

# The effect of citrate, oxalate, acetate, silicate and phosphate on stability of synthetic arsenic-loaded ferrihydrite and Al-ferrihydrite

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## Abstract

The effect of the organic species oxalate, citrate and acetate and the inorganic species silicate and phosphate on release of As(V) from synthetic arsenic-loaded ferrihydrite and Al-ferrihydrite in the pH range 4–8 was investigated. For ferrihydrite, the organic species increased %As(V) extraction in the order: acetate < oxalate << citrate. In each case, the %As(V) extraction increased when acidity changed to pH's lower than 6, but remained unchanged when the pH increased from 6 to 8. For Al-ferrihydrite, the trend for %As release as a function of pH in the presence of acetate and oxalate was similar to that for ferrihydrite. However, unlike the ferrihydrite case, in the presence of citrate the %As extraction went through a minimum at pH 6. This is postulated to be related to the solubility equilibria of Al-ferrihydrite as a function of pH. The co-presence of silicate or phosphate with each of the organic species enhanced As(V) extraction in the order  $\text{SiO}_3^{2-} > \text{PO}_4^{3-}$ . Competitive adsorption of the investigated organic and inorganic species on ferrihydrite and Al-ferrihydrite could explain the enhanced release of As(V) into solution. However, disproportionate adsorption of other species relative to amount of As(V) release occurs, suggesting that mechanisms other than competitive adsorption are also operative. The results could best be explained in terms of combination of competitive adsorption and processes involving pH-dependent dissolution of ferrihydrite/Al-ferrihydrite, formation of various complex ionic species involving Al(III), Fe(III), As(V),  $\text{SiO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{OH}^-$ ,  $\text{H}^+$  and organic species: acetate, oxalate and citrate.

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## 1. Introduction

Arsenic contamination in water is a worldwide problem [1]. This contamination can be classified as primary and secondary. The primary contamination results mainly from rock weathering, biological activity and volcanic emissions followed by transportation through the environment by water [2]. The secondary contamination is related to various human activities such as milling, combustion, wood preservation, and pesticide applications [3,4].

In recent years, several methods for arsenic removal from contaminated water have been developed. These include ion

exchange, reverse osmosis, lime softening, bio-conversion to arsine, and co-precipitation/adsorption on iron oxyhydroxides. The co-precipitation and adsorption on iron oxyhydroxides (e.g. ferrihydrite) is the most cost-effective and commonly used method for arsenic removal from contaminated drinking water and metallurgical waste liquors. In our recent studies, we have shown that removal of arsenic by adsorption on Al-ferrihydrite at its optimum Fe/Al ratio of 1:1 is more effective than on ferrihydrite. Residual As(V) concentration of <10 ppb is achieved in the pH range 6–7 [5]. However, this method yields solid residues which are highly concentrated in arsenic (approximately 18 mg/g for ferrihydrite and 23 mg/g for Al-ferrihydrite) and could be classified as hazardous wastes. The safe disposal of these toxic residues is of great concern in relation to their stability under the environmental conditions [6].

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The stability of the As-loaded residues when disposed to the environment in the form of landfills or residue ponds may be affected by three major types of actions. The first is related to the gradual transformation of amorphous hydroxides to corresponding well-crystalline minerals as time elapses, e.g. from ferrihydrite to goethite. These transformation processes lead to a decrease in surface area, and subsequent release of arsenic. The second is related to the pH variation and long term exposure of leachates which consist of organic and inorganic species such as acetate, citrate, oxalate, silicate, phosphate, etc. The third is related to the bio-reduction of As(V) to less stable As(III).

