

Evaluating a drinking-water waste by-product as a novel sorbent for arsenic

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Abstract

Arsenic (As) carcinogenicity to humans and other living organisms has promulgated extensive research on As treatment technologies with varying levels of success; generally, the most efficient methods come with a significantly higher cost burden and they usually perform better in removing As(V) than As(III) from solution. In the reported study, a novel sorbent, a waste by-product of the drinking-water treatment process, namely, drinking-water treatment residuals (WTRs) were evaluated for their ability to adsorb both As(V) and As(III). Drinking-WTRs can be obtained free-of-charge from drinking-water treatment plants, and they have been successfully used to reduce soluble phosphorus (P) concentrations in poorly P-sorbing soils. Phosphate and arsenate molecules have the same tetrahedral geometry, and they chemically behave in a similar manner. We hypothesized that the WTRs would be effective sorbents for both As(V) and As(III) species. Two WTRs (one Fe- and one Al-based) were used in batch experiments to optimize the maximum As(V) and As(III) sorption capacities, utilizing the effects of solid:solution ratios and reaction kinetics. Results showed that both WTRs exhibited high affinities for soluble As(V) and As(III), exhibiting Freundlich type adsorption with no obvious plateau after 2-d of reaction (15 000 mg kg⁻¹). The Al-WTR was highly effective in removing both As(V) and As(III), although As(III) removal was much slower. The Fe-WTR showed greater affinity for As(III) than for As(V) and reached As(III) sorption capacity levels similar to those obtained with the Al-WTR-As(V) system (15 000 mg kg⁻¹). Arsenic sorption kinetics were biphasic, similar to what has been observed with P sorption by the WTRs. Minimal (<3%) desorption of sorbed As(III) and As(V) was observed, using phosphate as the desorbing ligand. Dissolved Fe²⁺ concentrations measured during As(III) sorption were significantly correlated ($r^2 = 0.74$, $p < 0.005$) with the amount of As(III) sorbed by the Fe-WTR. Lack of correlation between Fe²⁺ in solution and sorbed As(V) ($r^2 = 0.2$) suggests reductive dissolution of the Fe-WTR mediating As(III) sorption. Results show promising potential for the WTRs in irreversibly retaining As(V) and As(III) that should be further tested in field settings.

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1. Introduction

In the past 20 years, the US EPA banned several inorganic As-based pesticides, such as arsenic acid, lead arsenate, lead arsenite, copper arsenate, and calcium arsenate. However, increased total As concentrations have already been detected in such pesticide-treated soils (total soil As

range of 7–970 mg kg⁻¹) (Sanok et al., 1994; Matschullat, 2000). Elevated As concentrations have been detected in soils located on former apple orchards with a prolonged history of arsenical-pesticide applications that are currently used for residential development (Murphy and Aucott, 1998). For more than two decades, animals were routinely dipped into vats containing sodium arsenite to control cattle ticks, resulting in significant As accumulation in the soil (Ng et al., 1993). Pressurized lumber is commonly treated with a water-soluble chromated copper arsenate preservative (CCA) in environments where rot or decay is likely to

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occur, raising serious health issues for CCA-treated lumber use and disposal (Gordon et al., 2002). Deposition in unlined construction and debris landfills can generate leachate enriched in As, which is susceptible to movement to the groundwater. Soils associated with playgrounds and under porches constructed with CCA-treated wood can become As point source pollution areas. The above point sources of As have resulted in significant As enrichment of surface- and ground-water supplies.

There are several treatment technologies available to reduce As concentrations in leachates of systems high in As (MacPhee et al., 2001). The most effective As treatment processes include adsorption, ion exchange, reverse osmosis, and nanofiltration (MacPhee et al., 2001). Iron (Fe) and aluminum (Al) salts in conjunction with polymers are commonly used for treating water contaminated with As (MacPhee et al., 2001). Other successful As treatment technologies include granular activated alumina (Rosenblum and Clifford, 1983), synthetic zeolites (Shevade and Ford, 2004), granular ferric hydroxide (Driehaus et al., 1998), fly ash and granular activated carbon (Pattanayak et al., 2000), or more recently, granular activated carbon impregnated by ferrous chloride (Gu et al., 2005).

The aforementioned As treatment technologies have been successfully applied to remove trace As concentrations from contaminated water, but most of them are cost-prohibitive for small communities or developing countries, which are likely to face expensive and technically imposing challenges to meet the maximum contaminant level of $10 \mu\text{g As l}^{-1}$. Waste recycling and re-utilization are two energy-efficient processes that have gained popularity due to their environmental friendliness and cost-reductive advantages. An example of such processes is the utilization of a waste by-product generated from the drinking-water treatment process as a cost-effective As sorbent. Addition of Fe, Al, or Ca salts to raw water removes colloids, color, sediment and contaminants from surface and groundwater supplies intended for potable water use; this process generates a by-product, the drinking-water treatment residuals (WTRs). These residuals are herein referred to as Al-WTRs (use of Al salt) or Fe-WTRs (Fe salt) (O'Connor et al., 2001). Drinking-water treatment residuals (WTRs) are physical mixtures of either Fe or Al hydr(oxides) or CaCO_3 that also contain natural organic matter, activated carbon, and polymer that can be obtained free-of-charge from drinking-water treatment plants (Elliott et al., 1990). The drinking-water treatment industry in the US generates more than 2 million tons of WTRs every day (Prakash and Sengupta, 2003). Land-application of WTRs seems a viable alternative as opposed to landfill/sanitary-sewers disposal or direct discharge to streams (Chwirka et al., 2001).

Recent literature has shown that WTRs are cost-effective amendments that reduce excess soluble P concentrations in systems high in P (Makris et al., 2004; Dayton and Basta, 2005). Drinking-WTRs can dramatically reduce soluble P in soils and runoff from areas amended with dif-

ferent P-sources, either in the short-term (Gallimore et al., 1999; Haustein et al., 2000), or in the long-term (up to 80 d) (Makris et al., 2005). However, little is known about As(V) or As(III) sorption by WTRs and their potential effectiveness in reducing soluble As concentrations in As-contaminated soils.

Similarities in the chemical nature of phosphate and As(V) molecules (tetrahedral geometry; atomic radii; bonding radii; ionization potential; and electronegativities) led us to hypothesize that WTRs would exhibit high affinity for As(V), as well as As(III). To the best of our knowledge, there is no study investigating both As inorganic species sorption by WTRs. The objectives of this study were: (i) to determine maximum As(III) and As(V) sorption capacities, and (ii) evaluate the effects of solid:solution ratios and reaction time on As(III) and As(V) sorption by two WTRs that have previously shown high affinity for P (Makris et al., 2005). The desorption potential of sorbed As from WTRs was evaluated using a soluble P concentration (1 mg P l^{-1}) commonly encountered in soil solution.

