ARSENIC ADSORPTION AND REDUCTION IN IRON-RICH SOILS NEARBY LANDFILLS IN NORTHWEST FLORIDA

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Abstract: In Florida, soils are mainly composed of Myakka, an acid soil characterized by a subsurface accumulation of humus and Al(III) and Fe(III) oxides. Downgradient of the landfills in Northwest Florida, elevated levels of iron and arsenic observations had been made in the groundwater from monitoring wells, which was attributed to the geomicrobial iron and arsenic reduction. There is thus an immediate research need for a better understanding of the reduction reactions that are responsible for the mobilization of iron and arsenic in the subsurface soil nearby landfills. Owing to the high Fe(III) oxide content, As(V) adsorption reactions with Fe(III) oxide surfaces are particularly important, which may control As(V) reduction. This research focused on the investigation of the biogeochemical processes of the subsurface soil nearby landfills of Northwest Florida. Arsenic and iron reduction was studied in batch reactors and quantified based on Monod-type microbial kinetic growth simulations. As(V) adsorption in iron-rich Northwest Floridian soils was further investigated to explain the reduction observations. It was demonstrated in this research that solubilization of arsenic in the subsurface soil nearby landfills in Northwest Florida would likely occur under conditions favoring Fe(III) dissimilatory reduction.

Keywords: As(V), Fe(III), Reduction, Adsorption, and Landfill

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INTRODUCTION

Nearby the landfills of Northwest Florida, elevated levels of iron and arsenic, especially iron observations had been made in the groundwater from monitoring wells downgradient of the landfills, which was attributed to the geomicrobial iron and arsenic reduction (Wang *et al.*, 2012). In Florida, soils are mainly composed of Myakka, an acid soil characterized by a subsurface accumulation of humus and Al(III) and Fe(III) oxides. In Northwest Florida, iron content is much higher than the rest of the state with a range of 20 to 200 mg/g soil (Williams *et al.*, 2012). In the subsurface soil, iron exists in the form of Fe(III) oxides. When reducing conditions occur, Fe(III) is reduced to Fe(II) and released. Researchers have discovered that *Shewanella* and *Geobacter* species are capable of conserving energy for growth with the structure Fe (III) bound in smectite clay as the sole electron acceptor (Kostka *et al.*, 2002). Nearby the landfills, arsenic release has been proven to be from unlined construction and demolition debris (C&D) landfills (Wang *et al.*, 2012). When coming out of circulation as construction debris, wood treated with chromated copper arsenate (CCA) for protection from fungus, water damage and termites is primarily disposed within these unlined C&D landfills (Saxe *et al.*, 2007; Hawley *et al.*, 2009). In the subsurface soil, As(V) and As(III) are the most commonly found arsenic species (Hawley *et al.*, 2009). Thermodynamic calculations and experimental results indicate that at high redox levels (pe + pH > 10), As(V) is the predominant arsenic species; while under moderately reduced conditions (pe + pH < 8), As(III) is the most abundant form of arsenic (Keaton and Kardos, 1940). As(V) adsorbs strongly to Al(III) and Fe(III) oxides in the soil (Zeng *et al.*, 2008). Studies show that 90% of arsenic is closely associated with the iron fraction in the subsurface soil nearby landfills in the form of As(V) (Jambeck *et al.*, 2006; Saxe *et al.*, 2007). In Northwest Florida, owing to the high iron content, As(V) exhibits very little tendency to leach. However, As(V) readily undergoes reduction in anaerobic environments to As(III), which is predominantly driven by microbial mediated biogeochemical interactions (Jones *et al.*, 2000). After reduction, As(III) mainly exists in the form of H_3AsO_3 and is very mobile because of its neutral nature. So far, a handful of microorganisms capable of respiring As(V) have been isolated, which include *Sulfurospirillum*, *Clostridium*, *Caloramator*, *Clostridium*, and *Bacillus*, etc. (Anderson and Cook, 2004; Sau *et al.*, 2008; Baesman *et al.*, 2009). In addition, iron reducing bacteria such as *Shewanella* species are also able to reduce As(V) to As (III) (Jones *et al.*, 2000). As a dissimilatory process, arsenic reduction must be coupled to the oxidation of an energy source, most commonly organic carbon. Nearby landfills, the organic content of landfill leachate can serve as the carbon source (deLemos *et al.*, 2006; Zhang *et al.*, 2008; Dubey *et al.*, 2009).

