

A REVIEW OF ARSENIC INTERACTIONS WITH ANIONS AND IRON HYDROXIDES

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Abstract : Interactions between anions and iron hydroxides and effects of anions such as silicate, phosphate, and bicarbonate on arsenic adsorption by iron hydroxides, are discussed in this review paper. Arsenic is strongly adsorbed on the surface sites of iron hydroxides through the formation of inner-sphere complexes. When arsenic coexists with silicate or phosphate in the suspension of iron hydroxides, arsenic adsorption to iron hydroxides decreases due to competitive adsorption of the anions. Especially phosphate and arsenic exhibit similar chemical behavior and compete for the adsorption sites. Carbonate decreases the sorption capacity of arsenite [As(III)] on iron hydroxides. The affinity of the anions for the adsorption site of iron hydroxides decreases in the following order: arsenate [As(V)] > phosphate > As(III) > silicate > bicarbonate. Silicate, phosphate, and bicarbonate in separate solutions decrease As(III) adsorption at relatively low concentrations and surface site coverage whereas the anions have none or moderated effects on As(V) adsorption. However, As(V) adsorption is dramatically decreased in multi-anions solution.

Key Words : arsenic, iron hydroxides, anion effect, adsorption, interaction

INTRODUCTION

Naturally occurring arsenic in drinking water supplies may affect more than 100 millions of people in several countries such as Bangladesh, India, Taiwan, Vietnam, and the United States.¹⁻⁸⁾ Arsenic is found as As(III) and As(V) species, as well as monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA) in natural systems.⁹⁻¹¹⁾ While As(V) is the predominant species in oxygenated waters¹²⁾, As(III) can be the prevalent species in anoxic water and groundwater.^{8,13)} Both As(III) and As(V) species are often found in the groundwater.^{1,14,15)} Organic arsenic species are generated from inorganic arsenic via biological methylation by fungi and

bacteria.^{10,11,16)}

Since As(III) removal is more difficult than As(V) removal and As(III) has a lower affinity than As(V) for iron hydroxides, the oxidation of As(III) to As(V) is required prior to treatment in order to enhance the extent of arsenic removal.¹⁷⁾ Oxygen and oxidants can be used to oxidize As(III) to As(V). The oxidation of As(III) by oxygen is kinetically very slow, whereas the oxidation of As(III) is rapid when oxidants, such as free chlorine, permanganate, hypochlorite, ozone, and hydrogen peroxide, are used.¹⁸⁾ As(III) can also be oxidized both abiotically and biologically. Manganese oxides¹⁹⁻²¹⁾ and lake sediments²²⁾ have been shown to oxidize As(III) to As(V). As(III) can also be oxidized biologically by bacteria isolated from soil.¹¹⁾

As(III) is more mobile and toxic than As(V).²³⁻²⁴⁾ Organic arsenic compounds are far

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less toxic than the inorganic arsenic species.²⁵⁾ The order of toxicity from greatest to least is arsine (AsH_3) > As(III) > As(V) > MMAA > DMAA.^{11,26)} Studies on long-term human exposure show that arsenic in drinking water is associated with liver, lung, kidney, and bladder cancers, as well as skin cancer.^{7,27,28)} In order to minimize the carcinogenic effect of arsenic, the U.S. Environmental Protection Agency (USEPA) adopted a new maximum contaminant level (MCL) of arsenic at 0.01 mg/L on January 22, 2001.

The most common technique for the removal of arsenic is coprecipitation with ferric salts. However, the removal of arsenic from Bangladesh groundwater is more difficult than the removal of arsenic from US groundwater due to the elevated concentration of silicate and phosphate in Bangladesh groundwater.¹⁵⁾ This review paper summarizes the interactions between arsenic and anions such as silicate, phosphate and carbonate with iron hydroxides and the effects of anions for arsenic adsorption on iron hydroxides.

