  –  $3.7 \times 10^{-3}$  eq/L; initial As(V) = 62 or 71 µg/L; initial NOM = 7.0 or 7.4 mg C/L; initial silica = 0–50 mg SiO<sub>2</sub>/L).

practical observations by Edwards (1994) and McNeill *et al.* (2002), who noted the simplified Langmuir isotherm could be adapted to describe As(V) removal as a function of Fe(OH)<sub>3</sub> formed even in many waters with pH well above 9.0 if the *K* value was appropriately adjusted.

The surface complexation model reduces to a linear isotherm when there is a great excess of surface sites relative to the sorbate concentration and electrostatic components of adsorption are relatively constant (Hering *et al.* 1996; McNeill & Edwards 1997). For the water samples tested by McNeill & Edwards (1997), the model predicted that silica and TOC always occupied less than 30% of the total available surface sites on the iron. Thus, the assumption regarding excess surface sites is valid considering the µg/L levels of As(V) in the raw waters. Likewise, we note that, in water treatment practice, effective agglomeration and removal of particles will not be obtained if surface charge



**Figure 3** | Comparison between prediction of As(V) removal using a model considering monomeric silica only in Swedlund & Webster (1999) versus a model that also considered dimeric silica (this work). (a) Arsenate removal in the presence of 1.8 mM of silica (108 mg/L as SiO<sub>2</sub>) and 0.1 M NaNO<sub>3</sub>; total Fe(OH)<sub>3</sub>(s) = 1 mM (55.8 mg/L Fe); initial As(V) = 4000 µg/L. (b) Actual silica adsorption density reported in Swedlund & Webster (1999) versus modeled silica adsorption density.

differs greatly from neutrality, and it is possible that this practical constraint explains why electrostatic forces could be relatively constant for the data collected. In any case, this analysis confirms that, for a fairly wide range of practically relevant circumstances, predictions based on more complicated surface complexation models can be closely approximated by simple linear isotherms.

### Arsenate removal more strongly influenced by pH

Pilot testing of As(V) removal via coagulation–microfiltration in water from Albuquerque, New Mexico demonstrated that, in at least some practical circumstances, As(V) removal could not be described by a linear isotherm. That is, although 1–3 mg/L of iron was dosed in that work, for the experimental data presented in Figure 5 and in other data collected during the study (Tong 1997; Clifford *et al.* 1997, 1998; Ghurye *et al.* 1998), the percentage As(V) removal was more sensitive of coagulation pH and less

**Table 3** | Additional and modified equilibrium expressions for solution reactions and surface complexation reactions for a wide pH range

Solution acid–base reactions	
$\{\text{H}_2\text{AsO}_4^-\} = K_{a1\_As5} \{\text{H}_3\text{AsO}_4\} \{\text{H}^+\}^{-1}$	$K_{a1\_As5} = 10^{-2.24}$ (Dzombak & Morel, 1990)
$\{\text{HAsO}_4^{2-}\} = K_{a1\_As5} K_{a2\_As5} \{\text{H}_3\text{AsO}_4\} \{\text{H}^+\}^{-2}$	$K_{a2\_As5} = 10^{-6.96}$ (Dzombak & Morel, 1990)
$\{\text{AsO}_4^{3-}\} = K_{a1\_As5} K_{a2\_As5} K_{a3\_As5} \{\text{H}_3\text{AsO}_4\} \{\text{H}^+\}^{-3}$	$K_{a3\_As5} = 10^{-11.50}$ (Dzombak & Morel, 1990)
$\{\text{SiO}_2(\text{OH})_2^{2-}\} = K_{a1\_Si} K_{a2\_Si} \{\text{Si}(\text{OH})_4\} \{\text{H}^+\}^{-2}$	$K_{a2\_Si} = 10^{-12.6}$ (Stumm & Morgan, 1996)
Arsenate adsorption	
$[\equiv\text{FeH}_2\text{AsO}_4] = K_{sL1\_As5}^{\text{app}} [\equiv\text{FeOH}] \{\text{H}_3\text{AsO}_4\}$	$K_{sL1\_As5}^{\text{app}} = K_{sL1\_As5}^{\text{int}}$
$[\equiv\text{FeHAsO}_4^-] = K_{sL2\_As5}^{\text{app}} [\equiv\text{FeOH}] \{\text{H}_3\text{AsO}_4\} \{\text{H}^+\}^{-1}$	$K_{sL2\_As5}^{\text{app}} = K_{sL2\_As5}^{\text{int}} E_{-1}^*$
$[\equiv\text{FeAsO}_4^{2-}] = K_{sL3\_As5}^{\text{app}} [\equiv\text{FeOH}] \{\text{H}_3\text{AsO}_4\} \{\text{H}^+\}^{-2}$	$K_{sL3\_As5}^{\text{app}} = K_{sL3\_As5}^{\text{int}} E_{-2}$
$[\equiv\text{FeOHAsO}_4^{3-}] = K_{sL4\_As5}^{\text{app}} [\equiv\text{FeOH}] \{\text{H}_3\text{AsO}_4\} \{\text{H}^+\}^{-3}$	$K_{sL4\_As5}^{\text{app}} = K_{sL4\_As5}^{\text{int}} E_{-3}$
Silica adsorption	
$[\equiv\text{FeSiO}_3(\text{OH})^{2-}] = K_{sL3\_1Si}^{\text{app}} [\equiv\text{FeOH}] \{\text{Si}(\text{OH})_4\} \{\text{H}^+\}^{-2}$	$K_{sL3\_1Si}^{\text{app}} = K_{sL3\_1Si}^{\text{int}} E_{-2}$

$$^*E_{-i} = \exp\left(\frac{zeF\psi}{RT}\right); i = 1, 2, 3, n \text{ or } n + 1$$