2. Materials and methods

2.1. WTR collection

Two WTRs were used in this study: one was Al-based, and the other was Fe-based. The Al-WTR was obtained from the drinking-water treatment plant in Bradenton, FL, USA. Additions of alum and a small amount of a copolymer of sodium acrylate and acrylamide, produced the Al-WTR. The Hillsboro River water treatment plant in Tampa, FL, USA provided the Fe-WTR, where $\text{Fe}_2(\text{SO}_4)_3$ is used as the coagulant. The WTRs were originally sampled from stockpiles that were formed within 1 year of production. All WTR samples were allowed to air-dry, and were subsequently passed through a 2-mm sieve before analyses.

2.2. General physicochemical properties of the WTRs

General chemical characterization methods for the two WTRs have been reported elsewhere (Makris et al., 2004). In brief, pH and soluble reactive As concentrations of the WTRs were measured in a 0.01 M KCl solution at a 1:10 solid:solution ratio, after 10 d of reaction. Total C and N were determined by combustion at 1010°C using a Carlo Erba NA-1500 CNS analyzer. Total-recoverable P, Fe, Al, and As were determined by inductively-coupled plasma mass spectrometry (ICP-MS) following digestion according to the EPA Method 3050B (USEPA, 2000). Oxalate-extractable P, Fe, and Al were determined by ICP-MS after extraction at a 1:60 solid:solution ratio, following the procedures of McKeague et al. (1971). The toxicity characteristic leaching procedure (TCLP) was used to determine the toxicity characteristic concentrations of several metals and metalloids to ensure environmentally-sound land-application of WTRs.

2.3. As(V) and As(III) sorption and desorption by the WTRs

Arsenic sorption capacities of the WTRs were determined in batch equilibration studies, based on the work of Makris et al. (2004). Stock standard solutions of As(V) and As(III) were prepared in 0.01 M KCl from Na₂HAsO₄ · 7 H₂O (KR Grade, Aldrich, USA), and NaAsO₂ (KR Grade, Aldrich, USA), respectively. Stock As(III) standard solutions were purged with N₂, tightly capped and used within 1 week. Aqueous mixtures of As(III)/As(V) standard solutions can be stable for at least 3 weeks without significant interconversion of As(III) and As(V) (Tallman and Shaikh, 1980). Phosphate stock solution was prepared from NaH₂PO₄ · H₂O (Merck). The pH of the stock standard solutions was adjusted to pH 6 using small quantities of 1 M HCl. Initial screening study was performed to evaluate the effectiveness of both WTRs in removing As from solution at a fixed solid:solution ratio (1:10), as-is (no adjustment) pH, and contact time (48 h). Representative air-dried (< 2 mm) samples of the WTRs were reacted with inorganic As in 1:10 (g WTR:ml) solutions at As(V) or As(III) loads of 3750 mg As kg⁻¹ to 15000 mg As kg⁻¹ for 2-d to determine As sorption capacities and kinetics at 23 ± 2 °C. The initial 1:10 (g:ml) solid:solution ratio was selected upon earlier P sorption experiments with WTRs (Makris et al., 2004). In the case of As(III) sorption/desorption, extra care was taken to remove the air from test tubes by purging N₂ gas and immediately capping. The absence of As(V) in selected samples of the As(III) sorption experiments was confirmed using the colorimetric method by Cummings et al. (1999). Subsequently, detailed experiments were conducted to determine the effects of solid:solution ratio and shaking time on As(V) and As(III) sorption, as well as to evaluate phosphate-induced As desorption from both WTRs. A 10-d equilibration time was employed for the solid:solution ratio effects experiment, based on earlier work with P sorption by different batches of the same WTRs (Makris et al., 2005). Solid:solution ratios of 1:5, 1:10, 1:20, and 1:40 (g WTR:ml As solution) varied by fixing the mass of WTRs (1 g). To determine the effect of shaking time on As sorption, As(III) and As(V) solutions at four initial As loads (375, 750, 1500, and 3000 mg l⁻¹) were reacted with the WTRs using the optimized solid:solution ratio, by varying the contact time (0, 1, 2, 4, 8, 16, 32, 48 h). The range of the initial As concentrations was selected in an attempt to reach the maximum As sorption capacities for both WTRs.

For all experiments, pH was not controlled; however, the suspension pH did not fluctuate much during sorption experiments (±0.3 units from initial pH, see Table 1). Suspensions were shaken (120 rpm) in a rotary shaker during the equilibration period. Following shaking, the suspensions were centrifuged (3000g), filtered (0.45 μm pore size), and analyzed for As and P by ICP-MS.

After sorption, the supernatant was removed and WTR-containing tubes were filled with a phosphate solution con-

Table 1
General chemical properties of two WTRs

Source	Form	pH	KCl-As (mg kg ⁻¹)	Total				Oxalate (200 mM)				
				C (g kg ⁻¹)	N (g kg ⁻¹)	P (g kg ⁻¹)	Al (g kg ⁻¹)	Fe (g kg ⁻¹)	As (g kg ⁻¹)	P (g kg ⁻¹)	Al (g kg ⁻¹)	Fe (g kg ⁻¹)
Bradenton, FL	Al-WTR	5.6	bd ^a	188 ± 0.5	4.5 ± 0.3	3.2 ± 0.5	87.1 ± 16.0	4.6 ± 0.1	0.015 ± 0.002	2.98 ± 0.0	82.3 ± 1.9	4.1 ± 0.2
Tampa, FL	Fe-WTR	6.0	bdl	196 ± 0.1	7.8 ± 0.1	2.7 ± 0.2	1.34 ± 0.1	170 ± 13.6	0.013 ± 0.004	2.6 ± 0.05	0.36 ± 0.01	78.6 ± 8.0

Numbers are the mean of two replicates ± one standard deviation.

^a Below detection limit. GFAAS instrument detection limit is 2 ppb or <0.03 mg kg⁻¹, using a 1:10 solid:solution ratio.

taining 1 mg P l^{-1} (1 g WTR:5 ml P solution) to test the ability of phosphate on As desorption from the WTRs. Suspensions were reacted for 1, 2, 4, 8, 16, 32 and 48 h. The amount of As desorbed was calculated as the difference between As sorbed and As measured in solution after the desorption step. Dissolved Fe^{2+} concentrations during the As(V) and As(III) sorption experiments were determined using the ferrozine method (Viollier et al., 2000). In brief, filtered ($0.45 \mu\text{m}$) samples were reacted with the ferrozine solution and the sample absorbance was recorded at 562 nm.