Interactions between Arsenic and Iron Hydroxides

Arsenic has a high adsorption affinity on iron oxides such as amorphous iron hydroxide^{9,29,30)}, ferrihydrite³¹⁾, and goethite.^{32,33)} As(V) adsorption increases at low pH in the pH range of 4 to 9 while the adsorption of As(III) increases at high pH.^{34,35)} Generally, As(V) is more strongly adsorbed to iron hydroxides than As(III).³⁶⁾ On the other hand, As(III) adsorption is greater than As(V) adsorption on iron hydroxides³⁵⁾ when the solution pH is greater than 8. Raven et al.³¹⁾ also found that ferrihydrite adsorbed greater amounts of As(III) than As(V) at pH 4.6 and 9.2 with an initial arsenic addition of 13.3 mol As/Kg Fe. Oscarson et al.³⁷⁾ reported that As(III) adsorption was greater than As(V) adsorption on iron hydroxides after 12 h of reaction at pH 7.

Both macroscopic and microscopic test methods provide information on the mechanism of adsorption.²⁹⁾ Point of zero charge (PZC) shifts

and ionic strength effects have been included in macroscopic experiments. Adsorption decreases with increasing ionic strength when the ions form outer-sphere surface complexes, whereas ionic strength has little effect on arsenic adsorption when inner-sphere surface complexes are formed.³⁸⁾ On the other hand, Goldberg and Johnson³⁵⁾ have reported that As(V) adsorption on iron hydroxides increases with increasing ionic strength, indicating that inner-sphere surface complexes are formed. They have found that As(III) adsorption decreases on iron hydroxides when the ionic strength increases, indicating an outer-sphere adsorption mechanism. However, these researchers concluded that As(III) adsorption on iron hydroxides formed both inner-sphere and outer-sphere surface complexes based on results from microscopic experiments.

Direct experimental observation of the adsorption mechanism can be obtained using spectroscopic techniques. Extended X-ray absorption fine structure (EXAFS) studies have provided evidence that As(V) forms an inner-sphere bidentate surface complexes on goethite³⁹⁾ and ferrihydrite.⁴⁰⁾ Fourier Transformed Infrared (FTIR) spectroscopy³³⁾ has shown that As(V) forms inner-sphere surface complex with iron hydroxide sites in coprecipitated and adsorbed solids. Goldberg and Johnson³⁵⁾ observed inner-sphere surface complexes between As(V) and goethite with Raman spectroscopy. EXAFS³²⁾ and FTIR spectroscopy³³⁾ have shown that As(III) can be adsorbed by an inner-sphere adsorption mechanism to goethite.

Interactions between Silicate, Arsenic and Iron Hydroxides

Silicon is a semi-metallic element, is the second most common element on earth after oxygen, and can be found in nearly all natural waters.³⁴⁾ Silicate is naturally present at 1-20 mg/L as SiO_2 in surface water and 7-45 mg/L as SiO_2 in groundwater.⁴¹⁾ The iron oxide surface has a strong affinity for silicate. Sigg and Stumm⁴²⁾ have reported that approximately 0.7 mmol/L of aqueous silicate can be adsorbed

to 6 g/L of goethite at an initial concentration of 0.8 mmol/L of silicate.

Silicate can also affect the chemistry of iron hydroxides. Anderson and Benjamin⁴³⁾ found that ferrihydrite crystallized to goethite in less than 24 h in the absence of silicate, while the presence of silicate inhibited crystallization of ferrihydrite for 1-2 weeks. Silicate inhibits coagulation and crystallite growth of iron hydroxides.⁴⁴⁾ The surface chemistry of Si-containing iron hydroxides also depends on the Si content. When the silicate:iron molar ratio increases from 0 to 0.35, the PZC of the iron hydroxides containing silicate decreased from pH 8 to pH 4 approximately.⁴³⁾ In the presence of silicate, the crystallization and particle size of iron oxides can be impacted.^{41,43,45-47)} Davis et al.⁴¹⁾ have demonstrated that silicate sorption to iron hydroxides produces a highly negative surface charge, which leads to the creation of smaller iron particles from large particles. The iron concentration is less than 0.1 mg/L in water in contact with fresh iron hydroxides after passing through a 0.45 μm pore size filter, whereas a significant increase in iron concentration is observed after filtration of water in contact with aged iron hydroxides containing silicate.⁴¹⁾ Meng et al.⁴⁶⁾ also found that the soluble iron concentration increased significantly from 47 to 2040 $\mu\text{g/L}$ when the silicate concentration was 5 mg/L as Si and the pH was increased from 8.6 to 9.4.

