Abiotic reduction mechanism of As(V) by fulvic acid in the absence of light and the effect of Fe(III)

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Abstract

In this paper, the mechanism of the redox cycling of arsenic under dark conditions was studied to help explain the high prevalence of As(III) in groundwater where no photochemical redox cycling is expected to occur. Most research has focused on the photochemical oxidation and reduction of metals and metal ions with dark redox cycling not given as much attention. A full understanding of the geochemical cycle and speciation of arsenic makes it equally important to study reduction of As(V) to As(III) under dark conditions.

The reduction of As(V) by FA in the absence of light is hypothesised to occur via complexation, which can be greatly enhanced by the presence of iron. Fe(III) is envisaged to play two roles:

- It facilitates binding of arsenate by FA through intermetallic bridging which results in the reduction of As(V) to the intermediate As(IV).
- It can be reduced by FA to Fe(II) which then can reduce As(IV) to As(III). The reduction of As(V) is felt to occur in two one-electron steps, where the As(IV) is reduced by Fe(II).

In solutions with no added Fe(III), binding of the negative arsenate by the negative FA occurs through inter-metallic bridging by cationic metals inherent in the FA. Competition from H^+ ions for the binding sites on FA at lower pH results in the diminished reduction.

Keywords: abiotic reduction, mechanism, As(V), fulvic acid, Fe(III)

Introduction

Our previous study has demonstrated that As(V) can be reduced to As(III) by fulvic acid (FA) under both light and dark conditions in the presence and absence of Fe(III) (Tongesayi and Smart, 2006). This means that photochemical reduction is not the only mechanism by which As(V) can be reduced to As(III) by FA.

Most previous research (Wittbrodt et al., 1996; Hug et al., 1997; Fukushima et al., 1999; Gaberell et al., 2003; Dutta et al., 2005) has focused on photochemical Fe(III)-mediated oxidation or reduction of heavy metals in natural waters; however, redox cycling under dark conditions has not been given as much attention. Also the development of technologies to remove arsenic species from drinking water has attracted intense research efforts (Thirunavukkarasu et al., 2003). This work is important in groundwater systems where the presence of DOM and iron may result in As(III) contamination.

Materials and methods

Suwannee River Fulvic Acid (FA) was obtained from the International Humic Substances Society (IHHS) collection of reference humic materials. The As(V) solutions were prepared from SPEX Certiprep, Inc. (Metuchen, NJ) PEAS2-2X 1000 mg/ℓ As(V) in 2% HNO_3 in which As(V) was in the arsenate (AsO_4^{3-}) form, and the As(III) stock solution was prepared from As_2O_3 Fisher Scientific Certified (Chicago, IL). Fe(III) stock solution was prepared from iron(III) sulphate puratronic, 99.999% metal basis

from Alfa Aesar (Ward Hill, MA).

Amberlite-XAD-8 20-50 mesh (Fluka AG, Cheische Fabrik CH-9470 Buchs, Switzerland) was packed in an opaque glass column and was used to separate FA from the arsenic species before analysis (Tongesayi and Smart, 2006). Acid-washed (10% HNO_3) and oven-dried (160 to 170ºC) glassware and reagent-grade or higher chemicals (Fisher Scientific, Chicago, IL) were used in all experiments and all solutions were prepared with Milli-Q (millipore, Billerica, MA) deionised distilled water. All glassware was rinsed with 70% isopropyl alcohol before use. HCl (optima) and NaOH (50% w/w) were used for all pH adjustments as appropriate.

Nalgene Amber high density (HDPE) bottles (60 Ml, Fisher Scientific, Chicago, IL), acid-washed (10% HNO_3) and rinsed with 70% isopropyl alcohol were used for dark incubation reactions. Temperature was maintained constant during incubations using an Isotemp Immersion Circulator from Fisher Scientific. A model 2100 pH/Temp/mV meter (VWR Scientific Products, West Chester, PA) was used to measure the pH of solutions.

Reaction incubations

Aliquots from a stock solution of FA were equilibrated at the appropriate pH for 24 h prior to being spiked with a known concentration of As(V). Reaction mixtures in which Fe(III) was included were initially incubated for 24 h with only FA and Fe(III) in order to prevent precipitation of Fe. They were then equilibrated at an appropriate pH for 24 h before being spiked with a known concentration of As(V).