3. Results and discussion

3.1. General chemical properties of the WTRs

Both WTRs were acidic (Table 1). Total As concentrations of the WTRs were within the range of published values for other WTRs ($1.9\text{--}9.7$ and $8.5\text{--}17 \text{ mg kg}^{-1}$ for Fe- and Al-WTRs, respectively) (Jain et al., 2005). The KCl-extractable As concentrations were $<0.03 \text{ mg kg}^{-1}$, suggesting minimum risk for As dissolution from the untreated (no As added) WTRs. The KCl-extractable As represented a negligible fraction of total ($<0.01\%$). Total C values agreed with the range of organic C found in 21 WTRs nationwide ($23\text{--}205 \text{ g kg}^{-1}$) (Dayton and Basta, 2005). Total P content was also within the typical range for the WTRs ($0.3\text{--}4.0 \text{ g P kg}^{-1}$) (Dayton and Basta, 2005). Total P, as well as As concentrations measured in the WTRs comes from the raw water treated in drinking-water treatment plants and becomes a part of the WTR structure. Total $[\text{Fe} + \text{Al}]$ concentrations in both WTRs

Table 2

Toxicity characteristic values of several metals and metalloids measured in both WTRs, using the TCLP extraction method

Analyte	Al WTR (mg l^{-1})	Fe WTR (mg l^{-1})
Cr	$<0.0084^a$	<0.0084
Ni	<0.0810	<0.0810
Cu	<0.0468	<0.0468
Zn	<0.0027	<0.0027
Ag	<0.0110	<0.0110
Pb	<0.0546	<0.0546
S	64.3	20.04
Cd	<0.0083	<0.0083
B	<0.1172	<0.1172
K	4.64	3.77
Ti	<0.0027	<0.0027
Mn	0.41	0.57
Ca	36.53	>89.5
Co	<0.0087	<0.0087
Mg	6.87	1.26
As	<0.0253	<0.0253
Se	0.75	0.67
Ba	0.34	0.2
W	0.29	1
Hg	0.55	0.54

^a ICP-AES instrument detection limits.

were high and typical of WTRs produced nationally. X-ray diffraction analysis revealed no crystalline Al or Fe hydr(oxides) components, suggesting that both materials were amorphous (Makris, 2004). Oxalate (200 mM)-extractable P, Fe, and Al are usually associated with the non-crystalline (amorphous) phase of metal hydroxides. Oxalate-extractable Al concentrations were close to total (80–98% of total Al), consistent with an amorphous nature of the Al-WTR. The Fe-based WTR had lower

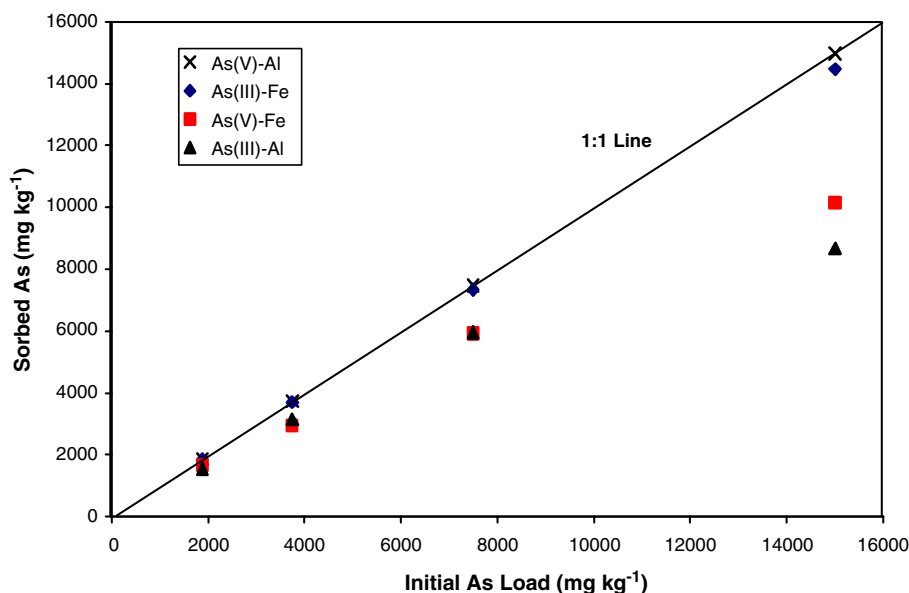


Fig. 1. As(V) and As(III) sorption isotherms ($23 \text{ }^\circ\text{C}$) for the Fe-, and the Al-based WTRs. Solid to solution ratio is 100 g l^{-1} , and shaking time of 2-d. The legend (AsIII-Fe) stands for AsIII sorption by the Fe-WTR, and (AsIII-Al) stands for AsIII sorption by the Al-WTR. Same applies for the legends of AsV sorption by both WTRs. The 1:1 line represents 100% removal of the initially added soluble As(III) or As(V) concentrations. Particles were $<2\text{-mm}$, and the pH was not controlled. Error bars represent one standard deviation of the mean ($n = 2$) and are smaller than the legend.

oxalate-extractable Fe values as a percentage of total Fe (64%) when compared with the Al-WTR. The TCLP values for As for both WTRs (Table 2) were well below the hazardous waste toxicity characteristic criterion (5 mg l^{-1}) as defined in Title 40 of the Code of Federal Regulations (CFR), Part 261.24. Similarly, TCLP values for several other metals (Pb, Zn, Cu, etc.) were well below the threshold values, thus, permitting land application of WTRs as an environmentally sound disposal method.

3.2. As(III) and As(V) sorption by the WTRs

Sorption isotherms (23°C) showed that both WTRs had a high affinity for As(III) and As(V) species (Fig. 1). The pH of both WTR suspensions in As sorption experiments was not controlled, ranging from 6 to 6.5. The Al-WTR

sorbed greater amounts of soluble As(V) than the Fe-WTR at all initial loads ($1875\text{--}15000 \text{ mg kg}^{-1}$), but the Fe-WTR sorbed greater amounts of As(III) than the Al-WTR, mainly at the higher As loads (7500 and 15000 mg kg^{-1}) (Fig. 1). Similar data were obtained by Dixit and Hering (2003) where As(III) was sorbed to a similar or greater extent than arsenate by HFO and goethite in the pH range of 6–9. After a 2-d reaction, the maximum amount of sorbed As(V) was 93% and 67% of the maximum initial As(V) load (15000 mg kg^{-1}) for the Al-WTR and the Fe-WTR, respectively (Fig. 1). The maximum amount of As(III) sorbed after a 2-d equilibration was 99% and 55% for the Fe-, and Al-based WTRs, respectively (Fig. 1).

The Al-WTR had a greater As(V) sorption capacity than that of the Fe-WTR, consistent with previous P sorp-