The 'hazardous waste' classification is usually determined by the Toxicity Characteristic Leaching Procedure (TCLP) developed by The Environment Protection Agency of the United States (USEPA). However, the TCLP test is not a comprehensive measure of a hazardous waste. It underestimates leachability of arsenic from solid residuals under real site conditions such as landfill and residue pond because it poorly simulates pH, low redox potential, long retention time, bio-reduction, and organic composition of mature landfill [7–9]. The extraction could be 10 times greater by actual landfill leachates than by the TCLP [9]. The arsenic extraction from As-loaded ferrihydrite tends to pass the EPA TCLP test owing partly to the fact that the TCLP extraction fluid consists of only weak acetic acid in pH range 3–5. Other active organic species such as citrate and oxalate, which are also commonly present in landfills and residual pond, are not considered. The effect of these organic species on arsenic extraction and dissolution of iron from the arsenic-rich residue, which is formed during removal of arsenic from contaminated water by adsorption on ferrihydrite and Al-ferrihydrite, has not received much attention and very few data in this area are available in the literature [9–11].

Apart from organic species, inorganic species such as silicate and phosphate are also usually present in contaminated water. For example, the typical Bangladesh tube-well water contains about  $1 \text{ mg L}^{-1}$  As, together with up to  $20 \text{ mg L}^{-1}$  Si (as silicate), and  $2 \text{ mg L}^{-1}$  P (as phosphate). The ability of  $\text{PO}_4^{3-}$  to compete with arsenate for goethite surface sites is well documented [12,13] since  $\text{PO}_4^{3-}$ , like arsenate, is sorbed as an inner-sphere complex via a ligand-exchange mechanism. Also, several studies have established that soluble silica exhibits high affinity for surfaces of aluminium and ferric oxides [14,15]. Species which result from Al(III) hydrolysis are also known to form complexes with Fe(III) and soluble Si(IV) [16]. A yellow-brown Fe–Al sol is reported to be formed by reaction of a ferrihydrite with the Al hydrolysis species at pH 4–4.2. This solution has been shown to be stable over long periods [16]. However, not much work has been reported on the effect of co-presence of both organic and inorganic species on the stability or leachability of arsenic from arsenic-loaded ferrihydrite sludges.

In this paper, we report the results of our investigation of the effect of the presence of organic species including citrate, oxalate, and acetate, on leaching of arsenic from synthetic As-

loaded ferrihydrite and Al-ferrihydrite in the pH range 4–8. The effect of co-presence of the inorganic species silicate and phosphate on arsenic release was also examined. The objective of this study was to determine how the stabilities and leachabilities of As-loaded ferrihydrite and Al-ferrihydrite were affected as a function of pH in the presence of each of the organic and inorganic species noted above. The investigated pH covers the range that is normally found under landfill conditions [7,9]. The concentration of organic species used in this study was comparable to the TCLP extraction in which 0.1 M acetate is used. The As-loaded ferrihydrite and Al-ferrihydrite were synthesized by using As(V) because it is in this form arsenic is usually removed by adsorption on solid adsorbents. As(III) is generally preoxidised to As(V) in arsenic removal process. [17].

## 2. Materials and methods

### 2.1. Synthesis of arsenic-loaded ferrihydrite and Al-ferrihydrite

For As-loaded ferrihydrite, a solution mixture of 0.1 M Fe(III) as  $\text{FeCl}_3$  and 5 mM As(V) as  $\text{Na}_2\text{HAsO}_4$  at pH 2 was first prepared. For As-loaded Al-ferrihydrite, the initial solution contained a mixture of 0.05 M Fe(III), 0.05 M Al(III) (Fe:Al = 1:1) and 55 mM As(V) as  $\text{Na}_2\text{HAsO}_4$ . The solution pH was then adjusted to 7 with sodium bicarbonate and maintained at this pH at room temperature for 4 h with constant stirring when the precipitation of arsenic-loaded ferrihydrite occurred. The precipitated material slurry was aged at  $70^\circ\text{C}$  in a temperature-controlled oven for 24 h [18,19]. After filtration, the precipitate was washed thoroughly with deionised water till free of As(V) and  $\text{Cl}^-$ , and dried at  $60^\circ\text{C}$  for 48 h. The composition of the precipitate was determined by dissolving 1 g of the residue in HCl and analysing for As, Fe and Al in the solution by inductively coupled plasma followed by atomic emission spectroscopy (ICP-AES). XRD spectra of the synthetic materials were obtained by using a Philips PW 2236/20 machine with a Co  $\text{K}\alpha$  radiation source.

