

Inorganic arsenic sorption by drinking-water treatment residual-amended sandy soil: effect of soil solution chemistry

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Abstract Previous studies in our laboratory have demonstrated that drinking-water treatment residuals are effective sorbents of arsenic V. However, the effect of soil solution chemistry on arsenic V sorption by drinking-water treatment residuals-amended soils remains to be explored. The current study uses a batch incubation experimental set up to evaluate the effect of soil solution pH, competing ligands, and complexing metal on arsenic V sorption by a sandy soil (Immokalee series) amended with two rates (25 and 50 g kg⁻¹) of aluminum and iron-based drinking-water treatment residuals. Experiments were conducted at three initial arsenic loads (125, 1,875, 3,750 mg kg⁻¹) and a constant solid: solution ratio of 200 g L⁻¹. An optimum equilibration time of 8 days, obtained from kinetic studies, was utilized for sorption experiments with both aluminum and iron drinking-water treatment residual-amended soil. Presence of phosphate decreased arsenic V sorption by both aluminum and iron drinking-water treatment residual amended soils, with a strong dependence on pH, drinking-water treatment residual

types, drinking-water treatment residual application rates, and phosphate concentrations. Addition of sulfate had no effect on arsenic V sorption by aluminum or iron drinking-water treatment residual-amended soil. A complementing effect of calcium on arsenic V sorption was observed at higher pH. Results elucidating the effect of soil solution chemistry on the arsenic V sorption will be helpful in calibrating drinking-water treatment residual as a sorbent for remediation of arsenic-contaminated soils.

Keywords Arsenic · Drinking-water treatment residuals · Batch incubation · Remediation · Sorption

Introduction

Given the widespread occurrence of arsenic (As) in soils and the potential human health risk posed by this carcinogen, it is imperative to develop cost-effective remediation strategies to treat soil As. 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 arsenic V [As(V)] immobilization. Addition of aluminum (Al) or iron (Fe) salts to raw water to remove colloids, color and sediment generates WTR that contains very high concentrations of Al- and/or Fe-hydroxides (Elliott and Dempsey 1991; Makris et al. 2005). Earlier soil incubation studies in our laboratory demonstrated the high As(V) sorption capacity of WTR in As-contaminated soils and low in Al and Fe oxyhydroxides (i.e., Immokalee and Millhoper series soils) (Sarkar et al. 2007; Nagar et al. 2009). The WTR-amended soils significantly ($p < 0.001$) increased the overall amount of As(V)-sorbed compared to that of unamended controls. The X-ray absorption spectroscopy

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studies by Makris et al. (2007) further supported the stability of sorbed As(V) by WTR, forming inner-sphere mononuclear bidentate complexes with WTR surface hydroxyls. However, thorough understanding on effect of soil solution chemistry on As(V) sorption by WTR-amended soils are crucial before further field trials of WTR application in As-contaminated soils.

Previous studies by Sarkar et al. (2007) showed the significant effect of solid solution ratio (SSR) and WTR application rates on As(V) sorption by two Florida soils amended with Al- or Fe-WTR. Arsenic(V) sorbed by WTR-amended soils significantly increased by increased WTR application rate from 2.5 to 10 %. Recent studies demonstrated that Al- and Fe-WTR performed well in removing As(V) from the aqueous solution that contains variable pH and plethora of interfering ions such as phosphate, sulfate, and calcium (Nagar et al. 2010). It was also reported that Al-WTR was more effective than Fe-WTR in removing As(V) under a variety of solution conditions, hence the effect of pH and phosphate competition was more pronounced for Fe-WTR, in comparison to Al-WTR. Several other studies have shown that sorption of As(V) on the soil depends on the variable charge developed on the soil surface, which is a function of soil solution pH (Goldberg 2002; Goh and Lim 2004). One of the most significant competing ions—phosphate, an analog of As(V), is often used in fertilizers in agricultural areas where As(V) may have been applied as a pesticide or herbicide (Williams et al. 2003). The presence of phosphate was reported to decrease As(V) sorption by Al/Fe hydroxides and soils (Manning and Goldberg 1996; Jain and Loepfert 2000, Goh and Lim 2004). Other anions such as chloride, nitrate, sulfate, and chromate hardly affect As(V) sorption by oxides and hydroxides in soil (Livesey and Huang 1981). Furthermore, sorption of As(V) on soil minerals depends on the residence time, which has been attributed to different sites of reactivity, surface nucleation–precipitation or diffusion into micropores of the sorbent (Sparks 1999). Several kinetic studies have shown that the sorption rate of As(V) on Fe/Al oxide minerals and WTR was initially rapid, but was followed by a slower phase (Raven et al. 1998; O'Reilly et al. 2001; Makris et al. 2006). Sarkar et al. (2007) observed linear As(V) sorption by WTR (without soil) for different As(V) loads (ranging from 225 to 7,500 mg As kg⁻¹ WTR) but proceeded slower thereafter, reaching 100 % after 48 h. There were numerous studies conducted on the effects of soil/solution chemistry on As(V) sorption by pure hydroxides, soils, and WTR (no soil) systems; to the best of our knowledge, no work has been conducted to investigate the effect of soil solution chemistry on As(V) sorption in WTR-amended soils.

The objectives of this study were to (1) evaluate As(V) sorption as a function of soil solution parameters,

namely, contact time and pH at different initial As(V) doses at two WTR application rates, and (2) determine effect of competing ligands (phosphate and sulfate) and complexing metal (calcium) on As(V) sorption in WTR-amended soil at an optimum SSR and two WTR application rates.