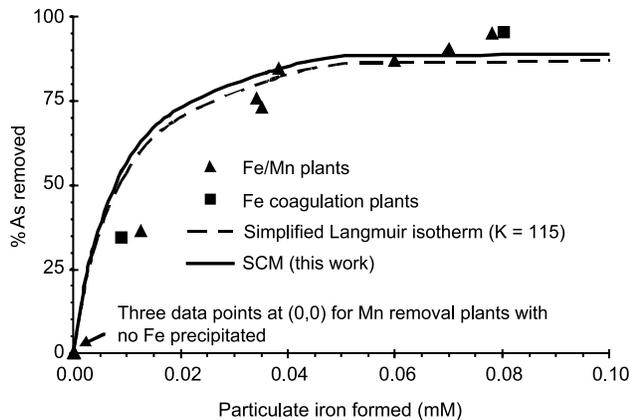
sensitive to coagulant dose. This water also contained a high concentration of silica (51 mg/L as SiO<sub>2</sub>).

The SCM developed in this work was able to predict the correct trend in removal observed in the Albuquerque study (Figure 5). The model also explains why pH was a more important factor in controlling As(V) removal in a water of this type. As a general rule, the lower the pH, the lower the

competition from silica due to both electrostatic considerations and availability of surface sites (Davis *et al.* 2002). For instance, in the Albuquerque water at pH 8.5, the SCM predicts that silica occupied 60% of the surface sites and that the surface potential on the iron was –117 mV. As the pH is decreased to 7.0, the model predicts that the surface potential increases to –64 mV and that only 47% of

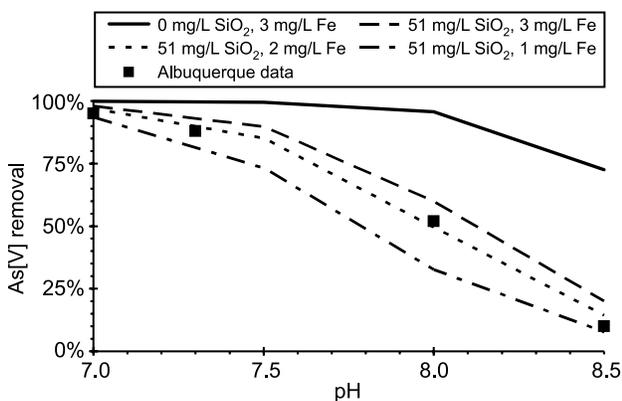
**Table 4** | Values of surface complexation model adsorption constants optimized to fit Swedlund & Webster (1999) data

As(V) adsorption constants					
$K_{sL1}$	$K_{sL2}$	$K_{sL3}$	$K_{sL4}$	$r^2$	
$2.54 \times 10^{10}$	0	$5.99 \times 10^{-2}$	$3.16 \times 10^{-10}$	0.999	
Silica adsorption constants					
$K_{sL1\_1Si}$	$K_{sL2\_1Si}$	$K_{sL3\_1Si}$	$K_{sL1\_2Si}$	$K_{sL2\_2Si}$	$r^2$
0	$2.33 \times 10^{-3}$	0	$2.11 \times 10^{12}$	$5.01 \times 10^5$	0.989



**Figure 4** | Predictions of As(V) removal as a function of coagulant dose using the simplified Langmuir isotherm of McNeill & Edwards (1997) and the SCM in this work for a representative water at pH 7.8 containing 5 mg/L of  $\text{SiO}_2$ , 3 mg/L of TOC and 200 mg  $\text{CaCO}_3$ /L of hardness. Data points represent percentage As(V) removal at seven full-scale treatments as reported by McNeill and Edwards with coagulation pH between 7.1–8.5, some of which were sampled more than once.

surface sites are occupied by silica. Both of these changes explain why a linear isotherm cannot accurately describe As(V) removal in Albuquerque water, as well as the observation that reduced coagulation pH can be a very effective means of improving As(V) removal even if coagulant dose is held constant (Figure 5). In such waters, depressing coagulation pH by bubbling  $\text{CO}_2$  or by dosing acid might be particularly helpful in enhancing As(V) removal.



**Figure 5** | Arsenate removal by coagulation–microfiltration in an Albuquerque pilot study. The water contained 51 mg/L of silica and the coagulant dose was 1–3 mg/L as Fe. Lines representing SCM predictions for different levels of Fe dosed indicate the primary importance of pH in controlling As(V) removal.

## CONCLUSIONS

- Surface complexation modeling is a useful tool in understanding competitive interference from silica and NOM during As(V) removal by adsorption.
- Consideration of dimeric silica adsorption in the SCM improves on previous models both conceptually and in terms of predictive accuracy.
- If silica concentrations are low and pH is about 7.8 or less, As(V) removal is not a strong function of pH and removal can often be described by a linear isotherm.
- If silica concentrations are high and pH is above about 7.8, silica occupies a significant number of surface sites and also reduces the surface potential, leading to more substantial interference with As(V) adsorption. In such cases, As(V) removal is a stronger function of pH and is not likely to be described by a linear isotherm.
- The model is also capable of estimating surface charge and surface potential—future work should attempt to test this in prediction of critical coagulant doses and particle settling efficiency via coagulation.

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