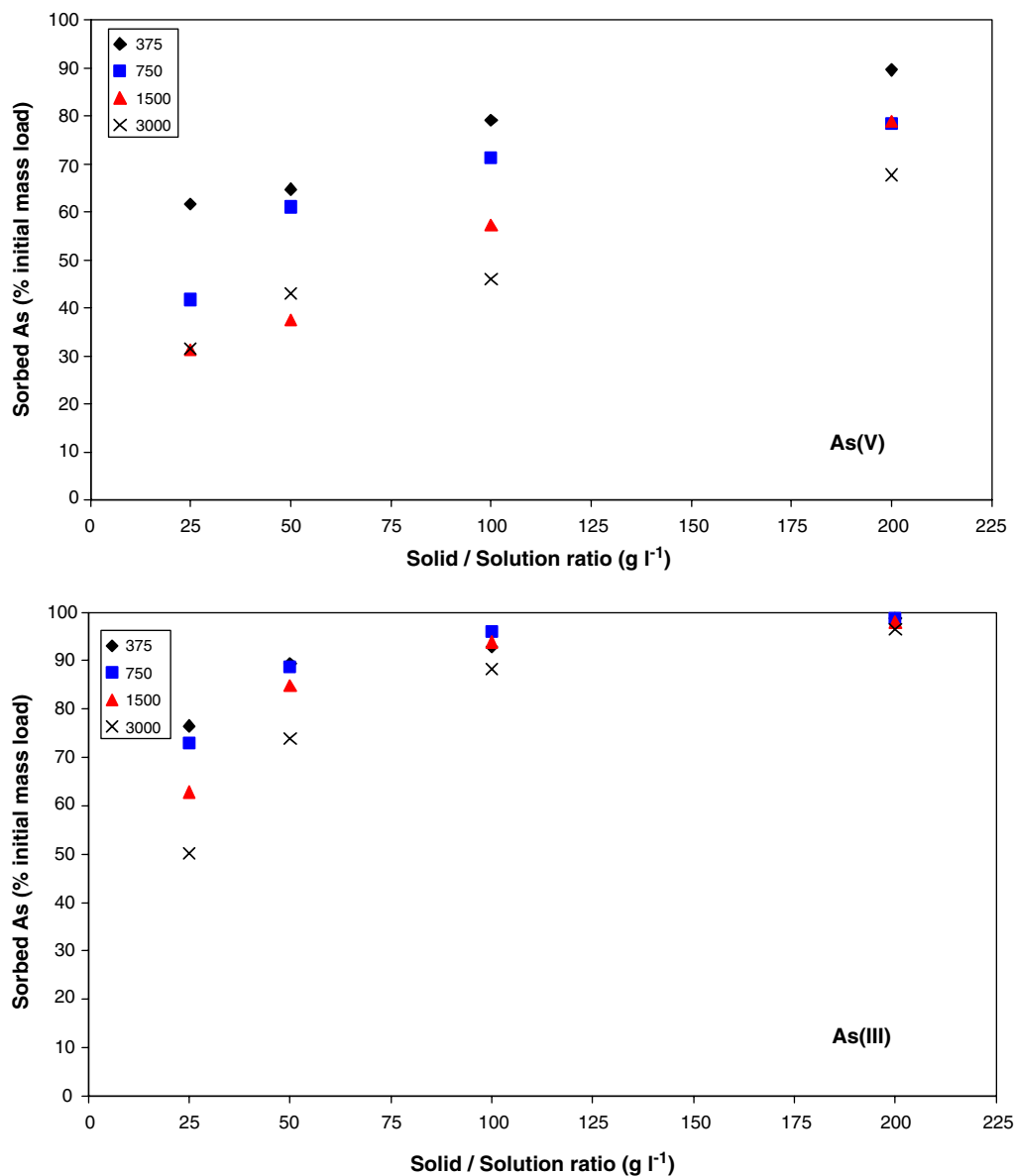


Fig. 2. Effect of solid:solution ratio on the amount of As(V) (top graph) and As(III) (lower graph) sorbed by the Fe-WTR after 2 d; the pH was not controlled.

tion experiments with different batches of the same WTRs (Makris et al., 2004). Greater external and internal specific surface area of the Al-WTR than that of the Fe-WTR could explain the greater affinity of the Al-WTR for As(V) (Makris et al., 2004). In the case of As(III), an abiotic reductive dissolution mechanism, which applies to the redox-sensitive Fe-WTR but not to the Al-WTR increases the amount of sorption sites by creating new surfaces, thereby accounting for the greater As(III) sorption by the Fe-WTR. Langmuir-based sorption maxima were not calculated for either WTR, because As(III) and As(V) sorption followed a linear or Freundlich type of adsorption isotherm (23 °C) over the range of concentrations used (375–3000 mg As l⁻¹).

Such high As(V) sorption capacity of the WTRs (~15000 mg kg⁻¹) are comparable, if not superior to that of other common industrial sorbents, such as, porous ferric hydroxide (As(V) sorption capacity of 17000 mg kg⁻¹)

(Driehaus et al., 1998), or granular ferric hydroxide (8000 mg kg⁻¹) (Badruzzaman et al., 2004). Iron-containing GAC had a As sorption capacity of 6570 mg As kg⁻¹ (Gu et al., 2005), and granular activated alumina particles exhibited As sorption maxima in the order of ~12000 mg kg⁻¹ (Lin and Wu, 2001), similar to As sorption capacities of the WTRs, suggesting that WTRs are effective As(V) and As(III) sorbents.

3.3. Effect of solid:solution ratio on As sorption by the WTRs

We attempted to identify the optimum solid:solution ratio for As(V) and As(III) sorption by the WTRs using four different initial As concentrations (375–3000 mg l⁻¹) (Figs. 2 and 3). Increasing the solid:solution ratios resulted in a significant ($p < 0.05$) increase in the amount of As(V) sorbed by the Fe-WTR, regardless of initial As