Materials and methods

Soil and WTR collection and soil amendment

Immokalee series soil, low in Fe–Al oxyhydroxides, having low As(V) retention capacity, was used for the study. Surface (0–15 cm) soil samples of Immokalee were collected from Southwest Florida Research and Education Center, Immokalee, FL, USA. The Fe- and Al-based WTRs were obtained from the drinking-water treatment plants in Tampa, FL and Bradenton, FL, USA, respectively. Soil and WTR samples were allowed to air-dry and were subsequently passed through a 2-mm sieve before being subjected to characterization and sorption experiments.

WTR (Fe- or Al-based) was thoroughly mixed with the soil at 25 and 50 g kg⁻¹ rates, the moisture content was adjusted to 70 % of water holding capacity and equilibrated for 7 days (7d). The application rates of WTR were chosen based on practical application rates of biosolids in agricultural fields (Elliott et al. 2002). Previous incubation studies have shown that Immokalee soil possesses a negligible As(V) retention capacity (Sarkar et al. 2007); therefore, control (0 % WTR) treatment was not included in the sorption experiments.

WTR and soil characterization

WTR and soil samples were characterized for several physicochemical properties as discussed in Nagar et al. (2009). In brief, solution pH, electric conductivity, and organic matter contents 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 (Loepfert and Inskeep 1996). An inductively coupled plasma mass spectrometer (ICP-MS; Perkin Elmer Elan 9000 model) was used for elemental determinations. Adequate blanks, duplicates and matrix spikes were used to meet quality assurance and quality control requirements.

Experimental design

Arsenic(V) sorption kinetics

Kinetic experiments were conducted at selected time intervals (1, 2, 4, 8, and 16 days) to determine the effect of

contact time on As(V) sorption by WTR-amended soil. Samples were reacted with As(V) solutions to attain initial As loads of 125, 1,850 and 3,750 mg kg⁻¹. This range of As loads was selected based on the previous studies on WTR-amended soils (Sarkar et al. 2007). Stock As(V) solutions were prepared in 0.01 M KCl using sodium hydrogen arsenate (NaH₂AsO₄·7H₂O, KR Grade, Aldrich, USA), and a SSR of 200 g L⁻¹ (Sarkar et al. 2007) was used. All samples were shaken at 120 rpm on a reciprocal shaker, and samples were collected at fixed definite time intervals, centrifuged at 4,000g for 25 min, filtered and analyzed for total soluble As with graphite furnace atomic absorption spectrometer (GFAAS). No pH control was imposed during kinetic experiments but the pH of the samples was measured before and after shaking. Optimum contact time obtained from this experiment was utilized for further sorption experiments.

Arsenic(V) sorption in absence of competing ligands and complexing metal

The effect of pH on As(V) sorption was studied by determining the amount of As(V) sorbed within the pH range of 3–9. After initial soil-WTR equilibration, representative samples were reacted with three initial As loads (125, 1,850, and 3,750 mg kg⁻¹) at a 200 g L⁻¹ SSR. Arsenic(V) sorption envelope was obtained by adjusting a series of pH levels (3–9) with predetermined amount of 1 M HCl or NaOH for each treatment.

Arsenic(V) sorption in presence of competing ligands and a complexing metal

Sorption envelopes for the reaction of As(V) with WTR-amended soil were obtained in the presence or absence of competing ligands (phosphate and sulfate) and a complexing metal (calcium) at an initial As concentration of 125 mg kg⁻¹ (lowest As load). The molar ratios of As to competing/complexing ligands were 1:1, 1:2, and 1:5. Stock solutions of phosphate and sulfate were prepared in 0.01 M KCl using sodium phosphate monobasic monohydrate (NaH₂PO₄·H₂O, Reagent Grade, Fisher, USA) and sodium sulfate decahydrate (Na₂SO₄·10H₂O, Reagent Grade, Fisher, USA), respectively. The source of calcium was calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O, Reagent grade, Fisher, USA). The solution was added to the soil samples at a 200 g L⁻¹ SSR, and pH was adjusted to desired levels (3–9).

Statistical analysis

Statistical analysis was performed using JMP IN version 5.1 (Sall et al. 2005). Two-way analysis of variance was performed to examine the effect of pH, contact time, initial

As loads, competing ligands (phosphate and sulfate), and complexing metal (calcium) on As(V) sorption by WTR-amended soil. Tukey–Kramer honest significant difference test was used to evaluate differences among treatment means. Treatment differences were deemed significant at $p \leq 0.001$.

Results and discussion

Soil and WTR characterization

General physicochemical properties of the Immokalee soil and WTR have been discussed elsewhere (Nagar et al. 2009). In brief, the soil and WTR samples were acidic (pH < 5.4) in nature. Immokalee soil, which was sandy in texture had very low oxalate-extractable Fe and Al contents (0.04 and 0.02 g kg⁻¹) compared to Fe-WTR (Fe content 78.7 g kg⁻¹) and Al-WTR (Al content 82.0 g kg⁻¹), suggesting the very low oxyanion sorption capacity of soil.

Effect of contact time on arsenic(V) sorption by WTR-amended soil

At the lowest initial As concentration (125 mg kg⁻¹), an apparent equilibrium state was reached in 1 day for Al-WTR-amended soils (Fig. 1). Increasing initial As load resulted in increased contact time to reach equilibrium (~4 days), and significant ($p < 0.001$) decreases in As(V) sorption. Sarkar et al. (2007) observed similar trends of As(V) sorption in WTR-amended soil with increasing initial As loads. Makris et al. (2006) reported that in absence of soil, As(V) sorption in Al-WTR (~100 % of As load of 7,500 mg kg⁻¹) reached an equilibrium in 2 days suggesting limited binding sites in Al-WTR-amended soils compared to Al-WTR (no soil). At 25 g kg⁻¹ application rate, 45 % of total As(V) was sorbed in the treatment with initial As load of 1,875 mg kg⁻¹, whereas 23 % sorption was observed in the treatment with initial As load of 3,750 mg kg⁻¹ (Fig. 1a). Increasing application rate to 50 g Al-WTR kg⁻¹ resulted in a significant ($p < 0.001$) increase in overall As(V) sorption (Fig. 1b). Maximum As(V) sorption at equilibrium was 58 and 47 % for 1,875 and 3,750 mg kg⁻¹, respectively.