HCl (Fisher Optima, Chicago, IL) or NaOH (50% W/W Fisher Certified, Chicago, IL) were used to adjust the pH of the reaction mixtures as appropriate. No buffer was added to the reaction mixtures as it was felt that this could alter the chemistry of FA. As a result, pH was periodically adjusted especially at higher pH

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(pH > 4) where pH slightly decreased with time. The incubated mixtures were examined after specific reaction times. Blanks were treated the same and the experiments were run in triplicate.

Arsenic analyses

The effect of each experimental parameter on the reduction of As(V) was inferred from the measured concentration of As(III). Square wave cathodic stripping voltammetry (SWCSV) at a hanging mercury drop electrode was employed using a BAS 100_B Electrochemical Analyzer (Bioanalytical Systems, Inc., West Lafayette, IN) coupled to a BAS Controlled Growth Mercury Electrode (Tongesayi and Smart, 2006).

Determination of Fe(II)

Samples for Fe(II) analyses were prepared using the o-phenanthroline method. The prepared samples were then analysed using UV/Vis spectrophotometry at 500 nm using the standard addition method.

Results and discussion

As shown in Fig. 1, substantial reduction of As(V) by FA occurs in the dark at pH 6. This suggests that photochemical reduction is not the only abiotic mechanism responsible for the production of As(III). The amount of reduction has also been shown to increase with an increase in FA concentration (see **Appendix**).

In order to determine the effect of iron on the reduction of As(V) by FA at pH 3 and 6, known amounts of Fe(III) were added to the reaction mixtures of As(V) and FA. The rate of As(V) reduction, r, can be written as shown in Eq. (1):

$$r = -d[As(V)]/dt = k_{obs}[As(V)] \qquad (1)$$

where:

k_{obs} is the pseudo first-order rate constant
The $[As(V)]_t$ at incubation time, t, was obtained by subtracting the [As(III)] measured from the initial $[As(V)]_i$

As shown in Table 1, the addition of Fe(III) increased the rate of As(V) reduction compared to the rate in the absence of Fe(III) at both pH, but the effect of Fe(III) is more pronounced at pH 3.

It has been reported that both humic and fulvic acid form complexes with arsenic (Mukhopadhyay and Sanyal, 2004). Because of their different charges, Fe(III) and As(V) will likely bind non-competitively at different sites on FA and also be non-competitively reduced by FA. This binding of the negatively charged As(V) and negatively charged FA has been suggested to occur through ternary complexation with cationic metals inherently present in the FA, and the higher the metal content the greater the extent of complexation (Redman et al., 2002).

As shown in Fig. 2, no As(III) was found prior to 120 h of incubation of As(V) in the absence of iron at pH 2, whereas in the presence of Fe(III) a small amount of As(III) was produced after 24 h. As the amount of Fe(III) was increased from 2 μM to 250 μM, a concurrent increase in the amount of As(III) was also observed after 24 h. After incubation times of 120 and 700 h in the absence of Fe(III), more As(III) was produced than when Fe(III) was added. This suggests that although Fe(III) is essential to the reduction of As(V), the net production of As(III) must depend on the relative rates of the reduction of As(V) and the re-oxidation of the As(III) produced. The redox reaction of dissolved organic matter (DOM) and many metal redox

TABLE 1
The effect of pH and Fe(III) on the reduction of As(V) by FA. Initial reaction conditions: 0.75 mg/ℓ FA, 0.50 μM As(V), 2.2 μM Fe(III), 25°C. (K_{obs} values are averages and standard deviations are too small to be included).

