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EFFECT OF SOLUTION CHEMISTRY ON ARSENIC
SORPTION BY Fe- AND Al- BASED DRINKING-WATER
TREATMENT RESIDUALS

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EFFECT OF SOLUTION CHEMISTRY ON ARSENIC SORPTION BY Fe- AND Al- BASED DRINKING-WATER TREATMENT RESIDUALS

ABSTRACT

Drinking-water treatment residuals (WTR) have been proposed as a low-cost alternative sorbent for arsenic (As)-contaminated aquatic and soil systems. However, limited information exists regarding the effect of solution chemistry on As sorption by WTR. A batch incubation study was carried out to investigate the effect of solution pH (3-9) on As(V) sorption by Al- and Fe- based WTR as a function of solid: solution ratio (SSRs) and initial As concentration. The effect of competing ligands (phosphate-P(V) and sulfate), and complexing metal (calcium) on As(V) sorption envelopes at the optimum SSR (200 g L⁻¹) was also evaluated. At 200 g L⁻¹ SSR, maximum As(V) sorption (~ 100%) exhibited by the Fe-WTR was limited at the pH range of 3-7, whereas, the Al-WTR demonstrated ~100% As(V) sorption in the entire pH range. The negative pH effect on As(V) sorption became more pronounced with increasing initial As concentrations and decreasing SSR. Sorption of As(V) by surfaces of both WTR decreased in the presence of P(V), exhibiting strong pH dependence. Only for the Fe-WTR, increased dissolved iron concentrations at pH > 7 supported a Fe-hydroxide reductive dissolution mechanism to account for the enhanced As sorption at alkaline pH. Addition of sulfate did not influence As(V) sorption by both WTR. A cooperative effect of calcium on As(V) sorption was observed at alkaline pH due to the formation of a calcium-arsenate phase. The constant-capacitance model provided reasonable fits to the sorption envelope data for both single-ion and binary-ion (As and P) systems, but it was unable to explain the enhanced As sorption by the Fe-WTR at pH >7.

Keywords: Arsenic, sorption, drinking-water treatment residual (WTR), water quality, remediation.

INTRODUCTION

Contaminant immobilization on a sorbent surface has gained wide public acceptance as a highly efficient and safe method for removing arsenic (As) from contaminated (waste)water. Well-known sorbents for immobilization of As include: granular-activated alumina (Rosenblum and Clifford, 1983; Lin and Wu, 2001), ferric (oxy)hydroxide (Driehaus et al., 1998, Wang and Reardon, 2001), laterite (Bhattacharya, 2002), activated carbon (Pattanayak et al., 2000), and more recently, granular-activated carbon impregnated with ferrous chloride (Gu et al., 2005), natural red earth (Vithanage et al., 2006), and some industrial by products such as red mud and red gypsum (Lombi et al., 2004). However, significant economic costs associated with the use of the above mentioned As immobilizing-agents hinders their application to developing countries, or individual municipalities of developed countries (Makris et al., 2006). The utilization of a waste by-product generated from the drinking-water treatment process (i.e. the drinking water treatment residual, or WTR) has been suggested as a cost effective method for As immobilization. Addition of iron (Fe) or aluminum (Al) salts to raw water to remove colloids, color and sediment generates WTR that contain very high concentrations of Fe-, or Al-hydroxides (Elliott et al., 1991; Makris et al., 2005).

Earlier batch experiments in our laboratory demonstrated the huge affinity of both Al- and Fe-hydroxide based WTR in removing As from aqueous solutions, reaching As sorption capacities of at least $15,000 \text{ mg kg}^{-1}$ (Makris et al., 2006). After 2d, nearly complete (99%) removal of As was achieved (at 1:5 solid: solution ratio or SSR), with minimum As desorption from the WTR (Makris et al., 2006). X-ray absorption spectroscopy showed strong, inner-sphere complexes between sorbed As and the Al- or Fe-hydroxide components of WTR (Makris et al., 2007). However, there is no detailed study on the effect of solution chemistry (pH, initial load,

SSR, competing ligands, or complexing metals) on As sorption by WTR. Solution chemistry parameters, such as, pH, initial As concentration, and co-occurrence of other ions strongly affect the binding dynamics of As to Al/Fe hydr (oxide) surfaces (Jain and Loeppert, 2000; Smith et al., 2002). Sorption of arsenate [As(V)] by amorphous Al/Fe hydroxides was highly pH-dependent, reaching maximum sorption at acidic pH (< 6) followed by a gradual decline with increasing pH (Manning and Goldberg, 1996; Jain and Loeppert, 2000; Burns et al., 2006). Variable, and often high concentrations of anions coexist with As(V), interfering with As sorption dynamics (Awual et al., 2008). Phosphate, whose concentrations in ground water typically exceed those of As, can be particularly effective in competing with As(V) for sorption sites on Al/Fe oxide mineral surfaces (Manning and Goldberg, 1996; Jain and Loeppert, 2000). A suite of surface complexation models have been successfully used to predict the competitive sorption of As(V) and P(V) on Fe/Al oxide surfaces (Manning and Goldberg, 1996; Meng et al., 2000).

Other anions such as chloride, nitrate, carbonates, and bicarbonates showed insignificant effect on As(V) sorption by possible formation of outer-sphere surface complexes with Fe/Al hydr(oxides) (Livesey and Huang, 1981; Fuller et al., 1993; Meng et al, 2000; Tanada et al., 2003; Yang et al., 2006; Ramesh et al., 2007). Few studies have shown, however, that sulfate, a major component in most surface and subsurface aquatic systems (Awual et al., 2008), influenced As(V) adsorption on alumina as well as iron oxides (Allard and Grimvall, 1988; Wilkie and Hering, 1996). Other studies have shown a cooperative effect of complexing ions, such as, calcium on As(V) sorption in hydrous ferric oxide surfaces (Smith et al., 2002). It is not clear, however, whether similar trends could be expected for the WTR. WTR is primarily amorphous masses of Fe and Al hydr(oxides), that also contains small quantities of sediments, activated carbon, and humic substances produced from the raw water, that are produced during

the water purification processes (Elliott and Dempsey, 1991; Makris et al., 2005). Oxyanion (As or P) sorption by WTR was influenced by specific physicochemical properties of WTR, such as, specific surface area, total C content and porosity (Makris et al., 2005). On the other hand, increasing SSR from 25 to 200 g L⁻¹ showed significant increase in the amount of sorbed As by WTR (Makris et al., 2006). Increasing initial As concentrations in solution decreased As sorption by both Al- and Fe-based WTR and this effect became more pronounced with decreasing SSR (Makris et al., 2006). However, these studies were conducted at a single pH and none of our earlier studies investigated possible interactions between pH, SSR and initial As concentration on the amount of sorbed As by WTR. Previous studies showed pH-dependent sorption of phosphate-P(V) [a chemical analogous of As(V)] by an Al-based WTR in the absence and presence of sulfate and chloride (Kim et al., 2002; Yang et al., 2006; Razali et al., 2007). Similarities between the chemical characteristics of P(V) and As(V) molecules led us to hypothesize that P(V) exerts a significant influence on As(V) sorption by WTR.

The present study aimed at evaluating As(V) sorption by WTR (Al- and Fe-based) as a function of pH at different initial As concentrations, and SSRs. The effect of competing ligands (P(V) and sulfate) and complexing metal (calcium) on As(V) sorption was also investigated at an optimum SSR. Finally, surface complexation modeling (SCM) was performed using the constant capacitance model (CCM) to fit As(V) sorption data on Al- and Fe-WTR surfaces for the single ion (only As), and binary ion [As+ phosphorus (P)] systems. The set of constants optimized for the P single ion system were used as fixed parameters to predict competitive sorption of As/P binary data. The WTR was modeled as a composite of mainly Al- or Fe-hydr(oxides) for the Al-, or Fe-based WTR, respectively.

MATERIALS AND METHODS

WTR Collection and Characterization

The Fe- and Al-based WTR samples were obtained from drinking-water treatment plants in Tampa, Florida. and Bradenton, Florida, USA, respectively. After air-drying and passage through a 2-mm sieve, WTR samples were characterized for several physicochemical properties as earlier discussed in Nagar et al. (2009). In brief, solution pH, electric conductivity, and organic matter content were measured using standard protocols (Ben-Dor and Banin, 1989; Hanlon et al., 1997a,b). Oxalate-extractable Fe and Al concentrations were determined using Tamm's reagent (Loeppert and Inskeep, 1966). Adequate blanks, duplicates and matrix spikes were used to meet quality assurance and quality control requirements.