### 2.2. Leaching procedure

Stock solutions of silicate and phosphate were prepared from reagent-grade  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  and  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ , respectively. Approximately, 1 mL of chloroform per litre was added to all the solutions to prevent microbial breakdown of the organic acids. For each leaching experiment, 3 g of the prepared As-loaded residue were added to 150 mL of the appropriate extractant solution in a 250 mL glass conical flask. The extractant solution was 0.1 M with respect to the organic salt. Thus, the solid/liquid ratio (w/v) used was 1:50. When needed, the initial concentration of silicate was adjusted to  $22.3 \text{ mg L}^{-1}$  Si and that of phosphate at  $6.8 \text{ mg L}^{-1}$  P. The pH adjustment was made with dilute HCl or NaOH as necessary. The mixture in each flask was

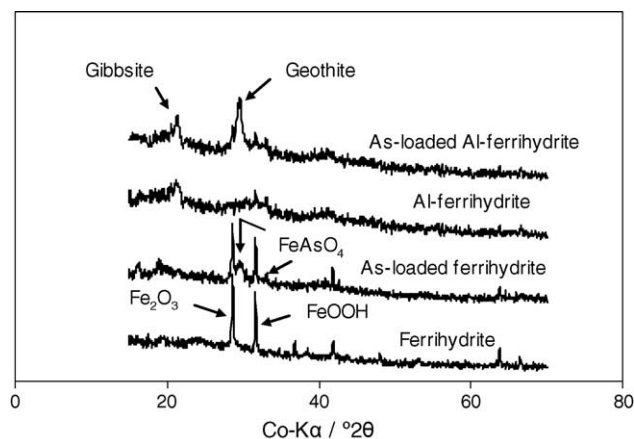


Fig. 1. X-ray diffraction patterns for ferrihydrite, As-loaded ferrihydrite, Al-ferrhydrite, and As-loaded Al-ferrhydrite.

shaken in an incubator for 24 h at 25 °C. Samples were taken at a regular interval and centrifuged at 9000 rpm for 20 min followed by filtration of the supernatant liquid through a 0.2 μm membrane filter. The filtrates were sent to the Marine and Freshwater Research Laboratory, Murdoch University for analysis of As, Fe, Al, Si, and P by ICP-AES. Each experiment was duplicated, and additional repetition of the experiment was conducted to ensure that the relevant standard deviation (RSD) was within 5%.

### 3. Results and discussion

#### 3.1. Characterisation of the synthetic ferrihydrite and Al-ferrhydrite

Fig. 1 shows XRD spectra of the ferrihydrite and Al-ferrhydrite materials. The spectra show that ferrihydrite and As-loaded ferrihydrite both have poorly crystalline with two peaks at  $2\theta$  values 28.66 and 31.67, indicating the presence of hematite ( $\text{Fe}_2\text{O}_3$ ) and goethite ( $\text{FeOOH}$ ) in the samples. These materials result from the partial transformation of ferrihydrite during the synthesis processes. The As-loaded ferrihydrite, showed two additional peaks at 29.75 and 33.10°, which could be assigned to the presence of  $\text{FeAsO}_4$  in the material [20]. The loading of As(V) on the ferrihydrite sample was found to be 18.6 mg/g, indicating the Fe:As molar ratio in the material to be 38:1.

The XRD spectra for both Al-ferrhydrite and As-loaded Al-ferrhydrite include a peak corresponding to gibbsite,  $\text{Al}(\text{OH})_3$ , at 21.40°. The peak at 31.68° for the As-loaded Al-ferrhydrite was assigned to  $\text{Fe}_2\text{O}_3/\text{FeOOH}$ . An elemental analysis of the arsenic-loaded Al-ferrhydrite indicated that the material contained 1:1 mole ratio of Fe to Al and the mole ratio of (Fe + Al) to As was 32:1. Thus, the arsenic loading on Al-ferrhydrite was 23.4 mg/g which was 25% higher than that on ferrihydrite.