Similar to Al-WTR-amended soil, maximum As(V) sorption for Fe-WTR-amended soil was achieved in 1 day for the lower initial As load (125 mg kg⁻¹) at both application rates (Fig. 2a, b). With increase in the initial As load, however, a significant ($p < 0.001$) decrease in As(V) sorption and an increase in equilibration time up to 8 days was observed. Longer equilibration time compared to Al-WTR-amended soil (4 days) is consistent with observations in previous studies (Makris et al. 2006; Sarkar et al. 2007; Nagar et al. 2010), and suggested that Al-WTR has greater

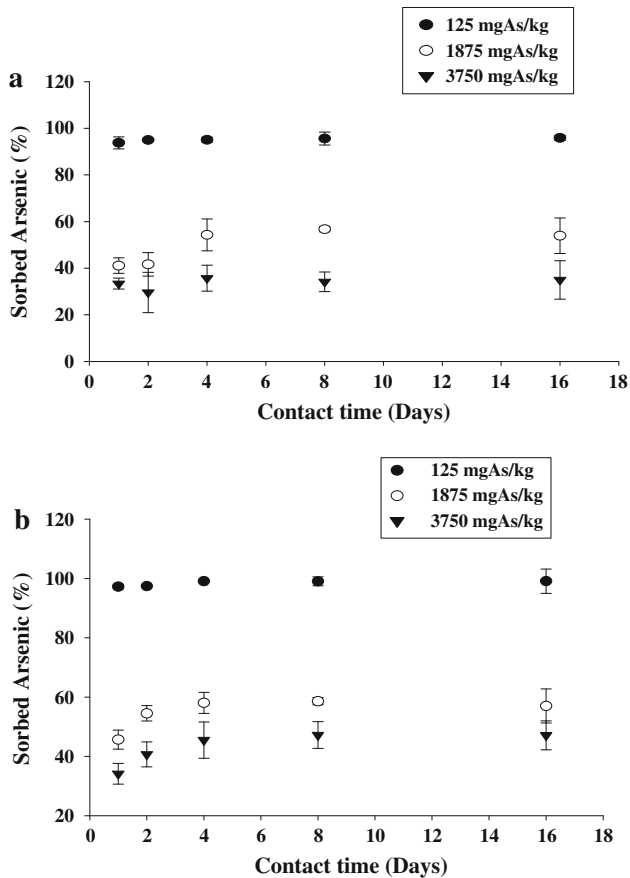


Fig. 1 Arsenate sorption by Al-WTR-amended soil, at 25 g kg^{-1} (a) and 50 g kg^{-1} (b) application rates, as a function of contact time and initial arsenic loads. Data are the mean of three replicates \pm one standard deviation

As(V) sorption capacity compared to the Fe-WTR. Arsenic(V) sorption kinetics by Fe-WTR (without soil) has shown that 2 days were required to reach an equilibrium state (Makris et al. 2006), which increased to 8 days in the present study in the presence of soil with minimal As(V) retention capacity. Similar to Al-WTR-amended soil, Fe-WTR-amended soil showed significant ($p < 0.001$) interaction between rate and initial As concentrations (data not shown). Even though maximum As(V) sorption onto Al-WTR-amended soil was observed after 4 days, further experiments for both the WTR-amended soil were conducted at an optimum reaction time of 8 days for consistency.

Effect of pH on arsenic(V) sorption by WTR-amended soil

For Al-WTR-amended soil (25 g kg^{-1} application rate), maximum As(V) sorption ($\sim 100\%$) for the lowest As load (125 mg kg^{-1}) was observed at a pH range 3.0–6.0, which gradually decreased to 84% with further increase in pH > 6 (Fig. 3a). This trend is similar to pH sorption

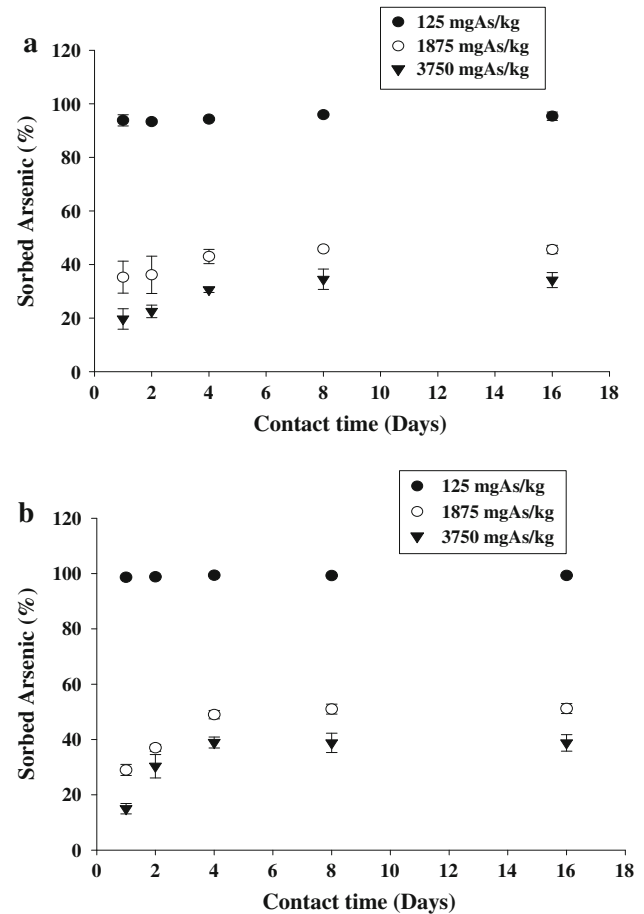


Fig. 2 Arsenate sorption by Fe-WTR-amended soil, at 25 g kg^{-1} (a) and 50 g kg^{-1} (b) application rates, as a function of contact time and initial arsenic loads. Data are the mean of three replicates \pm one standard deviation