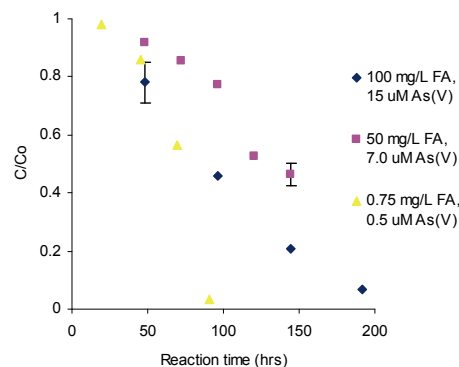| pH	k_{obs}/min	
3	4.3 x 10^{-5}	1.2 x 10^{-5} (no Fe(III))
4	8.7 x 10^{-5}	
5	3.0 x 10^{-4}	
6	6.0 x 10^{-4}	4.1 x 10^{-4} (no Fe(III))
7	5.8 x 10^{-4}	

Figure 1
Fraction of As(V) (C/C_o) remaining as a function of time at pH 6. Analysis was done in triplicate and error bars represent the standard deviations. Standard deviation is within symbol size for data without error bars.
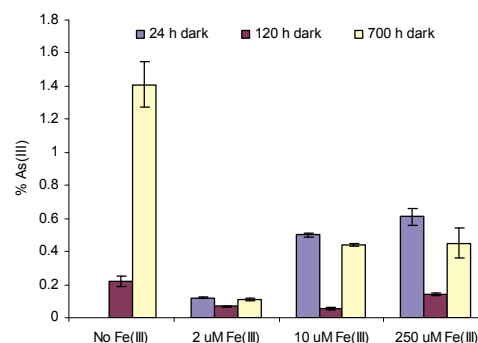

Figure 2
Percent As(III) produced by reduction of As(V) by FA at pH 2 and 28.8°C in the function of [Fe(III)]. Initial reaction conditions: 100 mg/ℓ FA standard, 15 μM As(V). Analysis was done in triplicate and error bars represent the standard deviations. Standard deviation is within symbol size for data without error bars.

couples have been reported to occur via one-electron transfer steps (Wittbrodt et al., 1996). Therefore, it seems likely that the first step in the reduction of As(V) to As(III) by FA should involve the unstable intermediate As(IV). Klaening et al. (1989) have reported the existence of As(IV) and observed that its rates of formation and disappearance are comparable.
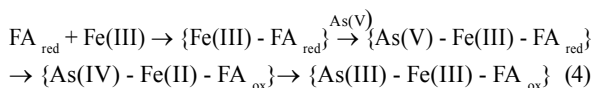
In our experiments, it can be hypothesised that the fate of As (IV) depends on the reaction conditions. Fe(III) can oxidise As(IV) but any Fe(II) produced in that reaction can also reduce the As(IV) back to As(III), as shown in Eq. (2) and Eq. (3) respectively, which implies that the relative ratio of Fe(II)/Fe(III) plays a very significant role in the net reduction of As(V) because the rates of these two reactions are similar (Emett and Khoe, 2001). The reaction represented by Eq. (2) does not occur

in the absence of Fe(III). This could explain the accumulation of As(III) in the absence of Fe(III) after incubation times of 120 h and 700 h as shown in Fig. 2.

$$As^{4+} + Fe^{3+} \rightarrow As^{5+} + Fe^{2+} \qquad (2)$$

$$As^{4+} + Fe^{2+} \rightarrow As^{3+} + Fe^{3+} \qquad (3)$$

At pH 2 about 80% of the Fe(III) is reduced to Fe(II) by FA after 24 h as shown in Fig. 3. Voelker and Stulzberger (1996) reported approximately 70% reduction of Fe(III) after 100 min at pH 3 with similar concentrations of Fe(III) and FA. This implies that the Fe(II)/Fe(III) ratio is high and the reduction of As(IV) {As(IV) + Fe(II) → As(III) + Fe(III)} should occur; however, less than 1.5% As(III) was produced at Fe(III) concentrations ranging from 2 to 250 µM.