Experimental Design

Arsenic(V) Sorption Experiments in the Absence of Competing Ligands and Complexing Metal

Arsenic sorption envelopes were constructed by adjusting a series of 7 pH levels (3-9) with a predetermined volume of 1M HCl and NaOH. Preliminary experiments were conducted with periodical pH adjustments to determine the total amount of 1M HCl and NaOH required for the final desired pH. Samples were reacted with four initial As concentrations (375, 750, 1500 and 3000 mg L⁻¹) at three SSRs (50, 100, and 200 g WTR L⁻¹). Stock solution of As(V) was prepared in 0.01 M KCl using sodium arsenate heptahydrate (Na₂AsO₄·7H₂O- KR Grade, Aldrich, USA). Samples were shaken (120xg) on a reciprocal shaker for 48 hrs (equilibrium time optimized from previous studies, Makris et al., 2006). Following shaking, the suspensions were centrifuged (4,000xg), filtered (0.45 μm), and the final pH was recorded. All the samples were analyzed for As by an inductively coupled plasma mass spectrometer (ICP-MS), Perkin Elmer.

Arsenic(V) Sorption in the Presence of Competing Ligands and Complexing Metal

Sorption envelopes of As sorption by WTR were also obtained in the presence of competing ligands (P(V) and sulfate) and complexing metal (calcium) at a constant initial As concentration. Initial molar ratios of As to ligands were 1:1, 1:5, 1:10, and 1:20. Stock solutions of P(V) and sulfate were prepared in 0.01M KCl using sodium phosphate monobasic monohydrate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, reagent grade, Fisher, USA) and sodium sulfate decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, reagent grade, Fisher, USA), respectively. The source of calcium was calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, reagent grade, Fisher, USA). Solutions were prepared by adding As and the competing ligand or complexing metal salt, simultaneously. The initial As concentration for the competing ligand experiments was 1500 mg L^{-1} . The initial As concentration (1500 mg L^{-1} or 20 mmol L^{-1}) was chosen to provide near maximum surface coverage, according to previous specific surface area measurements for the WTR (Makris et al., 2004). For the competing metal experiments, initial As concentration was 750 mg L^{-1} .

Surface Complexation Modeling

The CCM was used to fit As(V) sorption as a function of pH for both Al- and Fe-WTR surfaces in the single ion (As or P) and binary ion (As+P) systems. This model assumes that all surface complexes were inner-sphere (Goldberg, 2002). The set of constants that were optimized for the P(V) single ion system were used as fixed parameters to predict competitive sorption of As(V) in the binary ion system (As+P). The computer program FITEQL 4.0 (Herbelin and Westall, 1999) was used. The surface parameters for the Al- and Fe-WTR used in the model simulations were obtained from the literature (Makris et al., 2004; Manning and Goldberg, 1996), and were listed in Table 1. Aqueous reactions and associated equilibrium constants for As(V) were listed in Table 2 (Goldberg and Johnston, 2001; Jing et al., 2003). Surface hydrolysis

constants for Al- and Fe-hydroxides (reactive surfaces for Al- and Fe-WTR, respectively) were also obtained from the literature (Table 2). In the present study, surface complexation constants for monodentate and bidentate As(V) species were determined in separate optimization reactions. The surface functional group was XOH, where X represented a reactive surface hydroxyl bound to a metal ion (Al or Fe) in the oxide mineral, such as, the Al- and Fe- hydroxide components of WTR. The assumption is made that the number of bidentate sites, is equal to half of the monodentate sites (Goldberg et al., 2005).

Statistical Analysis

Data were statistically analyzed using JMP IN version 5.1 (Sall et al., 2005). A two-way analysis of variance was performed to examine the effect of pH, contact time, initial As loads, P(V), sulfate, and calcium on As(V) sorption by WTR. The Tukey-Kramer honest significant difference test was used to evaluate significant differences among treatment means. Data were reported as the mean of triplicate measurements \pm one standard deviation.

RESULTS AND DISCUSSION

Effect of pH on Arsenic (V) Sorption by WTR

General physicochemical properties of the WTR have been discussed elsewhere (Nagar et al., 2009). Arsenate sorption envelopes for the Al-WTR at 200 g L⁻¹ SSR and the lowest initial As concentration (375 mg L⁻¹) indicated ~100% As sorption for the entire pH range (Figure 1a). This trend remained unchanged even after increasing the initial As concentration to 3000 mg L⁻¹ (40 mmol As kg⁻¹ WTR) (Figure 1a). This can be explained by the high external and internal specific surface area, hence the strong As(V) sorption capacity of the Al-WTR (Makris et al., 2006). At the intermediate SSR, As sorption remained at 100%, being independent of pH (Figure 1b). At the lowest SSR (50 g WTR L⁻¹), the magnitude of As sorption remained intact (100%) in

the 3-7 pH range, but at pH >7, a significant ($p < 0.001$) negative pH effect on the amount of As sorbed by the Al-WTR was observed as a function of the initial As concentration used (Figure 1c). At pH < pHzpc (zero point of charge), the positively charged surface of sorbent would likely prefer the sorption of the negatively charged As(V) (O'Neill, 1995; Jain et al., 1999). At pH > pHzpc, OH⁻ dominates the system, resulting in a charge reversal on the hydr(oxide) surfaces which led to electrostatic repulsion between As(V) and surface hydroxyls (generated by accumulation of OH⁻) (Goh and Lim, 2004). The pHzpc for Al-WTR was not determined in this study but literature indicated the pHzpc for Al-hydroxide ranging from 8.5-9.5 (Sparks, 1995). However, effect of pH on As(V) sorption by Al-WTR was only apparent at lowest SSR (Figure 1c). Previous studies on P(V) [a chemically analogous to As(V)] sorption by different Al-WTR also indicated a significant decrease in P(V) sorption with increase in pH from 4.3 to 9 (Kim et al., 2002, Yang et al., 2006).

The typical curvature observed in oxyanion sorption envelopes for amorphous metal hydroxides that was partially the case also for the Al-WTR was further corroborated by the Fe-WTR. The Fe-WTR exhibited a significant ($p < 0.001$) decrease in As(V) sorption as a function of solution pH, paralleling the trend of anion sorption envelopes for amorphous Fe hydroxides (Figure 2). Overall, the negative pH and SSR effect on As sorption was greatly pronounced for the Fe-WTR when compared to that of the Al-WTR. This could be partially explained by the relatively lower As(V) sorption capacity of the Fe-WTR when compared with the Al-WTR (Makris et al., 2006). At any initial As concentration with a 200 g L⁻¹ SSR, As(V) sorption for all initial As concentrations was almost 100% at a pH 3 to 4, decreasing to ~ 60% with a pH increase to 7 (Figure 2a). Arsenate sorption envelopes obtained in this study were similar to those of previous studies on amorphous Fe oxides (Pierce and Moore, 1982; Wilkie and Hering,

1996; Dixit and Hering, 2003). At the lowest SSR (50 g L^{-1}), maximum As(V) sorption (at pH 4) for the lowest As concentration (375 mg L^{-1}) was 90%, which decreased to 45% for the 3000 mg L^{-1} As concentration. When the pH increased to 7, As sorption further decreased to 15% for the 3000 mg L^{-1} As load (Figure 2c).

The present study showed an interesting pattern of increasing As sorption after pH 7 for the Fe-WTR (Figure 2). It was speculated that a reductive Fe-hydroxide (a major component of Fe-WTR) dissolution mechanism could be responsible for the increased As(V) sorption at higher pH levels. A gradual increase in the color of the supernatant with increasing pH led us to hypothesize a possible role of soluble Fe^{2+} being released during sorption of As(V). A gradual increase in soluble Fe^{2+} concentrations was observed only above a pH of 7 (Figure 3). These results were consistent with our previous Fe-WTR-As work at a pH of 6-6.5 where no evolution of soluble divalent Fe was observed (Makris et al., 2006). Previous studies showed that dissolution of iron hydr(oxides) primarily influenced by redox potential, pH, and microbial population (Bennett and Dudas, 2003; Campbell et al., 2006; Kocar et al., 2006). In a column study by Kocar et al. (2006), Fe^{2+} ions increased the retention of As(V) on the As-presorbed ferrihydrite under Fe-reducing conditions and a pH of 7.2. Enhanced retention of As(V) upon reductive dissolution of Fe-WTR may result from the formation of a Fe-As(V) precipitate. The precipitate may be the result of: i) partially utilizing some of the soluble Fe^{2+} ii) incorporation of As(V) in secondary precipitates (Kocar et al., 2006), or iii) creation of new Fe hydroxide surface sites at alkaline pH values (Figure 3). Manning et al. (2002) showed that dissolution of a Mn hydroxide solid and subsequent release of Mn^{2+} into solution created new sites for As(V) sorption. In a column set-up, Kocar et al. (2006) showed that As(V) retention by As-presorbed ferrihydrite coincided with the production of Fe^{2+} under biologically-mediated (by *S.*

putrefaciens) Fe-reducing conditions. Advanced instrumentation (X-ray absorption spectroscopy) and microbial studies are required for further corroborating the increased As(V) sorption by the Fe-WTR at alkaline pH.