envelope for As(V) sorption by Al-WTR (no soil) (Nagar et al. 2010). However, the effect of pH is more pronounced in the present study due to decrease in sorption sites in the presence of soil. With increase in As concentrations in solution, available sorption sites are saturated, resulting in a more pronounced effect of pH (Fig. 3a). Maximum As(V) sorption for higher As loads ($1,875$ and $3,750 \text{ mg kg}^{-1}$) was 76 and 66%, respectively, at pH 3, which decreased to 42 and 19% when pH increased to 9.0 (Fig. 3a). With an increase in application rate (50 g kg^{-1}), there was a significant ($p < 0.001$) increase in As(V) sorption, and the effect of pH became less pronounced (Fig. 3b). This could be explained by an increase in available sites by additional amounts of Fe/Al hydroxides at higher application rate of Al-WTR. The effect of the increased application rate became more pronounced at a higher initial As load due to significant ($p < 0.001$) interaction between rate and initial As loads (data not shown). For higher As loads ($1,875$ and $3,750 \text{ mg kg}^{-1}$), maximum As(V) sorption was 93 and 73%,

respectively, which decreased to 49 and 23 % with an increase in pH to 8.0 (Fig. 3b).

Similar to Al-WTR-amended soil, Fe-WTR-amended soil experienced a significant ($p < 0.001$) decrease in As(V) sorption with an increase in pH, and this effect became more pronounced with increasing As load (Fig. 3). Overall, As(V) sorption by Fe-WTR-amended soil was significantly ($p < 0.001$) lower than Al-WTR-amended soil, similar to trends observed in previous studies (Makris et al. 2006; Sarkar et al. 2007; Nagar et al. 2010). Maximum As(V) sorption (at pH 3) in Fe-WTR-amended soil (25 g kg⁻¹ application rate) for the lowest As load was ~100 %, which decreased to 57 % with increasing initial As concentration to 3,750 mg kg⁻¹. Arsenic(V) sorption further decreased to 30 %, with an increase in pH to 7.5 for 3,750 mg kg⁻¹ As load (Fig. 3c). In the present study, there was an interesting pattern of

increasing As(V) sorption after pH 7.0 and this effect was more prominent at a higher application rate (50 g kg⁻¹) of Fe-WTR (Fig. 3d). For 50 g kg⁻¹ application rate, As(V) sorption decreased to 67 and 23 % for 125 and 3,750 mg kg⁻¹ loads of As, respectively, at pH 7 which increased to 70 and 30 % with an increase in pH > 7 (Fig. 3d). This increase could be contributed by reductive dissolution of Fe-WTR at a higher pH (Nagar et al. 2010). The results were in accordance with our previous studies on As(V) sorption envelopes by Fe-WTR (no soil) (Nagar et al. 2010).

Effect of competing ligands on As(V) sorption by WTR-amended soil

Phosphate resulted in a significant decrease in As(V) sorption for Al-WTR-amended soils with a strong dependence