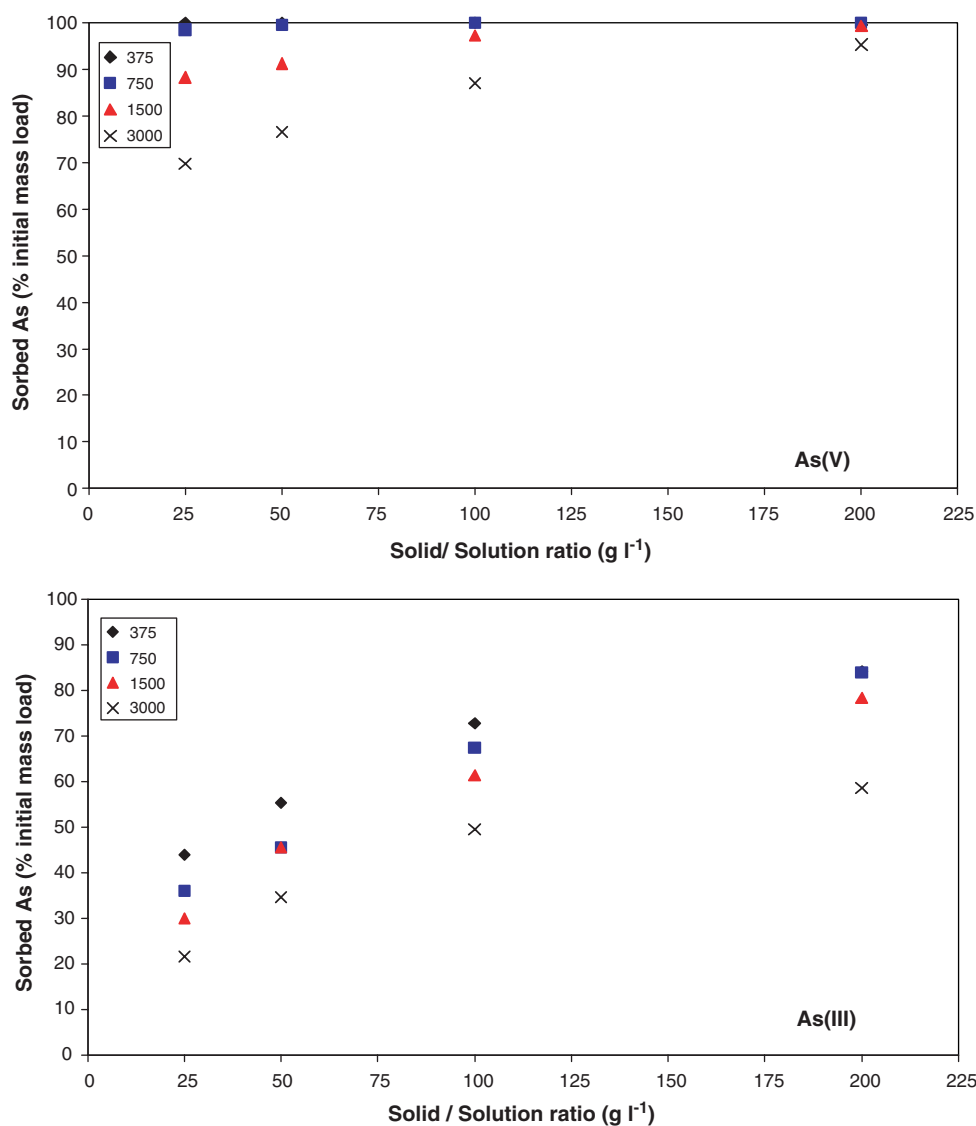


Fig. 3. Effect of solid:solution ratio on the amount of As(V) (top graph) and As(III) (lower graph) sorbed by the Al-WTR after 2 d; pH was not controlled.

concentrations (Fig. 2). The greater affinity of As(V) for the Al-WTR, when compared to the Fe-WTR, resulted in greater As(V) sorption by the Al-WTR at all solid:solution ratios (Fig. 3). There was a significant ($p < 0.001$) interaction between the initial As(III) concentrations and solid:solution ratios for the Fe-WTR, but not in the case of As(V) (Fig. 2). At relatively small solid:solution ratios ($25\text{--}50\text{ g l}^{-1}$), increases in the initial As(III) concentrations had a significant negative effect on the amount of As(III) sorbed by the Fe-WTR. However, increasing the solid:solution ratio to 200 g l^{-1} , there was no significant difference in the total amount of As(III) sorbed, removing nearly all of the added As(III) (Fig. 2). There was a significant ($p < 0.001$) interaction between the solid:solution ratios and the initial As(V) concentrations on the overall amount

of As(V) sorbed by the Al-WTR (Fig. 3). The amount of As(III) sorbed by the Al-WTR was less than that of the Fe-WTR, and there was no interaction between the solid:solution ratios and the initial As(III) concentrations on the overall amount of As(III) sorbed. Based on both As(III) and As(V) solid:solution ratio experiments, we selected the 200 g l^{-1} ratio as the solid:solution ratio that would maximize As sorption for both WTRs, and was subsequently used in the kinetic experiments.

3.4. Effect of equilibration time on as sorption by the WTRs

A kinetically-driven As(V) and As(III) sorption was documented for both WTRs (Figs. 4 and 5). Arsenic(V) sorption by the Fe-WTR was biphasic, showing an initially

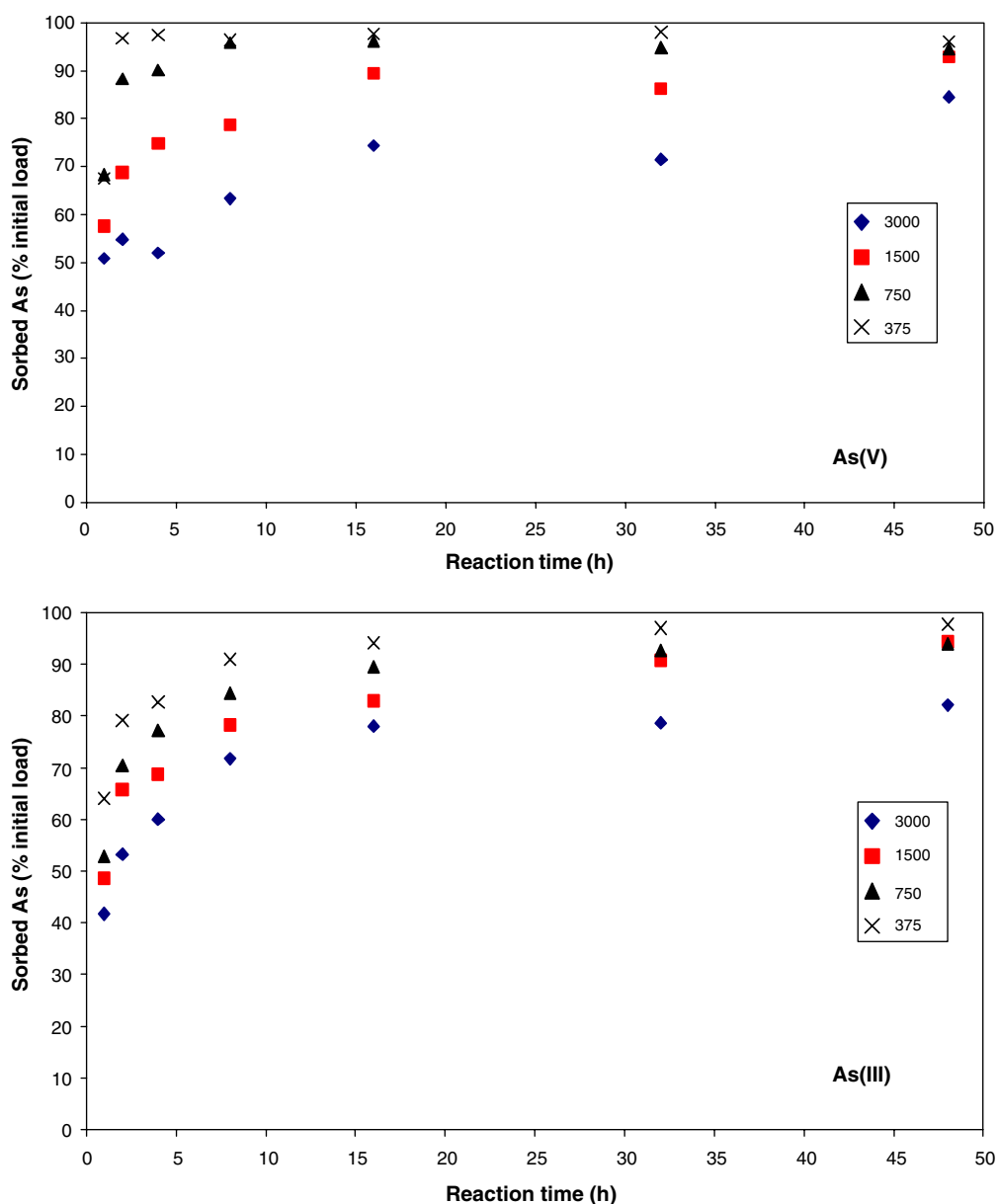


Fig. 4. Kinetics of As(V) (top graph) and As(III) (lower graph) sorption by the Fe-WTR, using different initial As(III) concentrations. Initial solid:solution ratio was 200 g l^{-1} . The pH was not controlled.