It is noted recently that there is an immediate research need for a better understanding of the reduction reactions that are responsible for the mobilization of iron and arsenic in the subsurface soil nearby landfills. Especially, adsorption reactions between As(V) and Fe(III) oxide surfaces are particularly important, which control arsenic reduction owing to the high Fe(III) oxide content in Northwest Florida. As(V) adsorbs strongly to Fe(III) oxides and subsequent arsenic reduction and release are severely constrained to iron reduction (Huang *et al.*, 2008). It has been proposed that solubilization of arsenic in the iron-rich subsurface soil would likely occur under conditions favoring Fe(III) dissimilatory reduction (Huang *et al.*, 2008). Although prior research has demonstrated that that microbial oxidation of organic matters, reductive dissolution of Fe(III) oxides/oxyhydroxides and As(V) can happen spontaneously, arsenic reduction reactions may still face competition from iron reduction. This research focused on the investigation of the biogeochemical processes of the subsurface soil nearby landfills of Northwest Florida. Arsenic and iron reduction was studied in batch reactors and quantified based on Monod-type microbial kinetic growth simulations. As(V) adsorption in iron-rich Northwest Floridian soil was further investigated to explain the reduction observations.

MATERIALS AND METHOD

Soil Collection and Characterization

The soil used for this research was collected from four landfills located in Northwest Florida, including Franklin County Landfill, Quincy-Byrd Landfill (Gadsden County), Baker Landfill (Okaloosa County), and Santa Rosa Central Landfill (Santa Rosa County). Soil samples were collected 1 to 3 feet below the surface, 100 to 300 feet away from the landfills. The collected soil samples were immediately placed in a Styrofoam cooler and sealed. All the soil samples were delivered to the laboratory immediately and stored under refrigeration at 4^oC until usage in the experiments. To assess the soil iron content, soil samples were first partially thawed and placed in an anaerobic chamber with a maintained H_2-N_2 atmosphere. The samples were then ground and the weighed samples were placed in a glass reaction vessel and purged with CO_2-scrubbed air, after which the samples were acidified with hot, 5% perchloric acid to dissolve carbonate precipitates such as siderite, calcite, aragonite, and carbonate forms of green-rust. Evolved CO_2 gas was carried to the coulometer cell containing a

CO$_2$-sensitive ethanolamine solution and quantitatively titrated. The samples were then reacted with 0.25 M hydroxylamine (NH$_2$OH) hydrochloride in 0.25 N HCl and incubated at 60°C for two hours for iron extraction (Lovley & Phillips, 1988; Roden & Zachara, 1996). Following the extraction, soil iron content was determined using spectrophotometric analysis techniques using a spectrophotometer at the wavelength of 447 nm (Shimadzu UV-1650 PC).

Adsorption Experiments

Batch adsorption of arsenate on iron-rich soil was carried out in autoclaved (121°C and 1 atm for 20 min) high-density polyethylene centrifuge tubes. A series of 40 ml vials containing 1×10^{-5}, 2×10^{-5}, 3×10^{-5}, 5×10^{-5}, 7.5×10^{-5}, and 1×10^{-4} M KH$_2$AsO$_4$ in 0.01 M KNO$_3$ background solution (to maintain constant ionic strength) including blank controls in the presence of 10 g air-dry soil (sealed with Teflon-lined screw caps) were agitated on a Wrist Action Shaker (Burrel Scientic, Model 75) for up to four hours to reach equilibrium. Above experiments were conducted at the same conditions as those of the reduction experiments. The suspension was then be centrifuged at 12 000 × g for 15 min, after which As(V) concentration in the supernatant was measured. The amount of arsenate adsorbed on the soil was obtained based on mass balance:

$$q = \frac{(C_i - C_e) \cdot V}{M}$$ **Equation (1)**

where q is the amount of As(V) adsorbed in the soil (mM/kg), C_i and C_e are the initial and equilibrium As(V) concentrations (mM/L), V is the volume of the aqueous phase (L), and M is the mass of the soil sample (kg).