At pH 2 Fe(III) is present in the form $FeOH^{2+}$, As(V) is present as $H_3AsO_4/H_2AsO_4^-$ (Cherry et al., 1979), and FA will be highly protonated, yet might still retain some negative charge. The addition of iron to FA produces the {Fe (III)-FA} complex (Voelker and Sulzberger, 1996; Bryan et al., 1997), which could facilitate the binding of As(V) by FA through inter-metallic bridging. This could then increase the reduction of As(V) by FA as shown in Eq. (4):

$$FA_{red} + Fe(III) \rightarrow \{Fe(III) - FA_{red}\} \overset{As(V)}{\rightarrow} \{As(V) - Fe(III) - FA_{red}\}$$
$$\rightarrow \{As(IV) - Fe(II) - FA_{ox}\} \rightarrow \{As(III) - Fe(III) - FA_{ox}\} \quad (4)$$

Alternatively, the iron might also bind the As(V) forming a positively charged complex {As(V) - Fe(III)}. This is then bound by FA as the {As(V) - Fe(III) - FA$_{red}$} complex resulting in the reduction of As(V). This complex formation would explain the increased rate of As(III) production in the presence of Fe(III) and the extent of As(V) reduction would then depend on the formation of these complexes.

The formation of these complexes will be limited by H$^+$ competition for FA at pH 2, and as a result, the rate of reduction of As(V) will be low. The large amount of Fe(II) produced together with the small amount of As(III) generated suggests that the Fe(II) is unable to reduce the As(V) at this pH, but can reduce the As(IV) intermediate. As a result, if experimental conditions do not favour the production of As(IV) in solution, which should occur after the binding of As(V) by FA, very little or no As(III) will be generated.

The situation is different at higher pH, where FA can reduce As(V) even in the absence of added Fe(III). In the presence of Fe(III), the Fe(II) produced will increase the rate of As(V) reduction by most likely acting on the intermediate As(IV). Although less Fe(II) was generated at pH 6, more As(III) was produced than at pH 2 under the same initial conditions as shown in Fig. 3. At higher pH, both As(V) ($H_2AsO_4^-/HAsO_4^{2-}$) and FA are more negatively charged and a larger fraction of the added iron will be bound by FA.. Therefore, more complex formation occurs through inter-metallic bridging, which results in higher reduction rates.

The values of k_{obs} shown in Fig. 4 decreased as the As(V) concentration increased, which implies that the reaction does not follow first-order kinetics. Reduction via complex formation implies that FA-As(V) and FA-Fe(III) should represent intermediates. Since the FA concentration is constant, the FA/As(V) ratio decreases with the initial concentration of As(V) which results in the apparent decrease in the reduction rate.

Conclusion

Abiotic reduction of As(V) to the more toxic As(III) by FA has been shown to occur to a significant extent in dark conditions
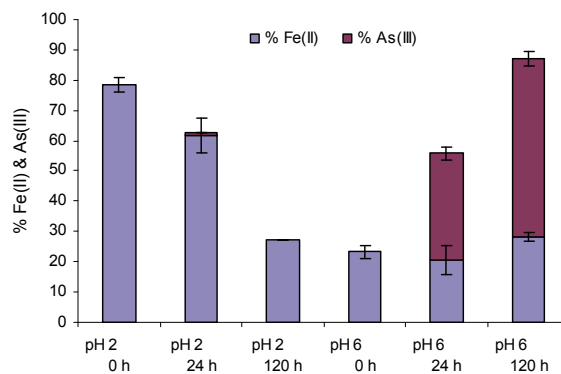

Figure 3
Percent Fe(II) and As(III) produced in a mixture containing 100 mg/ℓ FA, 15 µM As(V), and 250 µM Fe(III) at 28.8°C under dark conditions. The value for % Fe(II) is the height of the blue bar and the value for % As(III) is the height of the red bar (above the blue bar). Analysis was done in triplicate and error bars represent the standard deviations. Standard deviation is within symbol size for data without error bars. (Time was recorded after addition of As(V)).
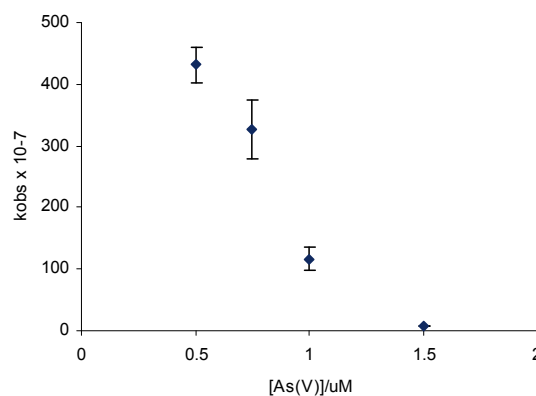

Figure 4
Effect of [As(V)]$_{initial}$ on k_{obs}. Other reaction conditions: 25°C, pH 3, 0.75 mg/ℓ FA, 2.2 µM Fe(III), dark. Analysis was done in triplicate and error bars represent the standard deviations. Standard deviation is within symbol size for data without error bars.

and the data support our hypothesis that reduction occurs via complex formation. This has serious environmental consequences since some of our experimental conditions are similar to groundwater conditions.