Based on the above As(V) sorption envelopes for both Al- and Fe-WTR, a 200 g L⁻¹ SSR was selected as the optimum SSR, because it exhibited the least pH variation in the amount of As sorbed, being always > 65%. The optimum 200 g L⁻¹ SSR was subsequently used for our competing ligand and complexing metal experiments.

Effect of Competing Ligands on Arsenic(V) Sorption by WTR

The co-existence of As (V) and P (V) anions in solution resulted in significant ($p < 0.001$) pH-dependent decrease in As(V) sorption for the Al-WTR (Figure 4a). At an equimolar concentration of P and As (20 mmol L⁻¹ each), near complete sorption of both oxyanions was observed from pH 3 to 7, illustrating the strong oxyanion sorption capacity of the Al-WTR (~12,000 mg kg⁻¹) (Figure 4a). Up to 1:5 As:P molar ratio, a significant ($p < 0.001$) decrease in As(V) sorption by the Al-WTR was observed only for pH > 7 (Figure 4a). At As:P molar ratios of 1:10 and 1:20, the decrease in As(V) sorption was evident throughout the pH range (3-9). These results were in agreement with previous studies that showed that decrease in As(V) sorption is dependent upon the magnitude of soluble P concentrations (Jain and Loeppert, 2000; Livesey and Huang, 1981). Similar deprotonation constants in solution and chemical structure between P(V) and As(V) hints for similar oxyanion effects on the surface charge of the solid (Hongshao and Stanforth, 2001). Ligand exchange with surface hydroxyl ions was the mechanism of P (V) sorption by Al-WTR (Yang et al., 2006). In the presence of equimolar concentration of As and P, P (V) sorption by the Al-WTR was higher than that of As(V) over the entire pH range (Figure 4a). However, this difference was more pronounced at a higher pH

(Figure 4a). These results were in accordance with previous studies, showing a slightly higher affinity of P (V) compared to As(V) for metal oxide surfaces (Hingston et al., 1971; Manning and Goldberg, 1996).

Similar to the Al-WTR, the Fe-WTR showed a significant ($p < 0.001$) decrease in As(V) sorption in the presence of P (V), although the effect was more pronounced (Figure 4b). The decrease in As (V) sorption was highly pH-dependent at both low (1:1 As:P) and high (1:10 As:P) soluble P (V) concentrations. At pH values 4, 6 and 7.5, the magnitude of As(V) sorption by the Fe-WTR in the presence of equimolar P was 99, 90, and 60%, respectively (Figure 4b), whereas under similar conditions, As (V) sorption by the Al-WTR was 99, 99, and 80%, respectively (Figure 4a). Similar to the Al-WTR, the Fe-WTR showed a slight preference for P (V) compared to As (V) as seen in the equimolar (As:P) treatment (Figure 4b). Similar to the untreated (no P added) experiment, there was an approximately 10% increase in As(V) sorption at $\text{pH} > 7$ in the case of the Fe-WTR, when P (V) was added to solution (Figure 4b). At the highest As:P molar ratio (1:20) – equivalent to 220 mmol anion L^{-1} , a large drop (80-90%) in As(V) sorption was observed for the entire pH range (Figure 4b). Increasing the molar As:P ratios from 1:1 to 1:20 led to further decrease in As(V) sorption due to the increased P(V) competition for surface binding sites.

Sulfate had no significant ($p < 0.001$) effect on As(V) sorption by the Al-WTR (Figure 5a). The maximum As(V) sorption by Al-WTR was 100% (equal to 7500 mg As kg^{-1} WTR) in the entire pH range, which remained unchanged despite the wide variation in added sulfate concentrations (20-400 mmol L^{-1}) (Figure 5a). This insignificant effect of sulfate on As(V) sorption could be explained by strong specific binding sites for As(V) on WTR surfaces, while sulfate might form weaker (outer- sphere) complexes (Meng et al., 2000; Yang et al., 2006).

Similar to the Al-WTR, there was no significant ($p < 0.001$) effect of sulfate on As(V) sorption by the Fe-WTR (Figure 5b). These results were also in accordance with previous studies, where researchers found no influence of sulfate on As(V) sorption by Fe-oxides (Jain and Loeppart, 2000; Manful et al., 1989; Meng et al., 2000). The documented slight increase in As(V) sorption by the Fe-WTR was unaffected by the added sulfate concentrations (Figure 5b).

Effect of Complexing Metal on As(V) Sorption by WTR

MINTEQ calculations showed that when As concentration was $>750 \text{ mg L}^{-1}$, a Ca-As mineral was formed (data not shown). Hence, initial As concentration was 750 mg L^{-1} to avoid the onset of precipitation in complexing metal experiments. Because of Al-WTR's extremely high As sorption capacity, As(V) sorption was not affected by incrementally increasing calcium concentrations in solution (Figure 6b). It has been demonstrated that soils exhibiting high As sorption capacities are not influenced by the presence of elevated Ca concentrations in solution (Smith et al., 2002). Conversely, the Fe-WTR showed a significant ($p < 0.001$) increase in As(V) sorption at $\text{pH} > 7$ in the presence of Ca (Figure 6b). At an equimolar ratio of As to Ca, As(V) sorption increased by 20% compared to the control (only As) (Figure 6b). Increasing the As:Ca molar ratio to 1:10, As(V) sorption further increased by 60% at $\text{pH} > 7$ (Figure 6b). Similar Ca-induced increase in As(V) sorption at a higher pH has been reported for both clay minerals and oxides (Wilkie and Hering 1996, Smith et al, 2002, Cornu et al 2003, Burn et al, 2006). An attempt to fit the experimental data by considering the specific sorption of Ca and sorption of various Ca-As species in FITEQL was unsuccessful (data not shown). Therefore, in the experimental condition of the present work (initial As(V) concentration- 750 mg As L^{-1}), a species calculation was performed using the ACT2 program of the Geochemist Workbench 6.0 software (Figure S-1, Supplementary Information). These calculations showed the formation of

calcium arsenate at $\text{pH} > 7$ for As:Ca molar ratios of 1:1 to 1:20 (Figure S-1). It led us to speculate that precipitation of calcium arsenate at a higher pH could be a possible mechanism behind the enhanced As(V) sorption at a higher pH in the present study.

Surface Complexation Modeling

Based on the CCM, surface complexation constants for both monodentate and bidentate surface binding sites of sorbed As(V) by WTR were optimized (Table 3). Single and binary anion experimental data and CCM lines for the Al-WTR using monodentate and bidentate binding mode assumptions were shown in Figure 7. The fit of the model to As(V) sorption data on Al-WTR in single ion system was excellent considering both monodentate and bidentate site assumptions (Figure 7). The model optimization was able to successfully fit the three monodentate and two bidentate surface complexation constants for both As(V) and P(V) (Table 3). Similarities between the As(V) and P(V) sorption envelopes and the observed competition for sorption sites invoked a similar sorption mechanism. The $\log K(\text{int})$ values for the P(V) single-ion system were used to predict experimental sorption envelopes in the binary systems. In binary ion system (As + P), the model fits were superior in quality (as measured by the goodness of fit) when monodentate As(V) surface species was used (Figure 7). In the case of bidentate site assumption, the model developed for the binary system (As+P) slightly underestimated As(V) sorption at $\text{pH} > 7$ (Figure 7).