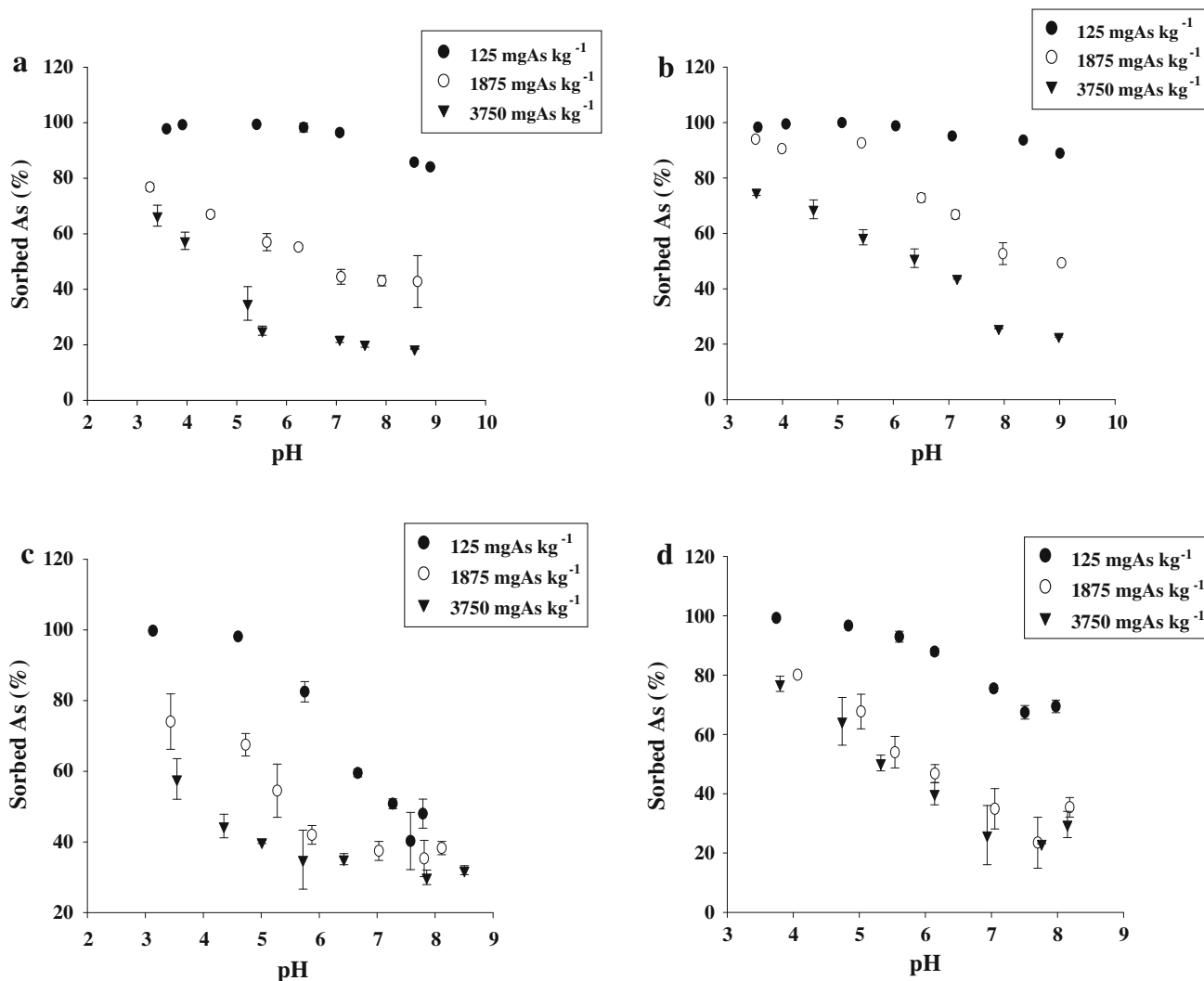


Fig. 3 Arsenic sorption by Al-WTR-amended soil at 25 g kg⁻¹ (a) and 50 g kg⁻¹ (b) application rates and by Fe-WTR-amended soil at 25 g kg⁻¹ (c) and 50 g kg⁻¹ (d) application rates as a function of

pH, and initial arsenic loads. Contact time was 8 days and SSR was 1:5. Data are the mean of three replicates ± one standard deviation

on pH (Fig. 4a, b). At an equimolar concentration of phosphorus (P) and As, As(V) sorption was almost 100 % at pH 3–7 for 25 g kg⁻¹ application rate (Fig. 4a). Arsenic(V) sorption significantly decreased to 80, 60, and 40 % with increasing pH values to 7, 8, and 9, respectively, compared to the control (without P) (Fig. 4a). This trend suggested that at a lower pH, sufficient sorption sites were present on the WTRs for phosphate and As(V) to sorb simultaneously. Increased pH, however, resulted in an increased negative charge on the WTR surface and more competition for potential binding sites (Jain and Loeppert 2000). Similar pH-dependent competition for As(V) sorption in the presence of phosphate has been reported in previous studies on oxide minerals with WTR (Manning and Goldberg 1996; Jain and Loeppert 2000; Nagar et al. 2010). With

increase in the As:P molar ratio to 1:5, a large drop in As(V) sorption was observed over the entire pH range, with only 20 % sorption at pH 8 (Fig. 4a). An increase in the Al-WTR application rate to 50 g kg⁻¹ increased potential binding sites for As(V) sorption resulting in a significant ($p < 0.001$) decrease in the competitive effect of P (Fig. 4b). Al-WTR-amended soil (50 g kg⁻¹) experienced no significant decrease in As(V) sorption with an increase in the As:P molar ratio to 1:5 at pH < 6. However, at pH > 6, As(V) sorption significantly ($p < 0.001$) decreased to 82, 65, and 40 % at As:P molar ratio of 1:1, 1:2, and 1:5, respectively (Fig. 4b).

For Fe-WTR-amended soil, a similar pH-dependent competition effect of phosphate was observed (Fig. 4). The effect of phosphate competition and pH, however, were