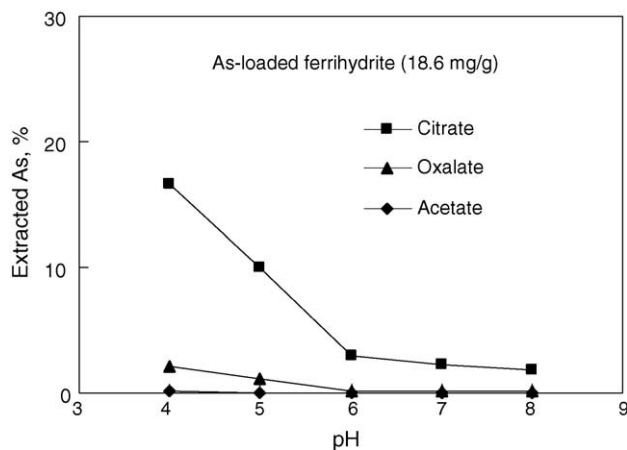


Fig. 2. %As extraction from As-loaded ferrihydrite as a function of pH in the presence of different organic species.

#### 3.2. Effect of presence of organic species on arsenic extraction

##### 3.2.1. As-loaded ferrihydrite

Fig. 2 compares %As extraction in the presence of each of citrate, oxalate, and acetate organic species as a function of solution pH. The %As extraction is strongly related to pH and is dependent on the nature of the organic species, and increases in the order acetate < oxalate << citrate. The %As extraction is quite low for acetate (<0.2%). In the presence of citrate and oxalate, arsenic extraction is remarkably higher than that for acetate, depending on solution pH. For example, the extraction, in the case of citrate, decreased rapidly from 17% at pH 4 to about 3% at pH 6 and then remained constant to pH 8. This could be the result of several competing mechanisms through which As is extracted. These could involve any one or several of the following processes.

- Formation of various soluble or insoluble species resulting from direct interactions between arsenic and the organic species, and partial dissolution of the solid phase as a function of pH.
- Competitive adsorption/desorption of As and organic species on the solid phase.
- Re-adsorption or desorption of arsenic resulting from new equilibrium reactions as a function of pH.

In order to gain some insight into the mechanism of As extraction, the concurrent % Fe extraction in each case was also measured. The results shown in Fig. 3 suggest that even though the magnitudes of %As and %Fe extractions are different, the trends are identical (Figs. 2 and 3). The extraction of both As(V) and Fe(III) was almost negligible at pH > 6. This suggests dissolution of ferrihydrite and consequent release of arsenic into solution. Further information on the mechanism of arsenic release comes from the consideration of residual Fe:As molar ratio in the solid phase. For example, if dissolution of the solid phase as a function

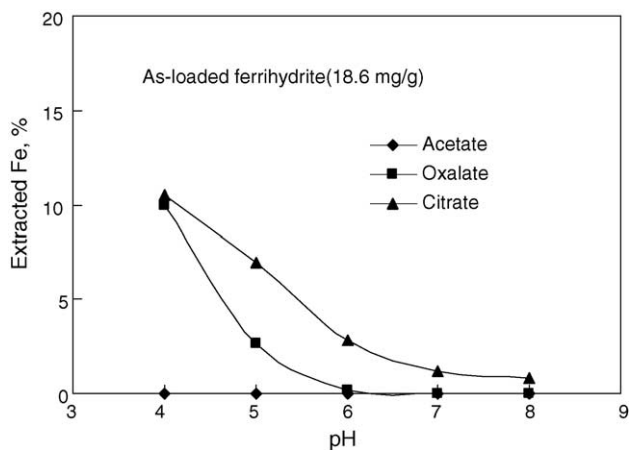


Fig. 3. %Fe extraction from As-loaded ferrihydrite as a function of pH in the presence of different organic species.