Similarly, the model provided semi-quantitative predictions of the sorption envelopes for the Fe-WTR in the single ion system (both As(V) and P (V)), although it did not perform well in the pH range of 7-9 (Figure 7). A similar trend was observed for As(V) sorption for binary ion systems, but the system did not converge for the model of bidentate sorption sites (Table 3). Although Fe hydroxides constitute a major component of the Fe-WTR's chemical composition,

there are several other constituents, such as, humic and fulvic acids along with other impurities (activated carbon, polymers, sediment). The plethora of WTR constituents interfering with As sorption might have caused the observed deviation of modeling fit from the experimental data. At the pH range of 7-9, a reductive Fe-hydroxide (major component of Fe-WTR) dissolution mechanism was presumably responsible for the increased As(V) sorption. This speculation was further supported by the lack of similar data in the case of the Al-WTR, which lacked of measurable Fe concentrations at alkaline pH. Inclusion of a Ca-As formed microcrystalline phase at pH>7 did not improve the model fits for the Fe-WTR, suggesting that classical precipitation was not responsible for the enhanced As(V) sorption at alkaline pH environment. Previous X-ray absorption spectroscopy showed that As(V) formed mononuclear bidentate surface complexes on the Fe-WTR surface (Makris et al., 2007), supporting our chemical modeling calculations that showed evidence of both bidentate and monodentate binding motifs.

CONCLUSIONS

Both WTR types performed well in removing As(V) from an aqueous solution that contained a plethora of sorption-interfering ions (P(V), sulfate and calcium) within a wide pH range (3-9). A pH-dependent sorption behavior of the Fe-WTR, typical of oxyanion sorption by amorphous metal hydroxides was observed for all SSR tested, being more prominent for the lowest SSR. No such pH-dependent behavior was observed for all, except for the lowest SSR of the Al-WTR because of its tremendous As sorption capacity. At the optimum SSR (200 g L^{-1}), As(V) sorption by the Al-WTR was nearly complete within the entire pH range (3-9), regardless of the initial As concentration (upto $3000 \text{ mg As L}^{-1}$). At pH>7, As sorption by the Fe-WTR increased without being affected by the presence of other common ions (P (V), sulfate and calcium), presumably due to a Fe hydroxide reductive dissolution mechanism. In the presence of equimolar dose of As

and P, the Al-WTR was capable of sorbing both anions simultaneously (12000 mg anions kg⁻¹ WTR) in the acidic pH range (3-7). The effect of P(V) competition and pH, however, were more pronounced for the Fe-WTR. The Al-WTR was more effective than the Fe-WTR in removing As from a suite of solution chemistry parameters. Arsenate sorption by both Al- and Fe-WTR was unaffected by the addition of sulfate. Precipitation of calcium arsenate at a higher pH increased As(V) sorption by Al- and Fe-WTR in the presence of calcium. The CCM was able to provide a reasonable fit to the experimental data for As(V) sorption in single and binary ion systems for WTR, confirming the formation of inner-sphere surface complexes. However, surface complexation modeling was unable to predict the enhanced As(V) sorption by the Fe-WTR at alkaline pH under the current study's experimental conditions. Advanced experimental and modeling studies are needed to investigate the enhanced As(V) sorption by the Fe-WTR at alkaline pH. Present study provides a thorough understanding of the As sorption by WTR at varying solution chemistry which is crucial in natural aquatic systems. This data set will be very useful in establishing a scientific framework for the use of WTR as an in-situ cost effective sorbent for contaminated aqueous media.

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Supplemental Information: There is a supplementary figure for this manuscript.

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Table 1. Solid and suspension properties used in the constant capacitance modeling of As(V) sorption by Al-WTR and Fe-WTR.

Parameter	Al-WTR	Fe-WTR
Surface Area (m ² g ⁻¹)¶	104.9	27.5
Site Density (site nm ⁻²) ¶	5.4	43.7
Total Surface Sites (mol L ⁻¹)	0.188	0.273
Suspension Density (g L ⁻¹)	200	200
Site types	Monodentate Bidentate	Monodentate Bidentate
Capacitance (F m ⁻²)¥	1.06	1.06

Note: Initial As concentration- 1500 mg L⁻¹, Background Electrolyte- 0.01 M KCl.

¶ Makris et al. (2004)

¥ Manning and Goldberg (1996)

Table 2. Protonation/deprotonation and aqueous reactions with equilibrium constants used in constant capacitance modeling of As(V) adsorption by Al-WTR and Fe-WTR. The Al- and Fe-WTR were modeled as composite of Al- or Fe-oxides, respectively.

Reactions	Log K	
	Al-WTR	Fe-WTR
Protonation/Deprotonation¶		
XOH → XO ⁻ + H ⁺	-9.09	-8.80
XOH + H ⁺ → XOH ₂ ^[+]	7.38	7.31
Aqueous Reactions¥		
H ₃ AsO ₄ → AsO ₄ ³⁻ + 3H ⁺	-20.70	-20.70
H ₃ AsO ₄ → HAsO ₄ ²⁻ + 2H ⁺	-9.20	-9.20
H ₃ AsO ₄ → H ₂ AsO ₄ ⁻ + H ⁺	-2.24	-2.24

¶ Goldberg and Johnston (2001)

¥ Jing et al. (2003)

Table 3. Surface complexation reactions and optimized intrinsic equilibrium constants ($\log K^{\text{int}}$) for the single ion (only As) and binary ion (As+P) systems using constant capacitance model. The set of constants that were optimized for P single ion system were used as fixed parameters to predict competitive adsorption of As/P binary data on WTR surfaces. Model considered both monodentate and bidentate site type assumptions for Al- and Fe-WTR.

Reactions	$\log K^{\text{int}}$	
	Al-WTR	Fe-WTR
Surface Complexation Reactions (Monodentate)		
$\text{XOH} + \text{H}_3\text{PO}_4 \rightarrow \text{XH}_2\text{PO}_4 + \text{H}_2\text{O}$	10.73	5.56
$\text{XOH} + \text{H}_3\text{PO}_4 \rightarrow \text{XHPO}_4^{[-]} + \text{H}_2\text{O} + \text{H}^+$	2.58	-2.36
$\text{XOH} + \text{H}_3\text{PO}_4 \rightarrow \text{XPO}_4^{[2-]} + \text{H}_2\text{O} + 2\text{H}^+$	-5.16	-10.2
$\text{XOH} + \text{H}_3\text{AsO}_4 \rightarrow \text{XH}_2\text{AsO}_4 + \text{H}_2\text{O}$	12.53	6.25
For system containing P	9.54	6.75
$\text{XOH} + \text{H}_3\text{AsO}_4 \rightarrow \text{XHAsO}_4^{[-]} + \text{H}_2\text{O} + \text{H}^+$	4.27	-1.70
For system containing P	1.69	-1.21
$\text{XOH} + \text{H}_3\text{AsO}_4 \rightarrow \text{XAsO}_4^{[2-]} + \text{H}_2\text{O} + 2\text{H}^+$	-3.61	-9.51
For system containing P	-6.25	-9.01
Surface Complexation Reactions (Bidentate)		
$2\text{XOH} + \text{H}_3\text{PO}_4 \rightarrow \text{X}_2\text{HPO}_4 + 2\text{H}_2\text{O}$	12.62	6.31
$2\text{XOH} + \text{H}_3\text{PO}_4 \rightarrow \text{X}_2\text{PO}_4^{[-]} + \text{H}^+ + 2\text{H}_2\text{O}$	4.57	-1.62
$2\text{XOH} + \text{H}_3\text{AsO}_4 \rightarrow \text{X}_2\text{HAsO}_4 + 2\text{H}_2\text{O}$	14.43	7.70
For system containing P	13.41	9.57
$2\text{XOH} + \text{H}_3\text{AsO}_4 \rightarrow \text{X}_2\text{AsO}_4^{[-]} + \text{H}^+ + 2\text{H}_2\text{O}$	4.58	-0.94
For system containing P	2.58	NC

Note: NC- Not converged.