Silica catalyzes the oxidation of Fe(II) to Fe(III).^{47,48)} Schenk and Weber⁴⁸⁾ observed that the rate of oxidation was increased as the concentration of silica increased in the pH range of 6.6 to 7.1. On the other hand, Rushing et al.⁴⁵⁾ have found that silica slows Fe(II) oxidation to Fe(III). At pH 6.5, more than 95% of the Fe(II) is oxidized after 30 min in the absence of silicate, however, only 66% of the Fe(II) is oxidized after 30 min in the presence of silicate.

Incorporation of silicate in iron hydroxides dramatically increases the binding strength of the iron hydroxides for cadmium but has a relatively little effect on copper, cobalt, or zinc.⁴³⁾ In contrast, cadmium adsorption on an iron hydroxide/silicate mixture is the same as on a similar amount of pure iron hydroxides.⁴⁹⁾

The adsorption of selenate decreases in the iron hydroxides containing silicate.⁴³⁾

Silicate competes with arsenic for the sorption sites of iron hydroxides.⁵⁰⁾ The adsorption of As(V) decreases with increasing pH and silicate concentration.³⁴⁾ Waltham and Eick⁵¹⁾ reported that silicate increased iron mobilization and interferes with arsenic removal. They postulated that this was due to a decrease in the surface potential of the iron hydroxides due to adsorption of silicate.

Interactions between Phosphate, Arsenic, and Iron Hydroxides

Phosphate adsorption on iron hydroxides has been investigated using modeling and FTIR spectroscopy.⁵²⁻⁵⁴⁾ FTIR spectroscopy has demonstrated that phosphate forms an inner-sphere bidentate binuclear complexes on iron hydroxides.^{52,54)} Persson et al.⁵³⁾ found that phosphate formed an inner-sphere monodentate mononuclear complex on iron hydroxides.

The structure and particle size of iron hydroxides can be affected by phosphate. Mayer and Jarrell⁴⁵⁾ have found that crystallite growth is slower in the presence of phosphate. They have reported the reduction of approximately 10% and 30% of phosphate sorption on iron hydroxides in the presence of 5 mg/L and 14 mg/L of silicate, respectively. Deng⁴⁸⁾ reported that color and structural differences were observed on iron colloid surface in the presence of phosphate. Transmission electron microscopy (TEM) was used to investigate the phosphate effect on the colloid structure of iron hydroxides.⁵⁵⁾ It was found that aggregated iron hydroxides had a three-dimensional branched chain structure; however, the formation of the chain structure of iron hydroxides was inhibited in the presence of phosphate. Lytle and Snoeyink⁵⁶⁾ observed the particle size of iron oxide suspension using photon correlation spectroscopy. They have found that phosphate decreases particle size of iron hydroxides.

The amount of phosphate sorption is correlated to iron hydroxides in sediment and soil.^{57,58)} Specifically, it has been reported that phosphate adsorption on iron hydroxides decreases in the presence of humic acid, magnesium, sulfate and fluoride at low pH, whereas calcium increased phosphate adsorption at high pH.^{59,60)} Geelhoed et al.⁶¹⁾ reported on the interaction between phosphate and citrate on iron hydroxides. They found that the presence of citrate decreased phosphate adsorption on iron hydroxides at pH below 7, whereas citrate adsorption decreases in the presence of phosphate on iron hydroxides over a wide pH range. The presence of phosphate reduces the amount of arsenic adsorption on iron hydroxides.^{22,30,34)}

Phosphate and As(V) exhibit similar chemical behavior and compete for specific adsorption sites.^{23,30,34,62)} Some researchers have reported desorption of arsenic on iron hydroxides in the presence of phosphate.^{9,16)} Arsenic release has been positively correlated to added phosphate concentration.^{9,62)} Violante and Pigna²³⁾ reported the competitive sorption of As(V) and phosphate on iron oxide. They have found that the sorption of As(V) is reduced by increasing the initial P/As(V) ratio. At an initial P/As(V) molar ratio of 1.5, approximately 72% of As(V) is adsorbed on iron hydroxides while 64% of P is adsorbed at an initial As(V)/P molar ratio of 1.5.