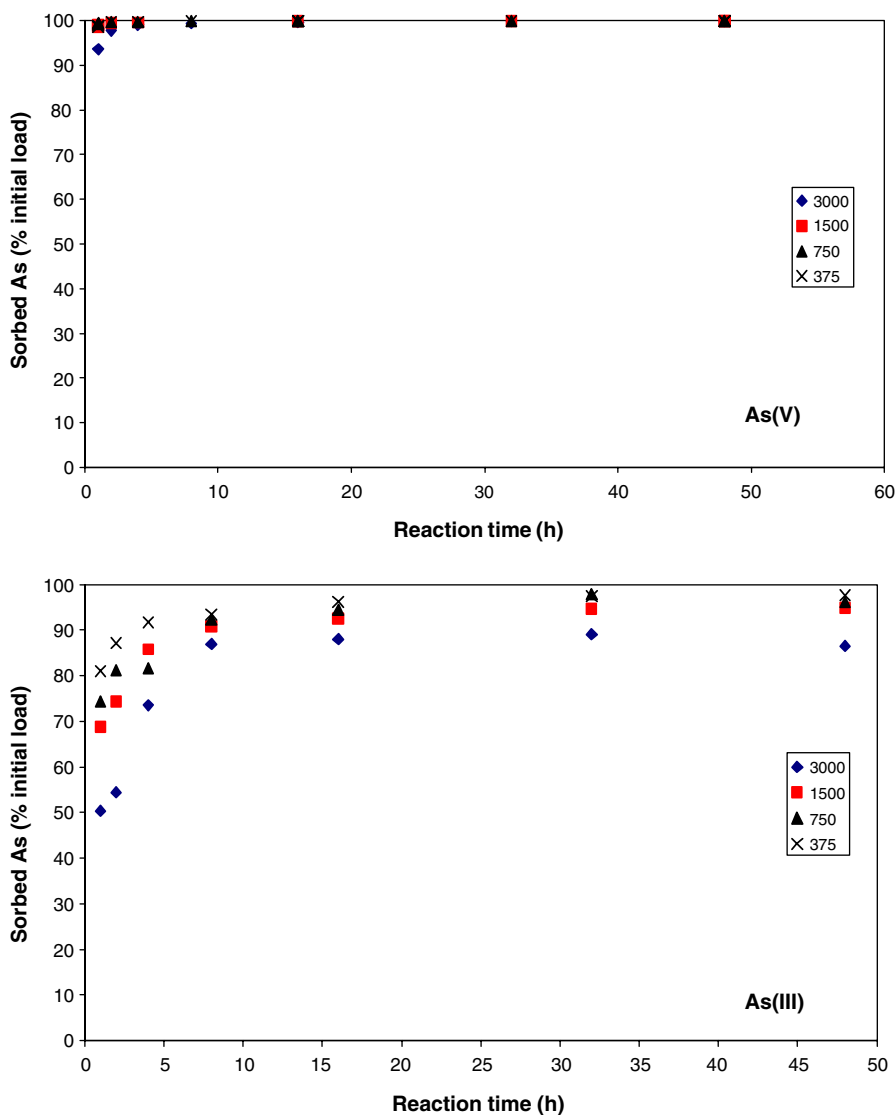


Fig. 5. Kinetics of As(V) (top graph) and As(III) (lower graph) sorption by the Al-WTR, using different initial As(III) concentrations. Initial solid:solution ratio was 200 g l^{-1} . The pH was not controlled.

Table 3

Pseudo-second-order reaction rate constants in WTRs suspensions after a $1500 \text{ mg As(V), As(III) l}^{-1}$ initial pulse input

Source	Form	As species	First-order rate fit (r^2)	Second-order rate fit (r^2)	Second-order reaction rate k ($\text{l h}^{-1} \text{ mg}^{-1}$) ^a
Bradenton, FL	Al-based	As(V)	0.84	0.98	3.5×10^{-2}
Tampa, FL	Fe-based	As(V)	0.79	0.84	1.4×10^{-4}
Bradenton, FL	Al-based	As(III)	0.71	0.87	9.3×10^{-4}
Tampa, FL	Fe-based	As(III)	0.94	0.98	2×10^{-4}

Second-order reaction rate coefficients were strongly dependent to initial As concentrations used. Contact time ranged from 1 to 48 h.

^a Where the slope of a linear fit to a n -order reaction equals: $(n - 1) * kn * C_0^{n-1}$.

fast, followed by a slower As sorption rate; same behavior was observed for As(III) sorption by the Fe-WTR, consistent with the biphasic P sorption kinetic data obtained for different batches of the same Fe-WTR used in this study (Makris et al., 2004) (Fig. 4). The amount of As(III) sorbed was greater than the amount of As(V) sorbed by the Fe-WTR, similarly to what Raven et al. (1998) showed, where, regardless of solution pH, As(III) was sorbed to a greater

extent than As(V), especially at high As concentrations (>1 and up to $13.3 \text{ mol As kg}^{-1}$ ferrihydrite).

Similar biphasic As(III) kinetic sorption data were obtained for the Al-WTR (Fig. 5). However, As(V) sorption kinetics for the Al-WTR revealed that As(V) was rapidly depleted from the solution, as approximately 98% of all initial As loads was sorbed within the first hour, and slowly proceeded to 100% sorption by the end of the

48-h period. The only exception was at the highest initial load (3000 mg As l⁻¹) where approximately 94% of the initial As load was sorbed within the first hour, and proceeded at a much slower rate thereafter (Fig. 5).

Kinetic data for both WTRs were best fit to a second-order reaction rate model (Table 3). The “fast” stage of As sorption would presumably encompass highly accessible surfaces (particle exteriors and macropores) (Van Rieemsdijk and Lyklema, 1980), while the “slow” stage could be associated with diffusion in micropores of the WTRs, as this was the case for P (Makris et al., 2004). A pore diffusion model was successfully applied to explain As(III) and As(V) sorption by activated alumina grains (Lin and Wu, 2001). The reaction period used here (up to 2-d) was significantly lower than the reaction period used for P sorption (up to 80 d) (Makris et al., 2005), but still shows a distinct time-dependent behavior. Arsenate sorption kinetics by a granular ferric hydroxide showed that 3 to >15 d were required to reach pseudo-equilibrium (Driehaus et al., 1998). Time-dependent As(V) sorption by porous ferric

hydroxide was explained on the basis of an intraparticle diffusion mechanism (Badruzzaman et al., 2004). Second-order rate coefficient for the Fe-WTR was smaller than that of Al-WTR, consistent with there being less As(III) and As(V) sorption per unit time for the second biphasic (longer-term) sorption stage (Table 3). It is worth mentioning here that the pseudo first-order kinetic model fit the data equally well ($r^2 = 0.94$) compared to the second-order rate model ($r^2 = 0.98$), possibly suggesting a different mechanism for As(III) sorption by the Fe-WTR, than for As(V) (Table 3).