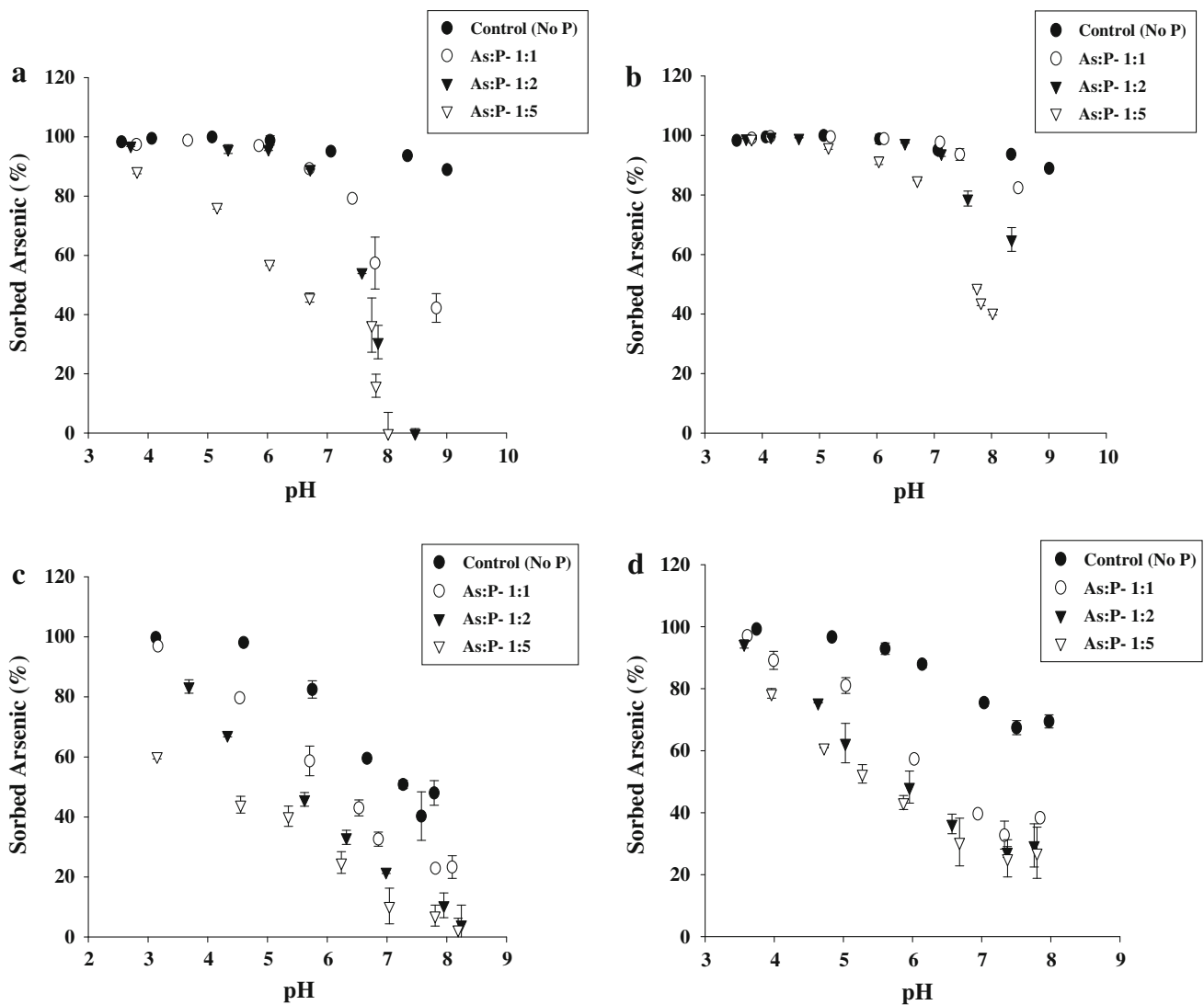


Fig. 4 Effect of competing ion (phosphate) on arsenate sorption by Al-WTR-amended soil at 25 g kg⁻¹ (a) and 50 g kg⁻¹ (b) application rates and by Fe-WTR-amended soil at 25 g kg⁻¹ (c) and 50 g kg⁻¹

(d) application rates as a function of pH. Contact time was 8 days and SSR was 1:5. Initial arsenic load was 125 mg kg⁻¹. Data are the mean of three replicates \pm one standard deviation