Reduction Experiments

The consortia were cultured using the sampled soil as the innocula under anaerobic conditions in the presence of enriched As(V) or Fe(III) separately. Specifically, 250 ml Teflon-sealed serum bottles equipped with CO$_2$ entrapping devices were used for the culturing. The serum bottles contained 100 mL mineral salts media that had a composition of KH$_2$PO$_4$, 160 mg/L; K$_2$HPO$_4$, 420 mg/L; Na$_2$HPO$_4$, 50 mg/L; NH$_4$Cl, 40 mg/L; MgSO$_4$·7H$_2$O, 50 mg/L; CaCl$_2$, 50 mg/L; FeCl$_3$·6H$_2$O, 0.5 mg/L; MnSO$_4$·4H$_2$O, 0.05 mg/L; H$_3$BO$_3$, 0.1 mg/L; ZnSO$_4$·7H2O, 0.05 mg/L; and (NH4)$_6$Mo$_7$O$_{24}$, 0.03 mg/L. Lactate at a concentration of 250 mg/L and KH$_2$AsO$_4$ at a concentration of 800 mg/L or FeCl$_3$·6H$_2$O at a concentration of 5 g/L were added to serve as the carbon source and electron acceptor, respectively. Resazurin (1 mg/L) was added as a redox indicator to indicate contamination by molecular oxygen and cysteine (3.0 g/L) was added to reduce the trace amount of oxygen remaining in the media after autoclaving. The

media pH was adjusted to 7.0 with 0.1 M Hcl or NaOH. Lactate was filter-sterilized and aseptically added to the autoclaved media. The headspace of the serum bottles was pressurized with ultra-pure nitrogen and the serum bottles were capped with butyl rubber septa and crimped with an aluminum seal. The inoculated serum bottles were put into a rotary-shaker (150 rpm at 35°C) in the dark for at least 1 week until the formation of black precipitate at the bottom and on the wall of the serum bottles was observed. Then 10 mL enriched culture was transferred into 100 mL fresh culture media amended with 250 mg/L lactate and corresponding electron acceptors for the second phase culture enrichment. After the fourth phase enrichment was completed, consortia were harvested by centrifugation (6000 × g for 15 min) and washed twice with a fresh electrolyte solution under an extra-pure nitrogen atmosphere. The electrolyte solution was prepared using analytical reagent-grade NaCl and nano-pure de-ionized water (NPDI, Barnstead, Dubuque, IA) at a concentration of 10^{-5} M. The concentrated cells were then re-suspended in a serum bottle containing fresh, electrolyte solution (10^{-5} M NaCl) to give a final concentration of approximately 5×10^8 cells/ml.

Laboratory arsenic and iron reduction experiments were conducted using 10 g collected soil samples reacting 2.5 mM of lactate and 5 mM of KH$_2$AsO$_4$ in the presence of the mixture of the cultured consortia and 100 mL mineral salts media in 250 ml serum bottles quipped with CO$_2$ entrapping devices. The headspace of the serum bottles was pressurized with ultra-pure nitrogen and sealed with butyl rubber stoppers and aluminum caps to keep an anaerobic condition. Control tests were conducted in the absence of consortia to quantify the abiotic losses in the system. Throughout the course of the experiments, lactate, ferrous iron, arsenate and arsenous acid concentrations were monitored by analyzing the extracted samples using a syringe. Lactate was analyzed by a HPLC equipped with an Agilent Hi-Plex H Column and a UV detector. Arsenate was quantified by ion chromatography (IC, DX-300 system, Dionex, CA) using a conductivity detector. Arsenous acid (H$_3$AsO$_3$) was indirectly determined by measuring the difference in As(V) concentration after oxidizing the sample by 9.1 mM H$_2$O$_2$. For ferrous iron quantification, 1,10-Phenanthroline Method was utilized (Williams *et al.*, 2012). In the presence of 1,10-phenanthroline (C$_{12}$H$_8$N$_2$·H$_2$O), ferrous iron formed a stable, orange-colored complex with the reagent:

$$Fe^{2+}(aq) + 3(ph)H^+ = Fe(ph)_3]^{2+} + 3H^+$$ **(2)**
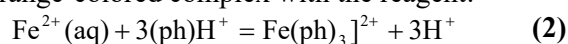
For this experiment, 0.0125 M 1,10-phenanthroline was used and ferrous iron concentrations were quantified using the spectrophotometer (Shimadzu UV-1650 PC) at a wavelength of 520 nm.

RESULTS AND DISCUSSION

Soil Characterization

The soil samples were characterized based on sieve analysis and were identified as loamy or fine sand. Based on sieve analysis, all the soil samples exhibited a poor grading, i.e., the soil particles were in general similar in size range. The finest particles were screened out by sieve 200 (~ 75μm). Santa Rosa County samples had the highest percentage fines of 6.01%. Gadsden County samples were determined to have the lowest percentage fines of 0.53%. Franklin County and Okaloosa County samples had medium values of 1.31% and 4.12% respective. The soil iron content for all the samples ranged from 39.4 mg/g (Franklin County), 65.8 mg/g (Gadsden County), 83.2 mg/g (Santa Rosa County) to 119.9 mg/g (Okaloosa County). The average iron content was 77.1 mg/g. It should be noted that only reducible iron contributes to the quantified iron content. There was a general trend that the soil iron content increased with the increase of percentage of finer particles. This is due to the increase in surface area available for iron accumulation.