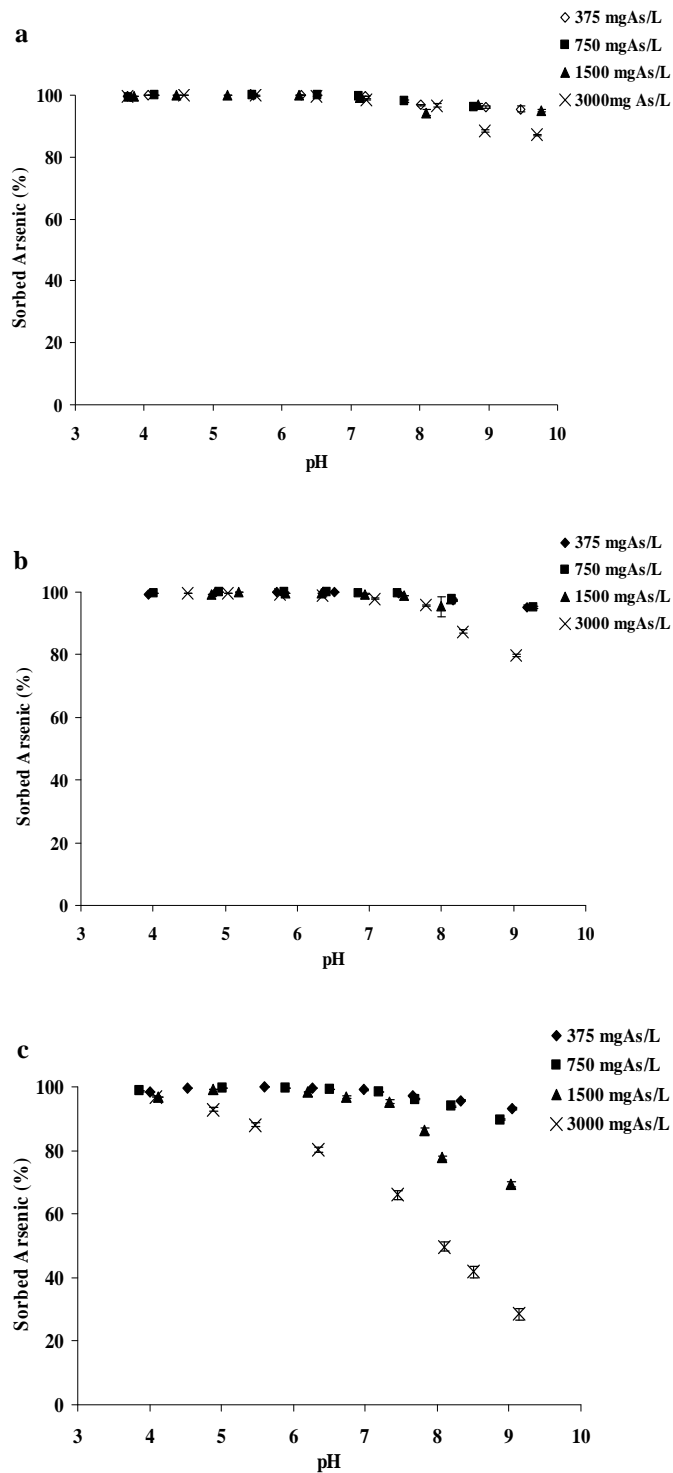


Figure 1. Effect of pH on the amount of As(V) sorbed by Al-WTR at (a) 200 g L⁻¹(a), (b) 100 g L⁻¹, and (c) 50 g L⁻¹SSRs, as a function of different initial As loads (375, 750, 1500, and 3000 mg As L⁻¹). Reaction time: 48 hrs, ionic strength buffer- 0.01 M KCl. Data are the mean of 3 replicates \pm one standard deviation.

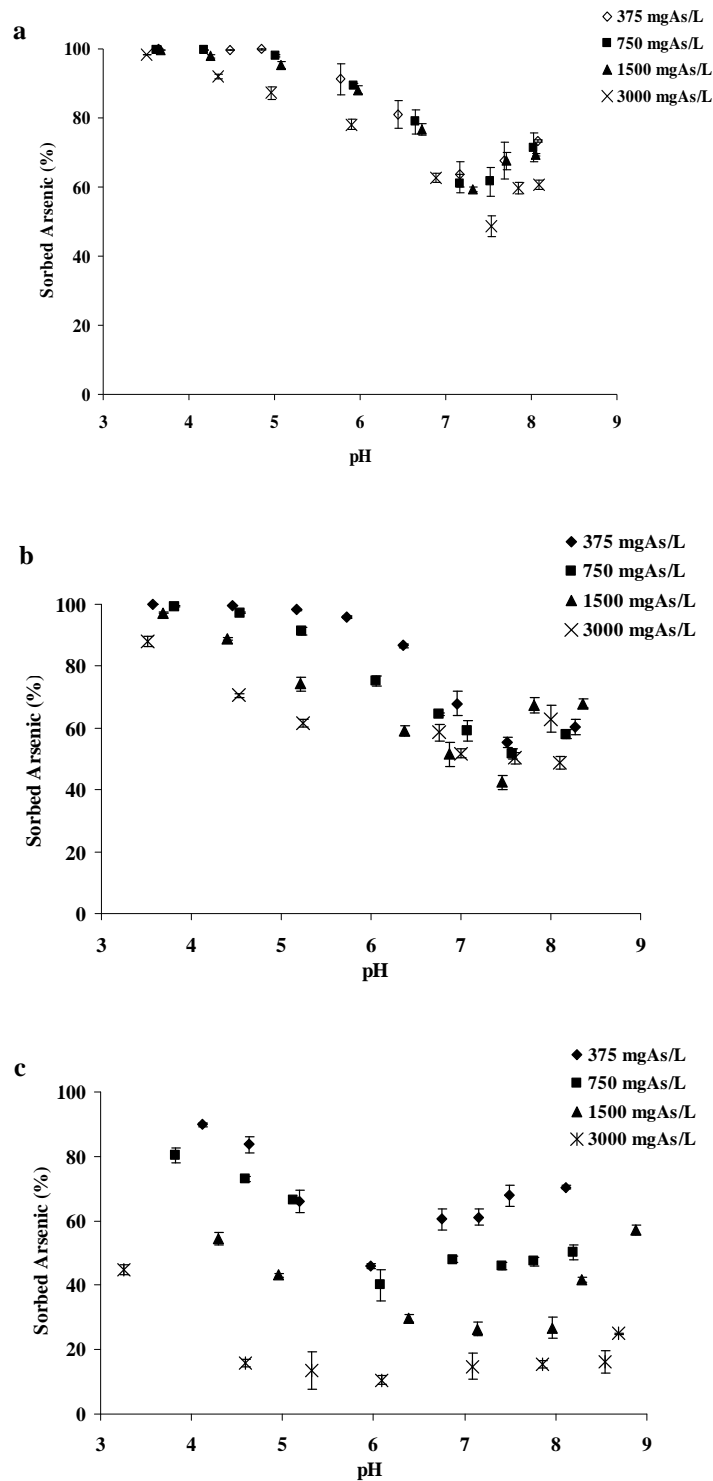


Figure 2. Effect of pH on the amount of As(V) sorbed by Fe-WTR at (a) 200 g L⁻¹, (b) 100 g L⁻¹, and (c) 50 g L⁻¹ SSRs, as a function of initial As loads (375, 750, 1500, and 3000 mg As L⁻¹). Reaction time: 48 hrs, ionic strength buffer- 0.01 M KCl. Data are the mean of 3 replicates \pm one standard deviation.