of pH were the only mechanism, the Fe:As ratio in solution and the solid phase should remain unchanged at 38:1 at each pH. Fig. 4 shows that the Fe:As ratio actually varied with the solution pH and also depended on the type of organic species. In the presence of citrate, the residual molar Fe:As ratio increased by about 10% on exposure to the extractant at pH 4. At pH 6, it increased by 2%. At pH's higher than approximately 6, the ratio became constant at about 39:1. The significant positive deviation from 38:1 before exposure to the extractant at pH lower than about 6 indicates that more arsenic relative to iron leached into the solution phase through some mechanism additional to the simple dissolution of solid phase. In the case of oxalate, the residual Fe:As ratio in the solid changed in the direction opposite of that for citrate (Fig. 4). The negative deviation suggests that while the dissolution of ferrihydrite occurs, less arsenic relative to iron is leached into the solution phase. Thus, arsenic was retained at the surface of the residual ferrihydrite through some other mechanism. In the case of acetate, the deviation for the resid-

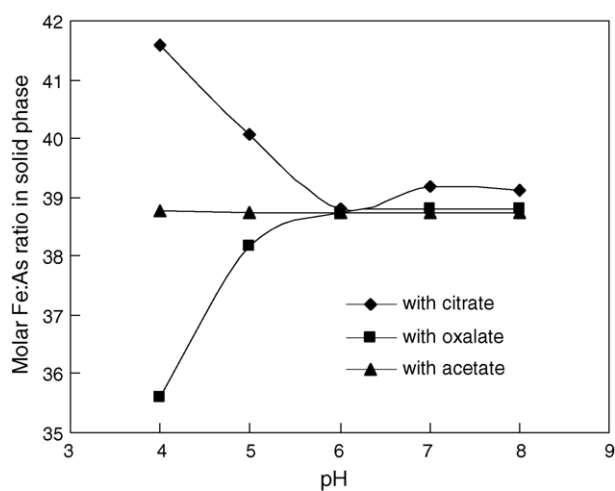


Fig. 4. Molar Fe:As ratios in the solid phase after leaching as a function of pH in the presence of various organic species.

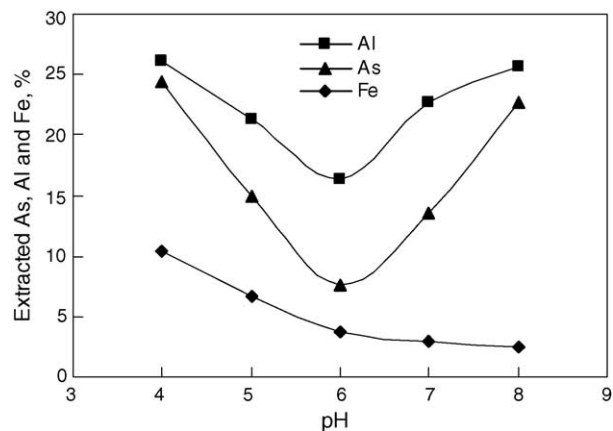


Fig. 5. Extraction of As, Al, and Fe from the As-loaded Al-ferrihydrite as a function of pH in the presence of citrate.

ual Fe:As ratio in the solid phase was about 2% positive over the entire investigated pH range.

### 3.2.2. As-loaded Al-ferrihydrite

Generally, the nature of the organic species and the solution pH both strongly affected the release of arsenic from the As-loaded Al-ferrihydrite. The behaviour was similar to that for the As-loaded ferrihydrite. However, the magnitudes of the effects were quite different for the two solids. For example, in the presence of citrate, approximately 7% more As extraction occurred from the As-loaded Al-ferrihydrite at pH 4, 3% at pH 6 and 22% at pH 8 than that from the As-loaded ferrihydrite under similar leaching conditions. The release of As(V) in the solution closely followed the concurrent release of soluble Fe(III) and Al(III) resulting from dissolution of Al-ferrihydrite. In particular, over the entire investigated pH range, the trends for As(V) and Al(III) release in solution were strikingly similar (Fig. 5). Both show a minimum at pH 6 (Fig. 5). The extraction of Fe(III) and Al(III) into solution in acidic media is not surprising because of the tendency of both iron(III) and Al(III) hydroxides to dissolve at  $\text{pH} < 7$  is well known. In alkaline media ( $\text{pH} > 7$ ), Al(III) is known to dissolve via the formation of various  $\text{Al}^{3+}\text{-OH}^-$  complex ionic species. Ligands such as citrate also form strong complexes with Al(III) ( $\log K = 6.8$ ) [21] and hence should influence the Al(III) solubility equilibrium. Consequently, the arsenic extraction should also be affected. Hence, the similarity of the two curves in Fig. 5 is not surprising.