Acknowledgements

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APPENDIX: Supporting data

Effect of FA concentration

Rate of reduction reaction of As(V), r, can be written as follows:

$$r = -d[As(V)]/dt = k_{obs}[As(V)] \qquad (1)$$

where:

k_{obs} is the pseudo-first-order rate constant.

Concentration of As(V) after a certain incubation period is obtained by subtracting the concentration of produced As(III) from the initial concentration of As(V).

Integrating Eq. (1) gives:

$$\ln\{([As(V)]_{initial} - [As(III)])/[As(V)]_{initial}]\} = k_{obs}t \qquad (2)$$

The effect of FA concentration on the reduction kinetics is shown in Fig.1. Values of k_{obs} were evaluated from the slopes of the lines according to Eq. (2). No reduction of As(V) was observed in the absence of FA. The amount of As(V) reduced increased with an increase in the FA concentration.

Rearranging Eq.(1) by considering concentration of FA gives:

$$r = -d[As(V)]/dt = k_{FA}[As(V)][FA] \qquad (3)$$

where:

k_{FA} is the empirical second-order rate constant.

From Eq.(1) and Eq.(3):

$$k_{FA} = k_{obs}/[FA] \qquad (4)$$

Eq. (4) shows a linear relationship between k_{obs} and FA concentration.

Salt effects

To determine the effect of a background electrolyte or salt effect on the kinetics of the reduction reaction, LiCl was used. From work done by Bonn and Fish (1993), lithium cation, of all the alkali metal cations, exhibited no specific binding with humic substances (HA) and was therefore appropriate for the purpose of this work. As shown in Fig. 2, the amount of As(V) reduced by FA decreased with an increase in the concentration of LiCl.

Since Li^+ ion is not likely to be bound by FA, this observation can be explained in terms of the salt ions interposing themselves between cation binding sites on FA and the anionic As(V) reducing chances of complex formation which precedes reduction of As(V).
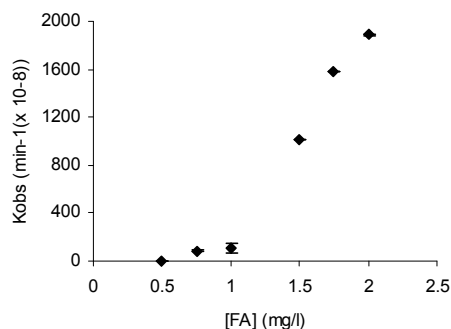

Figure 1

Effect of [FA] on the kinetics of the reduction of As(V) at pH 3 and 25 °C under dark conditions. Initial reaction conditions: 1.50 µM As(V), 2.2 µM Fe(III). Standard deviation (triplicate analysis) is within symbol size for data without error bars.
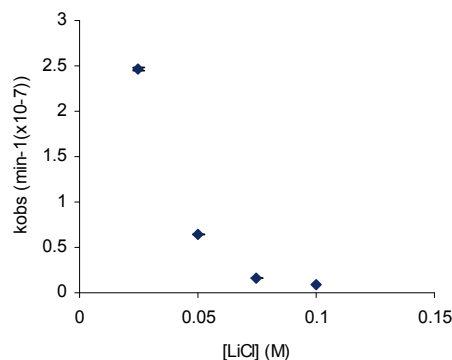

Figure 2

Effect of [LiCl] on the kinetics of the reaction at pH 3 and 25 °C under dark conditions. Initial reaction conditions: 0.50 µM As(V), 0.75 mg/L FA, 2.2 µM Fe(III). Standard deviation (triplicate analysis) is within symbol size for data without error bars.