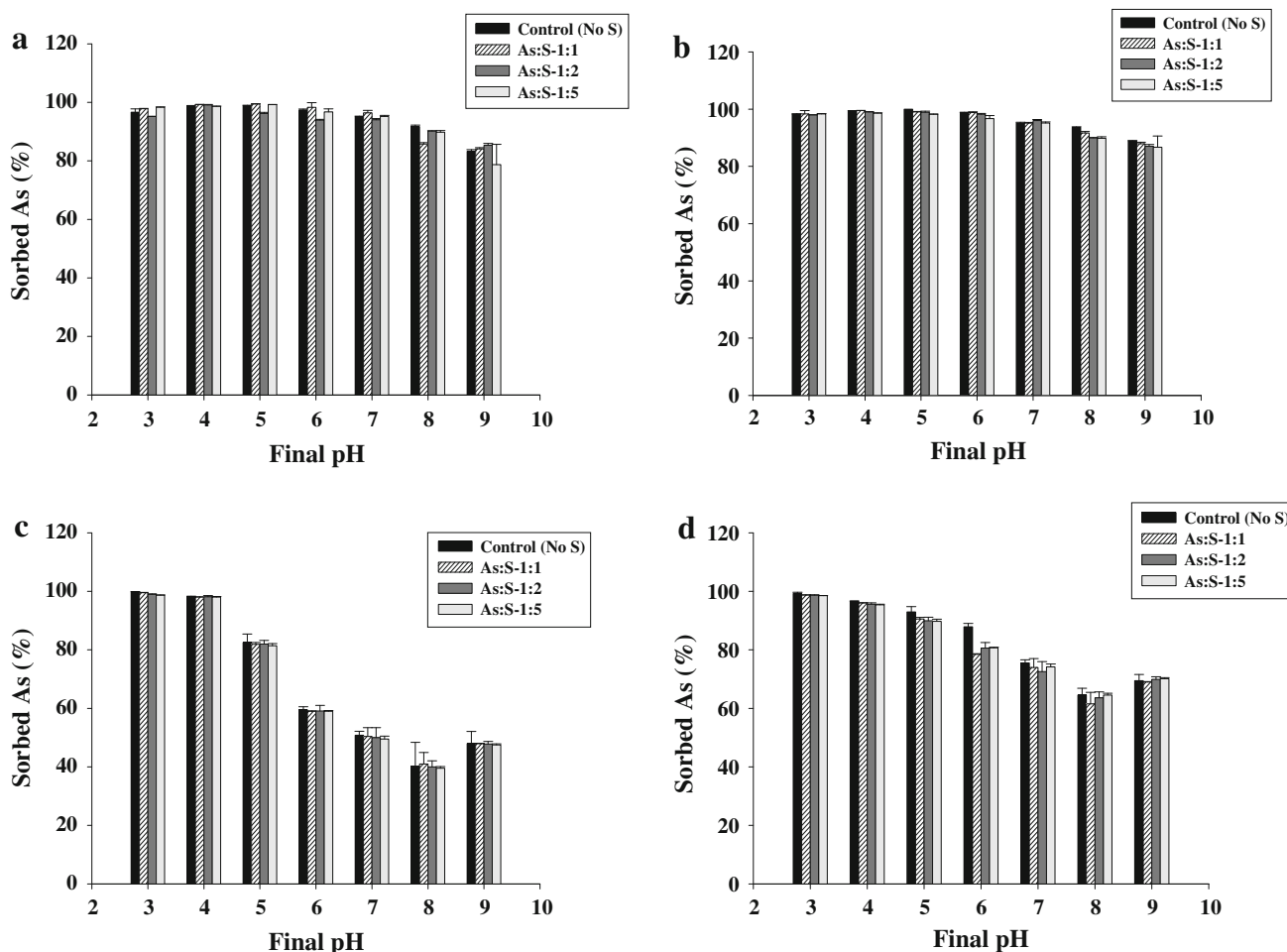


Fig. 5 Effect of competing ion (sulfate) on arsenate sorption by Al-WTR-amended soil at 25 g kg⁻¹ (a) and 50 g kg⁻¹ (b) application rates and by Fe-WTR-amended soil at 25 g kg⁻¹ (c) and 50 g kg⁻¹

(d) application rates as a function of pH. Contact time was 8 days and SSR was 1:5. Initial arsenic load was 125 mg kg⁻¹. Data are the mean of three replicates ± one standard deviation

more pronounced compared to Al-WTR-amended soil due to comparatively smaller external and internal specific surface area of Fe-WTR for anion sorption (Makris et al. 2004). Arsenic(V) sorption (at a 25 g kg⁻¹ application rate of Fe WTR) decreased to 97, 84, and 60 % at pH 3 and As:P ratios of 1:1, 1:2, and 1:5, respectively, which further decreased to 76, 57, and 55 % after increasing the pH to 8, compared to the control (without P) treatment (Fig. 4c). As a result of increased application rate to 50 g kg⁻¹, the effect of phosphate competition and pH became less pronounced. Maximum As(V) sorption at the lowest P load (As:P 1:1) was 99 % at pH 3, which decreased to 77 % with an increase in the As:P ratio to 1:5 (Fig. 4d). An increase in the pH to 7.5 resulted in further decrease in As(V) sorption to 67 and 23 % for the lowest and highest P loads, respectively. The present study showed an approximate 5–7 % increase in As(V) sorption above pH 7

(Fig. 4d). As discussed earlier, this increase in sorption might be the result of increased surface area due to the reductive dissolution of Fe-WTR at a higher pH (Nagar et al. 2010).

There was no significant effect of sulfate on As(V) sorption by Al- or Fe-WTR-amended soils at both the application rates (25 and 50 g kg⁻¹) with varying pH (Fig. 5). These results are in agreement with the previous finding of As(V) sorption by Al- and Fe-WTR (no soil), where addition of sulfate (20–200 mmol L⁻¹) had an insignificant effect on sorption at an entire pH range (Nagar et al. 2010). The unaffected sorption behavior of As(V) by sulfate could be explained by strong specific binding sites for As(V) on WTR surfaces (Yang et al. 2006; Makris et al. 2007), while sulfate may form outer sphere complexes. These results were also in accordance with previous studies where researchers found no influence of sulfate on