Interactions between Carbonate, Arsenic, and Iron Hydroxides

Carbonate can be encountered in all natural waters. Total carbonate is naturally present at the concentration of greater than 120 mg/L as C in some groundwater.³⁴⁾ Some researchers have measured carbonate adsorption on iron hydroxides.⁶³⁻⁶⁵⁾ Van Green et al.⁶⁴⁾ observed that the maximum adsorption of carbonate on iron hydroxides occurred at approximately pH 6. Villalobos and Leckie⁶³⁾ reported that the maximum surface coverage was about 1.2-1.4 $\mu\text{mol}/\text{m}^2$ in open systems. Increasing ionic strength decreases carbonate adsorption on iron.^{63,64)} These results indicate the formation of weak carbonate surface

complexes at the interface between water and iron hydroxides. The adsorption mechanisms of carbonate on iron oxide can be determined utilizing microscopic tests. Attenuated Total Reflectance Fourier Transformed Infrared (ATR-FTIR) data have shown that carbonate forms monodentate inner-sphere complexes on iron oxide.^{63,66)}

Zachara et al.⁶⁵⁾ found a competitive effect of carbonate on chromate adsorption on iron hydroxides. Van Green et al.⁶⁴⁾ have observed that the presence of carbonate decreases chromate adsorption on iron hydroxides. In contrast, carbonate promotes the adsorption of selenate and sulfate in the pH range of 6 to 8.⁶⁷⁾ Carbonate also forms ternary surface complexes with U(VI) and Pb(II).^{68,69)}

Fuller et al.⁷⁰⁾ reported that the presence of carbonate had little effect on As(V) sorption in coprecipitation experiments. Wilkie and Hering⁷¹⁾ reported that the addition of carbonate had a slight effect on As(V) adsorption at pH 9 and no effect on As(III) adsorption at pH 6. High arsenic concentrations in groundwater are correlated with high bicarbonate concentrations.^{72,73)} Appelo et al.⁷⁴⁾ have demonstrated, using model calculations, that carbonate in soil and groundwater, in particular, reduces the sorption capacity of arsenic on iron hydroxides. Holm³⁴⁾ also reported a similar effect of carbonate in As(V) adsorption to iron hydroxides.

Binding Affinity of Anions on Iron Hydroxides

The binding affinity of anions for the surface site of iron hydroxides can be used to describe the interactions between anion and iron oxide. Silicate adsorption is weaker than As(V) adsorption on iron hydroxides.⁵⁰⁾ Liu et al.⁷⁵⁾ reported that As(V) had a stronger affinity than phosphate for iron hydroxides. Meng et al.⁷⁶⁾ calculated the binding affinity of the anions such as phosphate, silicate, As(III), and As(V) on iron hydroxides. At constant pH, the binding affinity was determined by the apparent adsorption constant (K^{app}) from Eq (1).

$$K^{app} = \frac{[SH_q L^{(n-1-q)-}]}{[SOH][L^-]^m} = [H^+]^m K \quad (1)$$

($m=1$ to 4; $q=m-1$)

where [] indicates the concentration of the aqueous and surface species, SOH denotes the hydroxyl sites on iron hydroxide surface, L^- indicates the anions, and $SH_q L^{(n-1-q)-}$ represents the adsorbed anion as surface complexes.