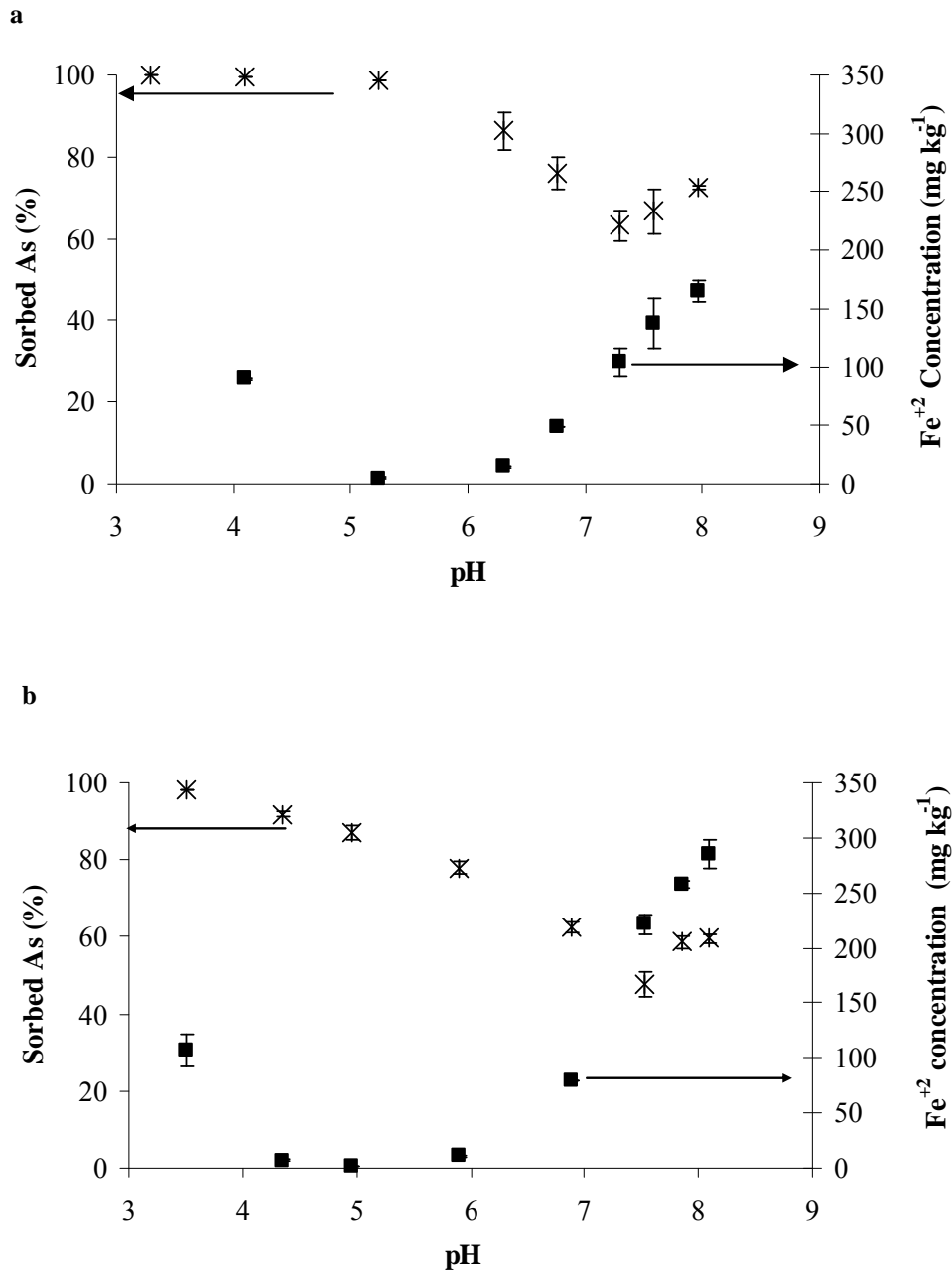


Figure 3. Monitoring dissolved Fe^{2+} concentrations during As(V) sorption by Fe-WTR as a function of pH at (a) 375 mg L^{-1} and (b) 3000 mg L^{-1} initial As concentrations. Similar trend was observed for other initial As concentrations, hence not shown. Reaction time: 48 hrs and solid: solution ratio: 200 g L^{-1} , ionic strength buffer- 0.01 M KCl . Data are the mean of 3 replicates \pm one standard deviation.

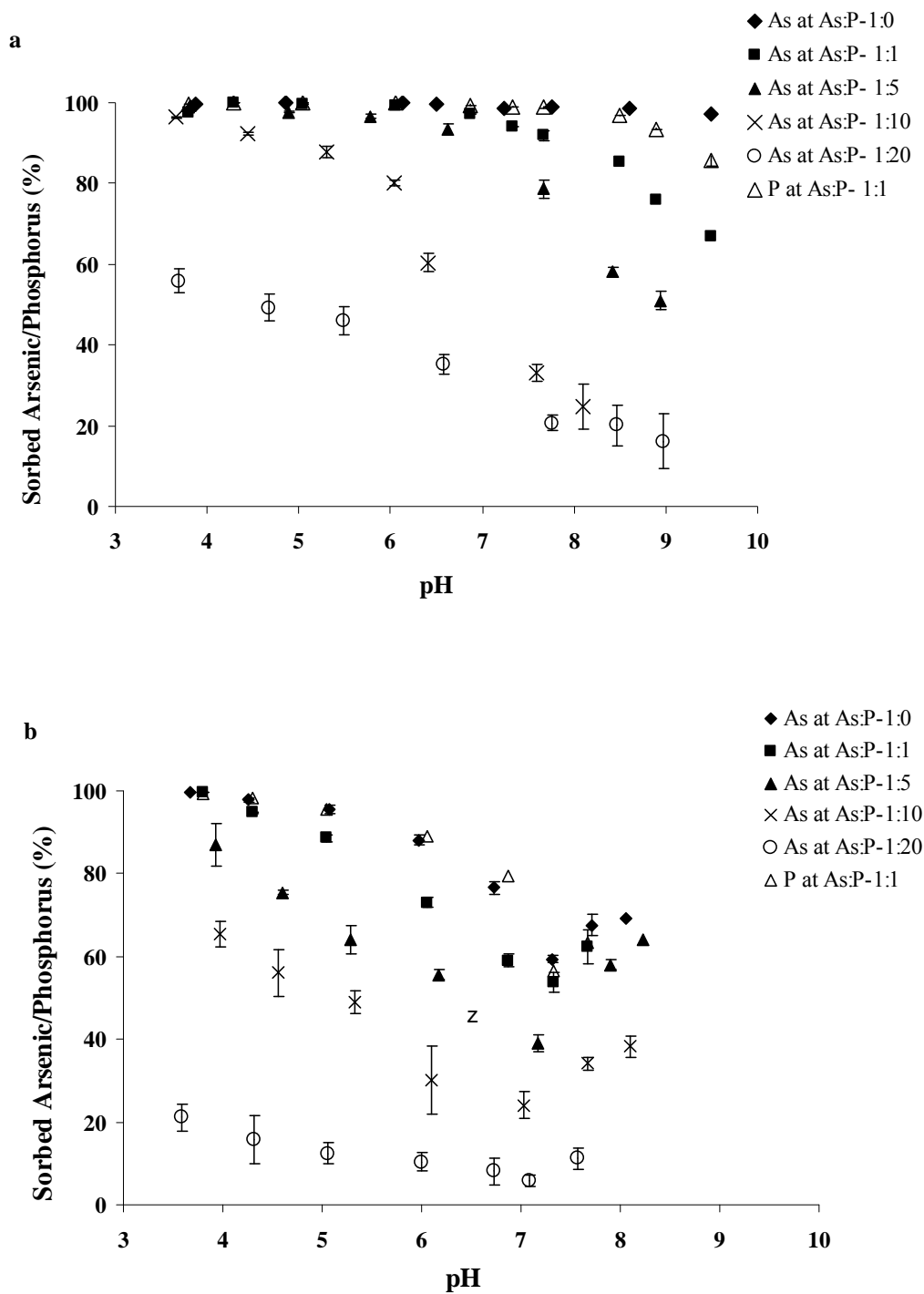


Figure 4: Effect of phosphate on As (V) sorption by (a) Al-WTR and (b) Fe-WTR as a function of pH and different As:P ratios. Initial As concentration – 1500 mg L^{-1} , Reaction time: 48 hrs and SSR: 200 g L^{-1} , ionic strength buffer- 0.01 M KCl . Data are the mean of 3 replicates \pm one standard deviation.