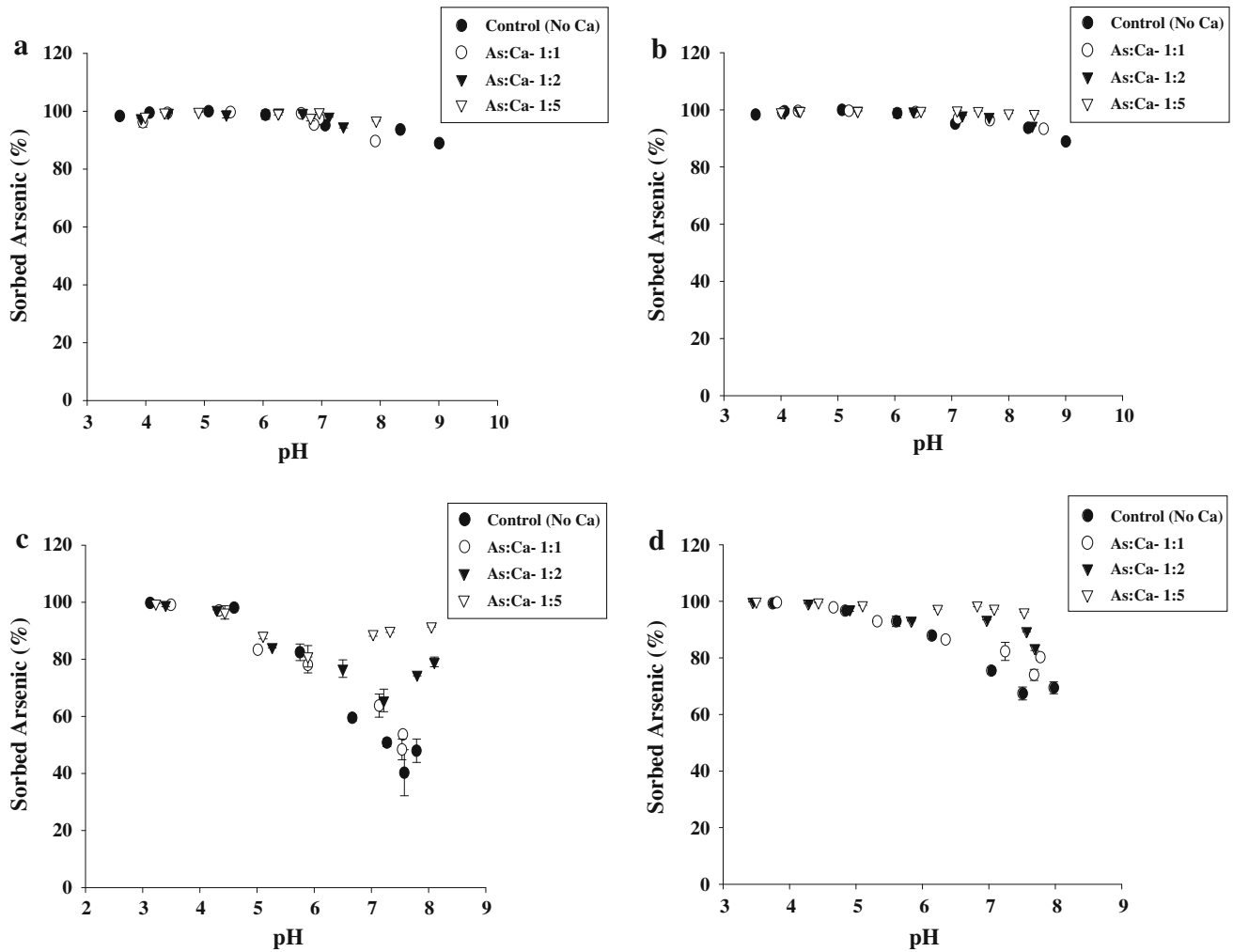


Fig. 6 Effect of complexing ion (calcium) on arsenate sorption by Al-WTR-amended soil at 25 g kg^{-1} (a) and 50 g kg^{-1} (b) application rates and by Fe-WTR-amended soil at 25 g kg^{-1} (c) and 50 g kg^{-1}

(d) application rates as a function of pH. Contact time was 8 days and SSR was 1:5. Initial arsenic load was 125 mg kg^{-1} . Data are the mean of three replicates \pm one standard deviation

As(V) sorption on ferrihydrite in the entire pH range (Jain and Loeppart 2000; Manful et al. 1989).

Effect of complexing metal on As(V) sorption by WTR-amended soil

The overall sorption of As(V) was enhanced in the presence of complexing ion, calcium (Ca), in the soil solution (Fig. 6). This effect was not significant ($p < 0.001$), however, for both application rates (25 and 50 g kg^{-1}) of Al-WTR, because most of the As(V) ($\sim 100 \%$) was already sorbed (Fig. 6a, b). Conversely, Fe-WTR-amended soil experienced a significant ($p < 0.001$) increase in As(V) sorption in the presence of Ca, and this effect was more significant at $\text{pH} > 7$ (Fig. 6c, d). At 25 g kg^{-1} application rate of Fe-WTR, As(V) sorption (without Ca) at $\text{pH} 7$ and 8 was 50 and 48% , respectively,

which increased to 65 and 80% , respectively, after the addition of Ca (As:Ca 1:2 ratio) into the system (Fig. 6c). When the As:Ca ratio increased to 1:5, As(V) sorption increased to 80 – 90% at $\text{pH} > 7$ (Fig. 6c). A similar trend was observed at 50 g kg^{-1} application rate of Fe-WTR, where As(V) sorption increased to almost 100% at the As:Ca ratio 1:5 compared to the control (without Ca) treatment (Fig. 6d). Precipitation of calcium arsenate could be the possible mechanism behind increased As(V) sorption at higher pH. Similar Ca-induced increases in As(V) sorption have been reported for Fe-WTR without soil (Nagar et al. 2010). The study showed that precipitation of calcium arsenate could be the possible mechanism behind increased As(V) sorption at higher pH, as calculated using ACT2 program of the Geochemist Workbench 6.0 software.

Conclusion

In our previous studies, WTR showed promising results in removing As(V) from aqueous solution with varying solution chemistry (Nagar et al. 2010). The present study demonstrated the effectiveness of WTRs in removing As(V) from a low Fe/Al hydroxide containing sandy soil under a varying set of soil solution chemistry. The Al-WTR-amended soil had a greater As(V) sorption capacity than that of Fe-WTR-amended soil, consistent with previous experiments (Makris et al. 2004; Nagar et al. 2010). For lowest As load (125 mg kg^{-1}), no pH-dependent effect was observed on As(V) sorption by Al- or Fe-WTR-amended soil at both application rates (25 and 50 g kg^{-1}). With increase in As load, As(V) sorption significantly decreased with increasing pH, being more prominent for lower application rate of WTR. Presence of phosphate decreased As(V) sorption by both Al- and Fe-WTR-amended soils with a strong dependence on pH and application rates. For Al-WTR-amended soils, there was no significant effect of phosphate addition at lower pH (3–6) at both application rates, but with increase in pH beyond 7, As(V) sorption significantly decreased. The effect of phosphate competition and pH, however, were more pronounced for the Fe-WTR-amended soil. Arsenic(V) sorption by both Al- and Fe-WTR-amended soil (at both application rates) was unaffected by the addition of sulfate. Addition of calcium resulted in increased As(V) sorption by Fe-WTR-amended soils, more prominently for the higher application rate of WTR. No apparent effect of calcium addition was observed in Al-WTR-amended soil, because most of the As(V) ($\sim 100\%$) was already sorbed by WTR surfaces. The present study provides an in-depth understanding of As(V) sorption by soil amended with Al- or Fe-WTR under varying soil solution chemistry, which is necessary to demonstrate the effectiveness of WTR application in the natural soil environment. Field-based experiments to validate the current results are necessary to further calibrate the application of WTRs in remediating As-contaminated soils.

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