The effect of oxalate on As(V) extraction was found to be quite unique. While significantly high amounts of Fe and Al were extracted into solution especially in acidic media (16–5% Al and 4–1% Fe, pH range 4–6), only 5% of the As(V), independent of solution pH in the range 4–8, was extracted. Thus, oxalate somehow enabled As(V) to remain attached to the solid phase. Further investigation indicated that about 80% of the added oxalate was located in the solid phase. Organic chelating species like oxalate are known to adsorb on Fe and Al hydroxide surfaces by forming surface complexes [22–25]. We postulate that a secondary phase

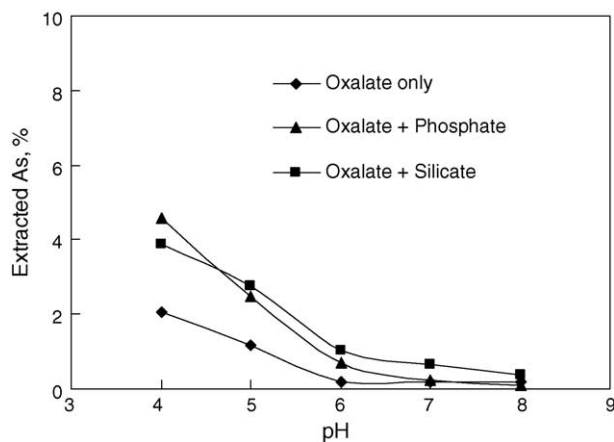


Fig. 6. %As extraction from As-loaded ferrihydrite as a function of pH in the presence of oxalate and oxalate together with either silicate or phosphate.

involving oxalate is formed on the surface of Al-ferrihydrite of Al-ferrihydrite which retains As(V) on it.

The presence of acetate had almost negligible effect on As, Fe and Al extraction. For example, less than 0.2% As and Al were extracted in the pH range 4–6 when acetate was present in the extractant media.

### 3.3. Effect of co-presence of silicate and phosphate with organic species

#### 3.3.1. As-loaded ferrihydrite

Typical results for the effect of  $\text{SiO}_3^{2-}$  and  $\text{PO}_4^{3-}$  on As(V) extraction when these ions are co-present with organic species can be seen from Fig. 6 where data for oxalate are shown. Clearly, co-presence of  $\text{SiO}_3^{2-}$  and  $\text{PO}_4^{3-}$  does influence As(V) extraction at all the investigated pH's. The effect on arsenic extraction is found to be in the order  $\text{SiO}_3^{2-} > \text{PO}_4^{3-}$ . The analysis of the final solutions indicated that almost all the added silicate and phosphate ended up into the solid from which arsenic was being leached. This suggested that the extraction of arsenic was enhanced at the expense of  $\text{SiO}_3^{2-}$  and  $\text{PO}_4^{3-}$  which competed with arsenic for adsorption sites on ferrihydrite. Jackson and Miller [26] have reported similar results for  $\text{PO}_4^{3-}$ . The ability of  $\text{PO}_4^{3-}$  to compete with arsenate for goethite surface sites is well documented [12,13], since  $\text{PO}_4^{3-}$ , like arsenate, is sorbed as an inner-sphere complex via a ligand-exchange mechanism. They are both oxyanions in aqueous solution with three similar acid dissociation constants. The acid dissociation constants for  $\text{H}_3\text{PO}_4$  are:  $\text{p}K_1 = 2.13$ ,  $\text{p}K_2 = 7.21$ ,  $\text{p}K_3 = 12.44$  and for  $\text{H}_3\text{AsO}_4$  are:  $\text{p}K_1 = 3.60$ ,  $\text{p}K_2 = 7.25$ , and  $\text{p}K_3 = 12.52$  [27]. A similar mechanism has been proposed by McNeill and Edwards [28]. An important point to note from Fig. 6 is that the amount of phosphate and silicate adsorbed on the ferrihydrite surface was not proportional to the amount of arsenic desorbed. This suggests that excess adsorption sites were available on the ferrihydrite surface where phosphate and silicate were accommodated.