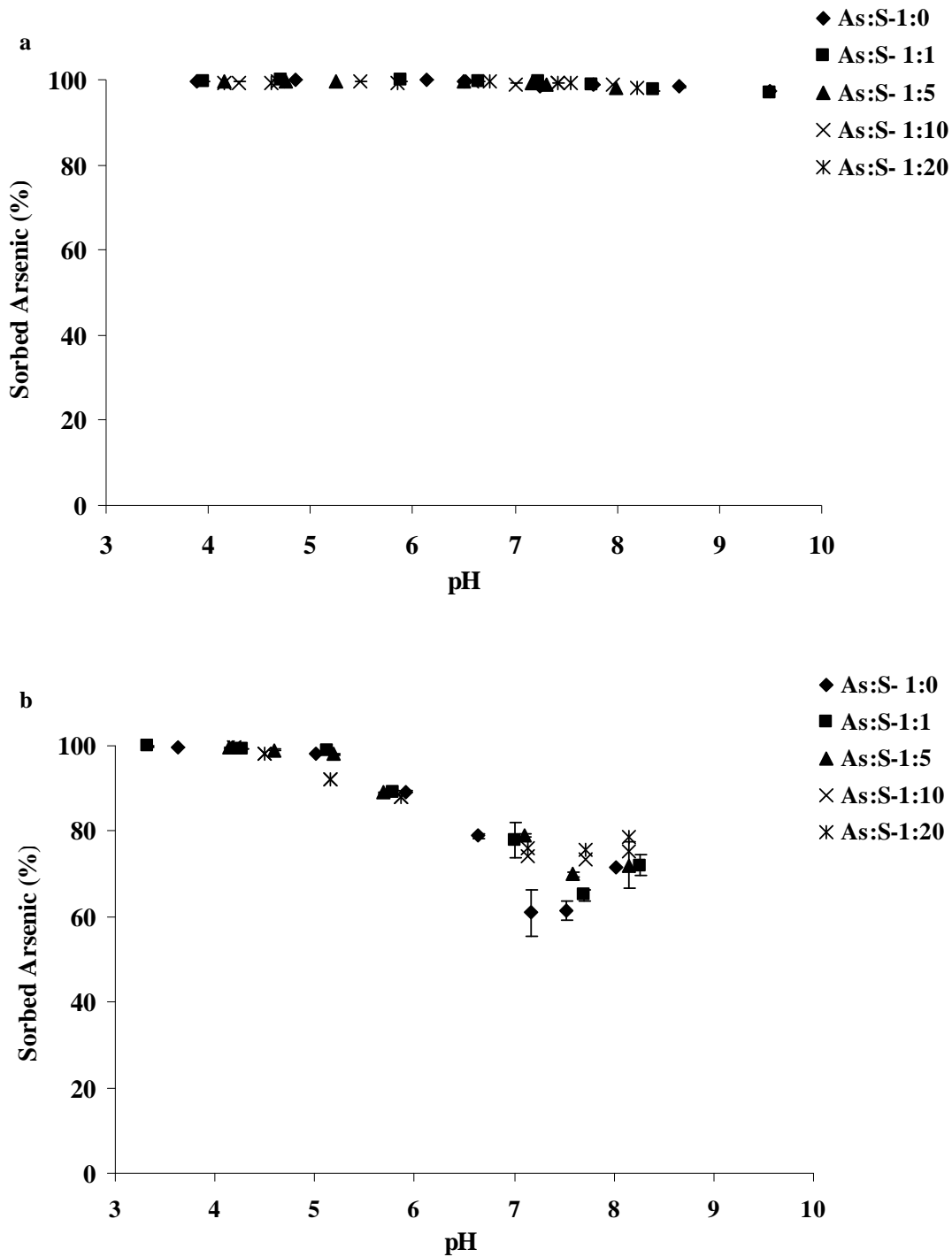


Figure 5: Effect of sulfate on As (V) sorption by (a) Al-WTR and (b) Fe-WTR as a function of pH and different As:S ratios. Initial As concentration – 1500 mg L⁻¹, Reaction time: 48 hrs and SSR: 200 g L⁻¹, ionic strength buffer- 0.01 M KCl. Data are the mean of 3 replicates ± one standard deviation.

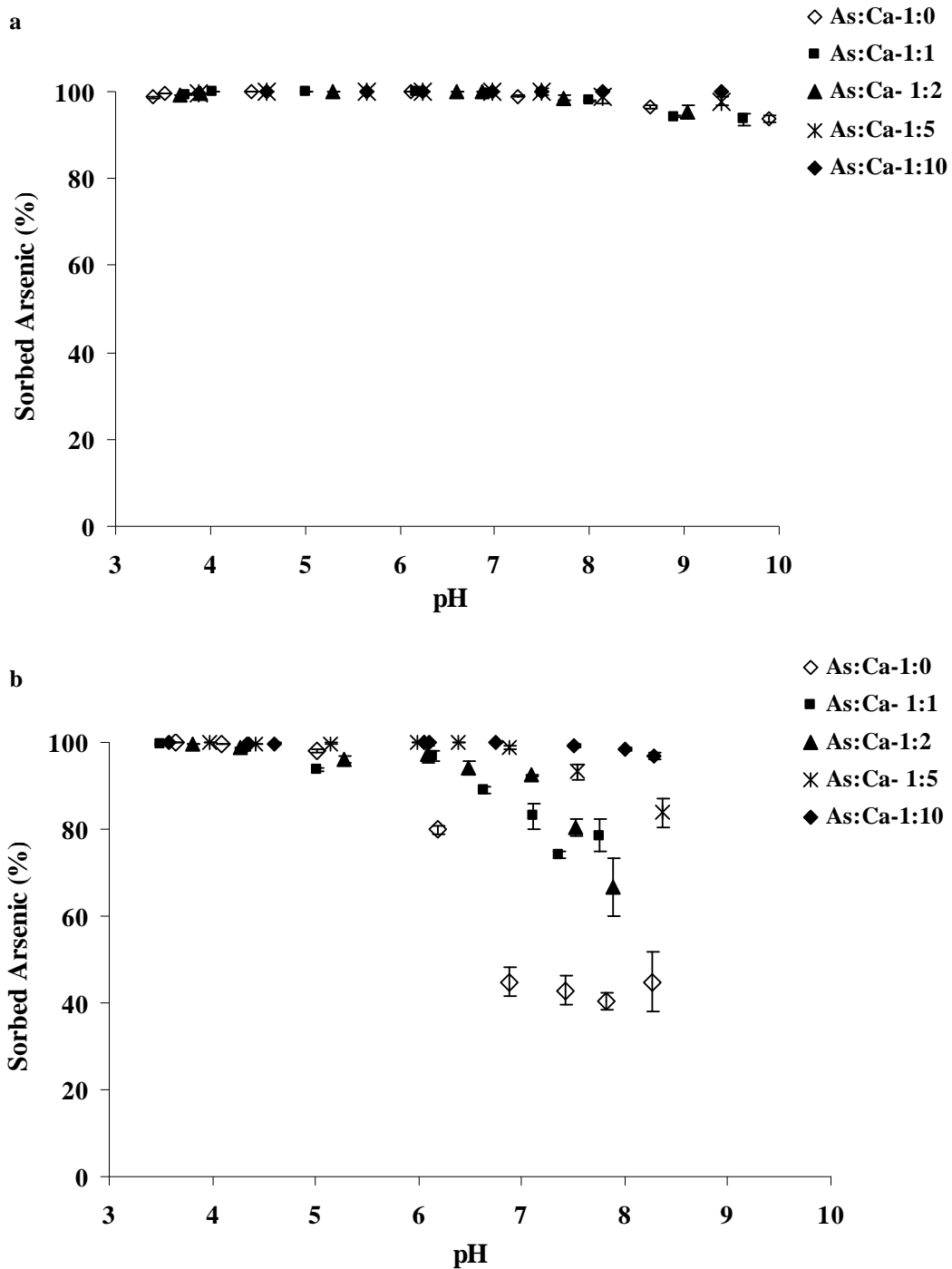
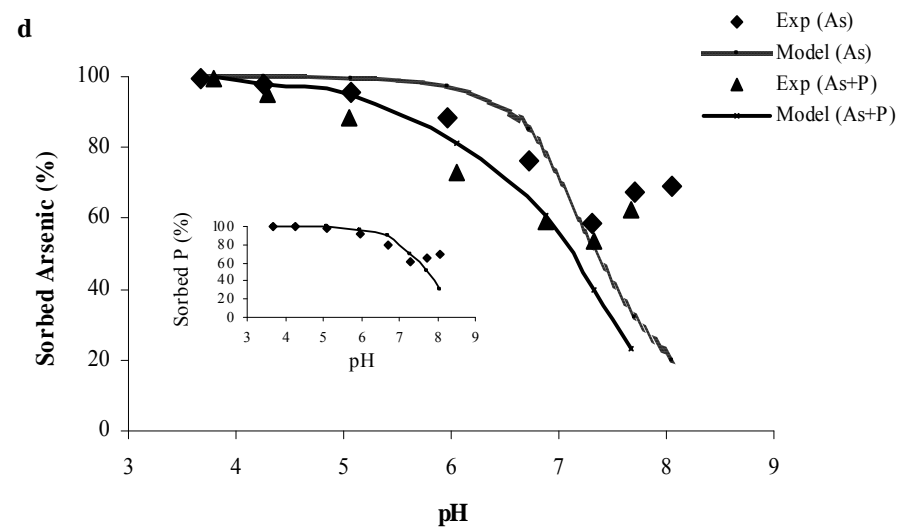
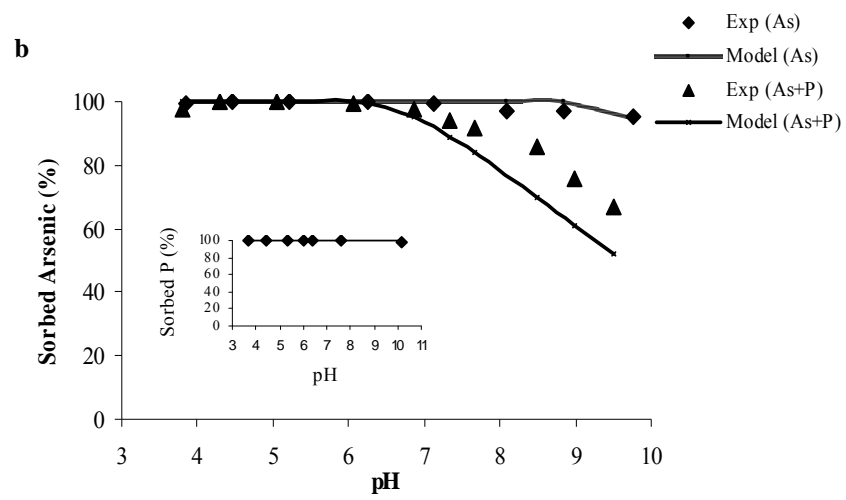
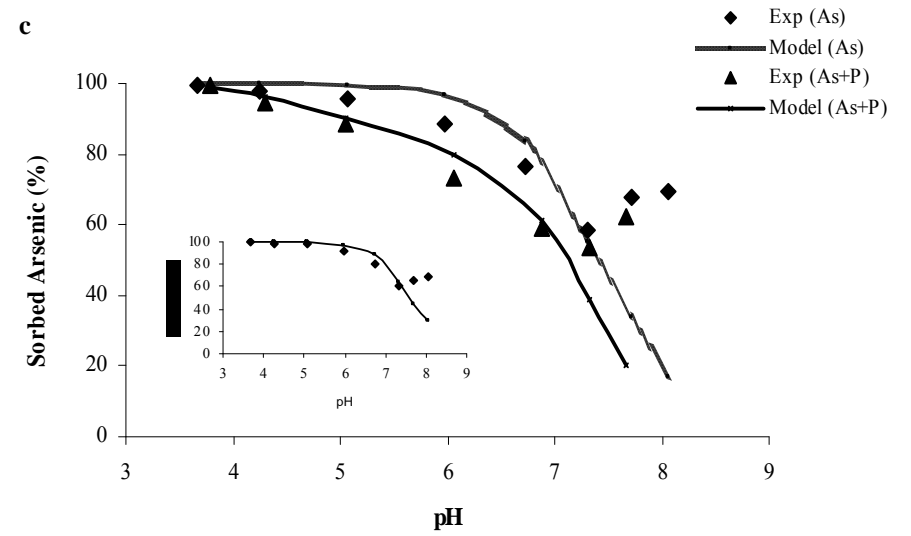
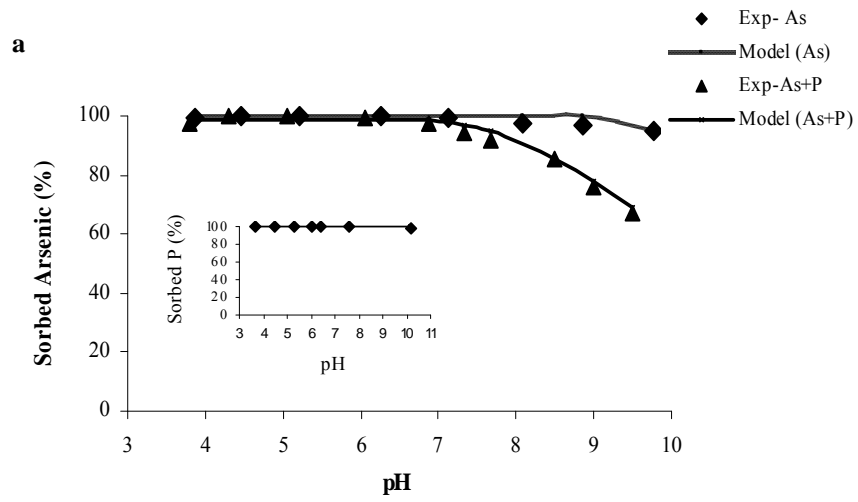