When total Fe(III) concentration in the suspension was 6.7 mg/L, the total surface site concentration was 0.108 mM and it was calculated based on the experimental results of Meng and Letterman.⁴⁶⁾ The affinity of the anions for iron oxide sites decreased in the following order arsenate > phosphate > arsenite > silicate at pH 6.8 (Table 1). The apparent adsorption constant of As(V) was 7, 60, and 800 times greater than phosphate, As(III), and silicate, respectively.

Combined Effects of Anions on Arsenic Adsorption by Iron Hydroxides

Arsenic adsorption on iron hydroxides was inhibited in the presence of silicate^{34,46,50,51)}, phosphate^{23,30,34,60)}, and carbonate.^{34,37,74)} Meng et al⁷⁶⁾ showed the combined effects of anions on As(III) and As(V) adsorption in multi-anions solutions (Fig. 1). Simulated Bangladesh groundwater containing the same arsenic, iron, cation, and anion concentrations as Bangladesh groundwater was used in their study. Overall As(III) adsorption decreased except in chloride solution. Silicate and bicarbonate concentrations were 160 and 550 times greater than As(III), respectively, whereas the binding affinity of As(III) was

higher than silicate and bicarbonate. In contrast, bicarbonate, phosphate and silicate had none or moderate effects on As(V) adsorption. This was attributed to the strong affinity of As(V) on iron hydroxides. However, As(V) adsorption decreased dramatically in multi-anions solution containing phosphate (Fig 1). As a result of the increased surface site coverage, the As(V) adsorption decreased when phosphate coexisted with silicate and bicarbonate. The presence of silicate and phosphate in the suspension of iron hydroxides decreased the As(V) adsorption.³⁾

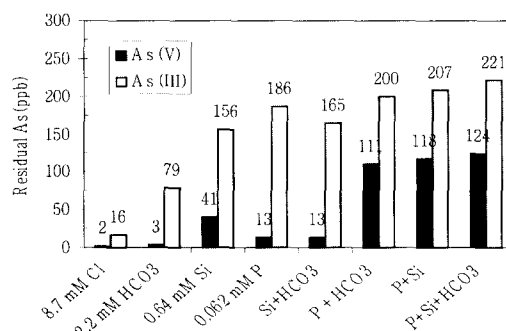


Figure 1. Combined effects of anions on As(V) and As(III) adsorption from simulated Bangladesh groundwater (2.5 mM $CaCl_2$, 0.82 mM $MgCl_2$, and 2.2 mM $NaCl$). Initial As = 0.004 mM; total Fe(III) = 0.12 mM; equilibrium pH = 6.9 ± 0.1 . (Modified from Ref 76)

Concluding Remarks

Extensive studies have studied the mechanisms of arsenic removal and the effects of anions for arsenic removal by iron oxides. Furthermore, combined effects as multi-anions have been reported recently. The purpose of this review has been to explain the mechanisms of

Table 1. Binding affinity of anions for iron hydroxides (from Ref 76)

	As(V)	P	As(III)	Si	HCO ₃
Total SOH sites (mM)	0.108	0.108	0.108	0.108	0.108
Initial anion concentration (mM)	0.010	0.010	0.010	0.010	NA
Equilibrium anion concentration (mM)	4.0E-5	3.0E-4	2.1E-3	7.5E-3	NA
K^{app}	2.5E6	3.4E5	3.8E4	3.1E3	NA
Affinity	High \longrightarrow Low				

*Equilibrium pH = 6.8, 2.5 mM $CaCl_2$, 0.82 mM $MgCl_2$, 2.2 mM $NaCl$.

arsenic adsorption on the surface of iron hydroxides and the effects of anions such as silicate, phosphate, and carbonate on the arsenic adsorption by iron hydroxides. The affinity of the anions for the adsorption site of iron hydroxides was also summarized and synergistic effects of multi-anions on arsenic adsorption was highlighted. Some controversial points presented in this review may be attributed to the synergistic effects and the interactions between anions and cations. Further research on the effects of cations on arsenic removal and the interaction between anions and cations on iron hydroxides may advance the understanding of the mechanism for arsenic adsorption on iron hydroxides.

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