In the case of co-presence of silicate or phosphate with citrate, the As(V) extraction increased by about 5% over the pH range 4–6.  $\text{PO}_4^{3-}$  and  $\text{SiO}_3^{2-}$  were both found to be adsorbed on ferrihydrite in the presence of citrate similar to that noted earlier for oxalate. This suggests that the mechanism of the effect of  $\text{PO}_4^{3-}$  and  $\text{SiO}_3^{2-}$  on As(V) extraction is similar irrespective of the identity of the organic salt. Surprisingly, silicate and phosphate when co-present with acetate had a small effect (<0.2%) on arsenic extraction over the whole investigated pH range 4–8. It is interesting to note that even though most of the added silicate and phosphate (98% silicate and 80% phosphate) were found to be located in the solid phase, the %As extraction was quite small unlike that for oxalate and citrate noted earlier. Obviously, some mechanism other than that postulated for citrate and oxalate operates in the case of acetate.

#### 3.3.2. As-loaded Al-ferrihydrite

The effects of the co-presence of  $\text{PO}_4^{3-}$  and  $\text{SiO}_3^{2-}$  with organic salts acetate, oxalate, and citrate on extraction of arsenic from As-loaded Al-ferrihydrite were found to be generally similar to those discussed for ferrihydrite. The results confirm that the inorganic ions compete with As(V) for adsorption sites resulting in enhanced release of As(V) into solution. For example, in the case of citrate, the ratio of the adsorbed silicate to the net increase in the extracted arsenic was found to be as high as  $5.8 \pm 0.2$  over the whole investigated pH range. A disproportionately high amount of  $\text{SiO}_3^{2-}$  is concentrated on the surface of solid Al-ferrihydrite, probably through formation of silicate polymers [29]. Partial precipitation of silicate as silica is also possible [30]. For phosphate, the molar ratio of phosphate adsorbed on the solid phase to the net increase in arsenic concentration in solution in the case of citrate media was found to be about 1.3 over the investigated pH range.

## 4. Conclusions

Organic species like oxalate, citrate, and acetate significantly affect release of arsenic from the arsenic-rich ferrihydrite and Al-ferrihydrite. The effect is pH-dependent. The order for the release of As(V) is citrate  $\gg$  oxalate  $>$  acetate. The %arsenic extraction decreases rapidly on change of pH from 4 to 6, beyond which the effect is generally small. The co-presence of silicate or phosphate with any of the organic species enhances the %As extraction in the order  $\text{SiO}_3^{2-} > \text{PO}_4^{3-}$ . The effect is particularly significant for citrate. Both the added silicate and phosphate are adsorbed on the surface of the solid ferrihydrite and Al-ferrihydrite resulting in competitive desorption of As(V). However, the extent of arsenic release is not always matched by the amount of other species which specifically get adsorbed on the surface of the solid. The arsenic release cannot be explained solely in terms of competitive adsorption/desorption. The desorption of arsenic probably occurs through a complex

mechanism involving competitive adsorption/desorption of arsenic, dissolution of iron and aluminium oxide/hydroxides, and complexation of Fe(III) and Al(III) with species such as As(V), OH<sup>-</sup> citrate, oxalate, silicate, and phosphate as a function of pH.

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