3.5. Arsenic desorption from the WTRs

Arsenic(V) desorption from the Fe-WTR was minimal, suggesting irreversible sorption (Fig. 6). For all initial As loads, As(V) desorption did not exceed 4% of previously sorbed As(V) by the Fe-WTR (Fig. 6). Arsenic(V) or As(III) desorption from the Fe-WTR was mostly unaffected by contact time (1 up to 48 h of desorption). Arsenic

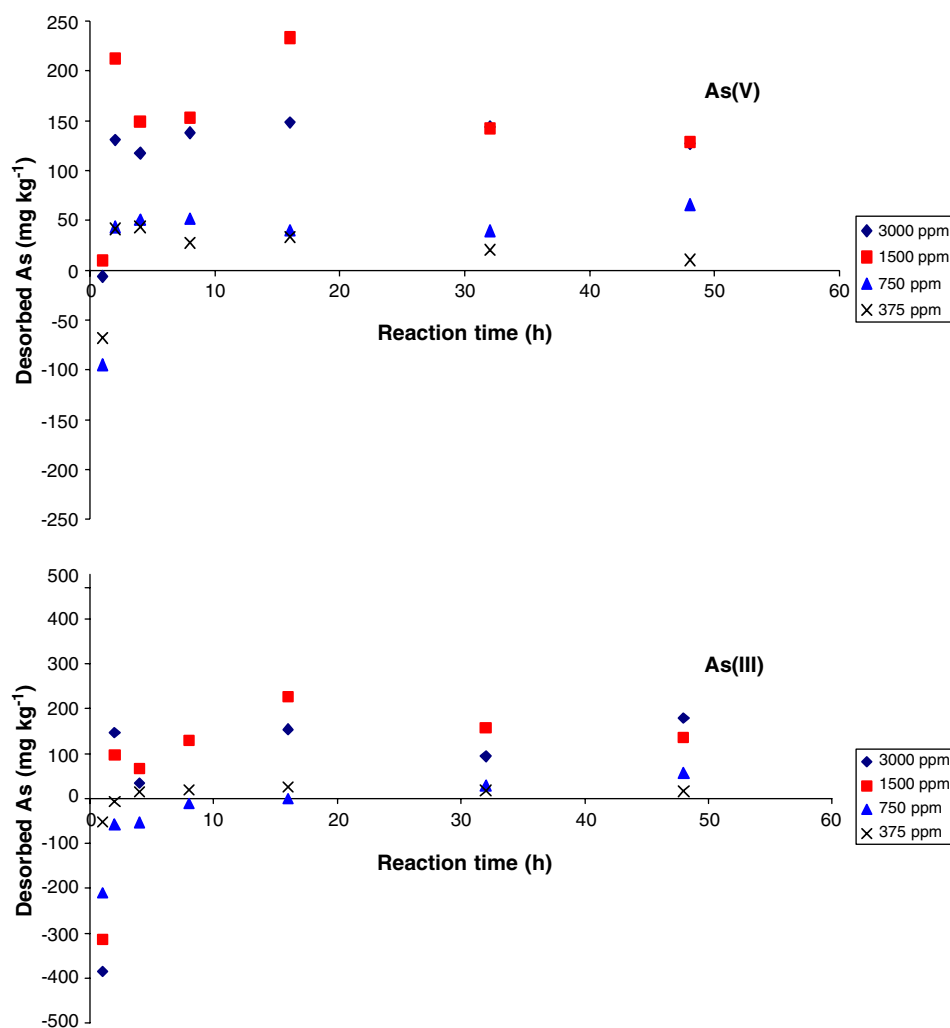


Fig. 6. Kinetics of As(V) (top graph) and As(III) (lower graph) desorption with a 1 mg P l⁻¹ solution from different As loads of the Fe-WTR at different times. Initial suspension was 200 g l⁻¹. Negative desorption numbers indicate continuous sorption during the desorption step. No data are presented for the Al-WTR, since As(V) and As(III) desorption trend lines were similar to the Fe-WTR.

desorption was initially negative, indicative of continuous non-equilibrium As sorption, but changed to positive within the first 2-h and stabilized thereafter up to 48 h of reaction (Fig. 6). Similar data were obtained for As sorbed by hardened paste of Portland cement where As sorption was unaffected by P additions ($10\text{--}1000\text{ mg l}^{-1}\text{ PO}_4$) during an 8-h reaction period (Kundu et al., 2004). Apparently, As(III) or As(V) sorbed by the Fe-WTR is chemisorbed on the WTR surfaces, similarly to what we observed with P sorption by WTRs (Makris et al., 2005), and hence, resists desorption by phosphate.

An abundance of sorption sites on the Fe-WTR suggests that P sorption to vacant sorption sites preempted P displacement of sorbed As during the desorption step; greater than 90% of the added P was sorbed (data not shown). In As and P ($<70\text{ }\mu\text{M}$) co-sorption batch experiments, P did not influence As(V) sorption by Fe hydroxide gel (Meng et al., 2002). However, at high surface site coverage of

the Fe hydroxides, phosphate significantly reduced As(V) sorption (Meng et al., 2002).

Similar results were observed for the Al-WTR; both As(V) and As(III) desorption levels were $<0.5\%$ (data not shown). At the two lowest As loads, phosphate-induced As desorption was $<0.03\%$ of previously sorbed As. At the two highest initial As loads, As desorption was $<0.5\%$ of the previously sorbed As. Such data are in close agreement with P desorption kinetics with a 5 mM oxalate solution from WTRs (Makris et al., 2004). Phosphorus desorption was minimal; materials that desorbed the greatest proportion of P also adsorbed the least amount of P (Makris et al., 2004).

The minimum amount of As desorbed in the presence of P is in agreement with the calculated second-order sorption rate coefficients for both WTRs. Generally, the higher the second-order rate coefficient, the lower the proportion of desorbed sorbate (Makris et al., 2005). The Al-WTR had