Figure 6: Effect of calcium on As(V) sorption by (a) Al-WTR and (b) Fe-WTR as a function of pH and different As:Ca ratios. Initial As concentration – 750 mg L^{-1} , Reaction time: 48 hrs and SSR: 200 g L^{-1} , ionic strength buffer- 0.01 M KCl . Data are the mean of 3 replicates \pm one standard deviation.

1



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Figure 7: Arsenate (single and binary ion) adsorption envelopes for Al-WTR with Constant Capacitance Model using (a) monodentate and (b) bidentate and for Fe-WTR using (c) monodentate and (d) bidentate site assumptions. Experimental conditions: 20 mM (1500 mg As L⁻¹), As to P molar ratio 1:1, ionic strength buffer- 0.01 M KCl. Inserts: Phosphate (single ion) adsorption envelope for monodentate or bidentate site assumption. Phosphate concentration 20 mM (620 mg P L⁻¹).

SUPPLEMENTARY INFORMATION

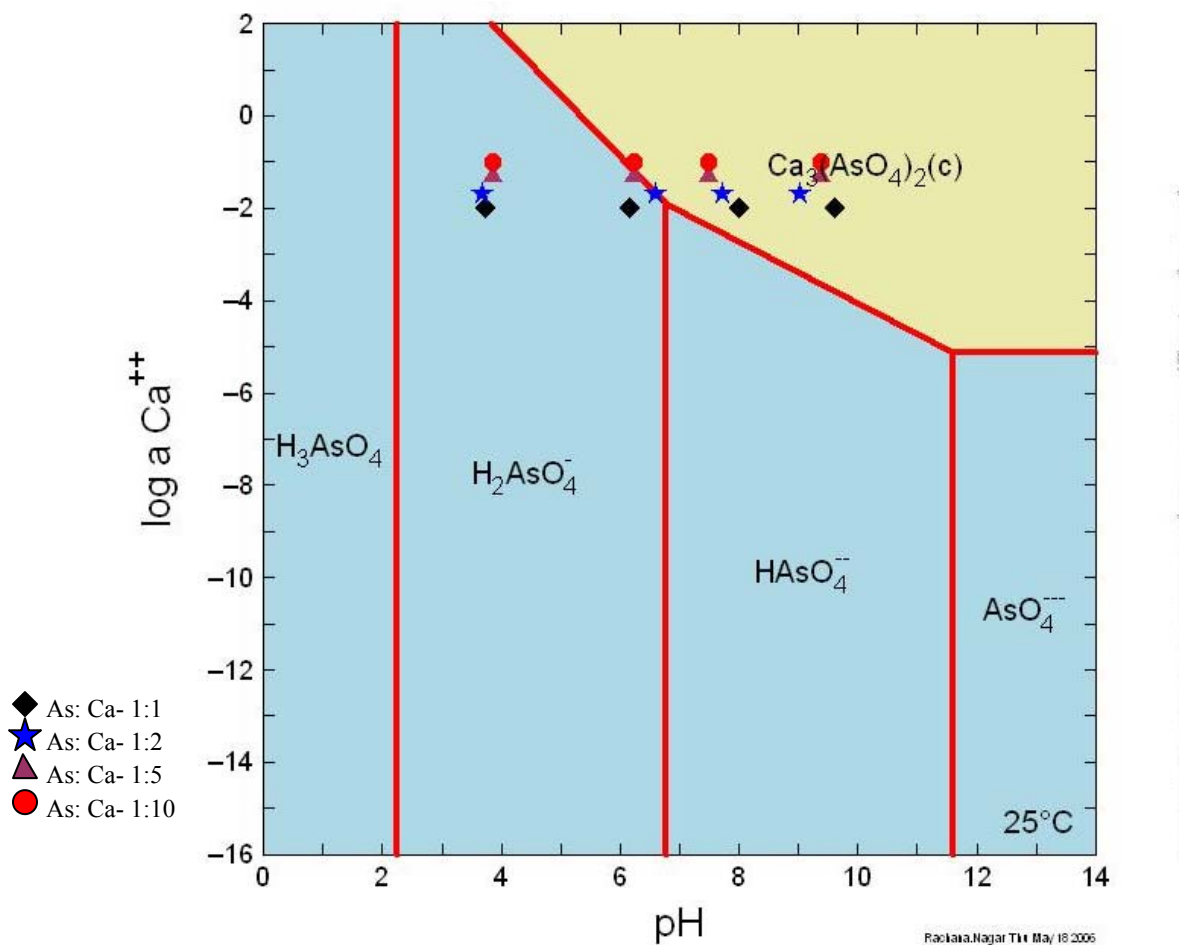


Figure S-1: Solubility diagram of Ca versus pH for the As(V) and calcium (at different molar ratios) using ACT2 program in Geochemist Workbench software, version 6.0. The yellow area represents the formation of calcium arsenate. Experimental conditions: Initial As concentration – 750 mg L^{-1} , As to Ca molar ratio varies from 1:1 to 1:20.