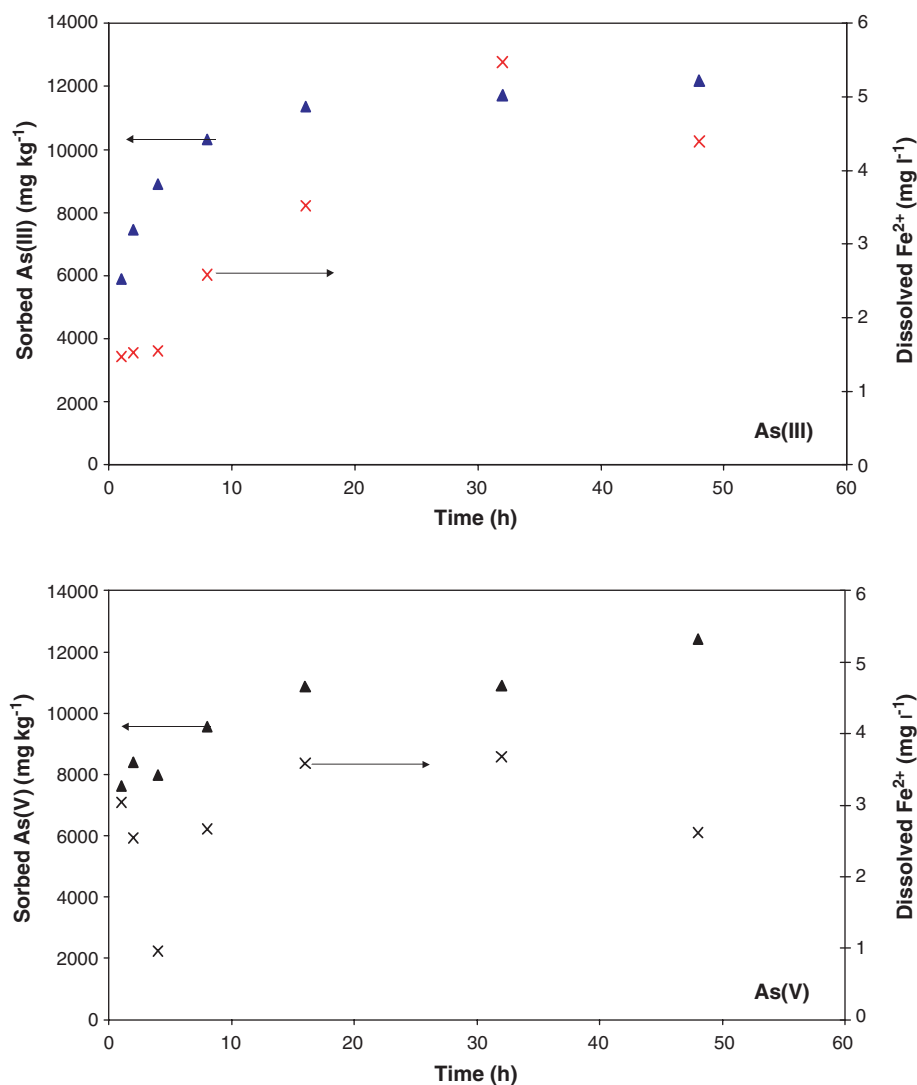


Fig. 7. Monitoring dissolved Fe^{2+} concentrations during the sorption kinetics of As(III) (top graph) and As(V) (lower graph) by the Fe-WTR. Initial suspension was 200 g l^{-1} and either As(III) or As(V) initial load was 15000 mg kg^{-1} . Similar relationships observed for other initial As loads and are not presented. Linear positive correlation between sorbed As(III) or As(V) and dissolved Fe^{2+} concentrations had R^2 values of 0.74 and 0.20, respectively.

higher second-order rate coefficients than the Fe-WTR, and also desorbed the least amount of sorbed As (Table 3). This is a favorable behavior with respect to stability of As sorbed to the retentive surfaces of the WTRs.

3.6. Effect of dissolved Fe^{2+} concentrations on As(III) sorption by the Fe-WTR

The greater affinity of the Fe-WTR for As(III) than for As(V) could imply that a surface redox reaction facilitated As(III) sorption. Electron transfer between As(III) and Fe^{3+} on the WTR surface could be responsible for the enhanced As sorption when As(III) was used instead of As(V). In addition, kinetic data for As(III) were fit equally well to both 1st and 2nd reaction rate models (Table 3), suggesting that another reaction might be taking place concomitantly with As(III) ligand exchange on the exterior and the interior of the Fe-WTR particles. A gradual increase in the color of supernatants with increasing amount of As(III) sorbed led us to infer a potential role of organic carbon and soluble Fe being released during As(III) sorption. We hypothesized that an abiotic reductive iron hydroxide dissolution mechanism was responsible for the increased As(III) sorption. Iron hydroxides are the major components of the Fe-WTRs (Makris et al., 2005). A microbially mitigated electron transfer mechanism is doubtful, since preliminary experiments showed no effect of aqueous sodium azide (1 mM) on As(III) sorption by either Al- or Fe-based WTRs, using the procedures of Lowry et al. (2004). Neither WTR is expected to be highly populated by microbes, since the WTR particles were extensively air-dried before initiating the sorption experiments.

We monitored the evolution of dissolved Fe^{2+} during the kinetic experiment for both As(III) and As(V) (as a control) by the Fe-WTR (Fig. 7). Results showed that there was a positive Fe^{2+} evolution with time (up to 48-h), paralleling As(III) sorption kinetics. Dissolved Fe^{2+} concentrations were within 10% of the total Fe concentrations ($Fe^{2+} + Fe^{3+}$) for all treatments. On the other hand, Fe^{2+} concentrations remained unchanged during the 48-h period of the kinetic experiment for As(V), suggesting no effect of Fe^{2+} on As(V) sorption. This was further supported by the significant linear correlation between the amount of As(III) sorbed with the dissolved Fe concentrations ($r^2 = 0.74$), and the poor correlation observed for As(V) ($r^2 = 0.20$). In effect, Fe^{2+} release from the Fe-WTR surfaces created new sites for As(III) sorption. Potential As(III) oxidation to As(V) during Fe-WTR dissolution is speculative, but not detectable in solution, because sorption isotherms showed that the Fe-WTR was able to remove both As(III) and As(V). Thus, abiotic Fe-WTR dissolution possibly induced particle transformations, creating newer sites for additional sorption of As(III). It is likely that this could be the reason of greater As(III) > As(V) sorption by the Fe-WTR. The Al-WTR is mostly comprised of Al hydroxides that usually are not involved in electron transfer reac-

tions. Manning et al. (2002) suggested that reductive dissolution of MnO_2 increased As(III) removal by oxidizing As(III) to As(V). Dissolution of MnO_2 during As(III) sorption released Mn^{2+} into solution that created new sites for As sorption. Arsenite sorption was greater than for As(V) by the synthetic birnessite as the result of As(III)-induced surface alteration (Manning et al., 2002). However, the majority of As(V) formed during As(III) oxidation (70–80%) was released into solution (Manning et al., 2002), which was not the case for the Fe-WTR. Ler and Stanforth (2003) considered a new type of surface precipitation where dissolution of the adsorbent (goethite) provides a continuous supply of Fe^{2+} to precipitate with P in solution. This phosphate “burial” resulted in decreased P availability with time. Our data provide only indirect evidence for an electron transfer mechanism; an EXAFS study on Fe-WTR before and after As(III) sorption is needed for verification of this hypothesis.

4. Conclusions

This study demonstrated that the WTRs are excellent low-cost sorbents for As(V) and As(III). Both Al- and Fe-based WTRs exhibited high As(III) and As(V) affinities with minimal As desorption. Beyond the obvious economic advantage, the major advantage of using WTRs is that As(III) removal is not followed by a concomitant increase of As(V) in solution. Both WTRs exhibited a Freundlich type As(III) and As(V) sorption at concentrations up to 3000 mg As l^{-1} , implying huge affinity of the WTR surfaces for both As species. This low-cost sorbent can be highly beneficial for small communities or developing countries while they strive to provide safe and As-free potable water. Even though an abiotic reductive dissolution mechanism could be responsible for the increased As(III) sorption by the Fe-WTR, spectroscopic evidence (EXAFS) is needed to elucidate the actual mechanism of the increased As(III) sorption by the Fe-WTR, when compared with As(V) sorption. Further studies are needed to document WTR efficacy in As remediation of contaminated waters/soils under field conditions.

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