Arsenate Adsorption

It was obvious that As(V) had a strong adsorption in the iron-rich Northwest Floridian soil (**Fig. 1**). The driving force of As(V) adsorption in the iron-rich soil was the attractive electrostatic interactions. The principal forms of mineralized Fe(III) in the soil of Northwest Florida included amorphous hydrous Fe(III) oxide ($Fe_2O_3 \cdot XH_2O$), maghemite (gamma-Fe_2O_3), lepidocrocite (gamma-FeOOH), hematite (alpha-Fe_2O_3), and goethite (alpha-FeOOH) (Williams *et al.*, 2012). As(V) can adsorb on most of these iron types. In general, Fe(III) oxides were the dominating iron in the adsorption of arsenate. As(V) adsorption was also pH dependent. In the near neutral pH range of the subsurface soil, Fe(III) oxides were positively charged while the clay minerals were negatively charged. Therefore, Fe(III) oxides were the important sorption "sinks" for As(V), which mainly existed in the form of negatively charged $H_2AsO_4^-$ or $HAsO_4^{2-}$. However, As(III) primarily existed as neutral H_3AsO_3. Therefore, As(III) was not strongly adsorbed under typical soil conditions.
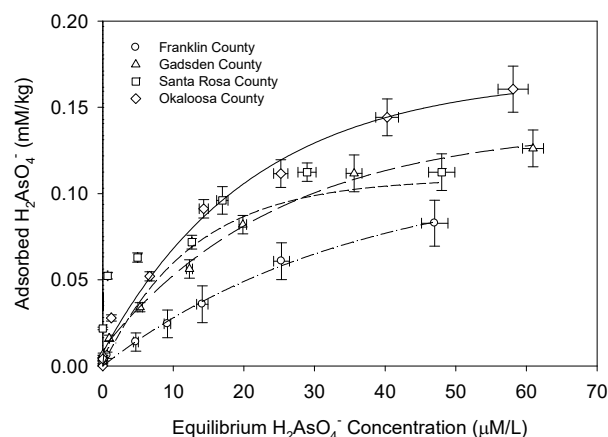

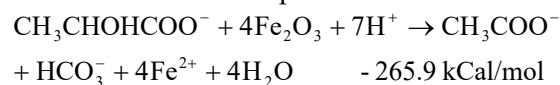**Fig. 1** As(V) Adsorption Isotherms in Landfill Soils.

Based on the kinetic investigation, it was found that As(V) adsorption in iron-rich soil reached the maximum value and becomes stable after 100 mins. The results demonstrated that equilibrium was reached after two hours of adsorption reaction for most cases. After adsorption equilibrium was reached, Okaloosa county soil had the most As(V) adsorption, followed by Santa Rosa County, Gadsden County and Franklin County. As(V) followed Langmuir adsorption isotherms in iron-rich soil under the pH range investigated for this research:
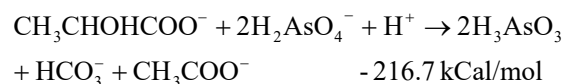
$$S = \frac{\alpha K C_e}{1 + K C_e} \qquad (3)$$

where S is the adsorbed As(V) in the iron-rich soil (M/g soil); α is the mass of As(V) required to completely cover a unit mass of soil (M/g soil); C_e is the As(V) equilibrium concentration (M); and K is the Langmuir adsorption constant, which increases with the increase of the binding energy of adsorption (M^{-1}). The α values and K values were obtained using numerical simulation against **Eq. (3)**. As(V) had α values of 0.89 mM/kg for Okaloosa county soil, 0.74 mM/kg for Santa Rosa County soil, 0.54 mM/kg for Gadsden County soil, and 0.38 mM/kg for Franklin County soil. A greater α value suggested higher iron contents in the soil. Therefore, Okaloosa county soil had the most iron content, followed by Santa Rosa County, Gadsden County and Franklin County, which was consistent with the soil characterization. The K values were $3.6 \times 10^{-3} M^{-1}$ for Okaloosa county soil, $3.2 \times 10^{-3} M^{-1}$ for Santa Rosa County soil, 2.9×10^{-3} 1/M for Gadsden County soil, and $2.5 \times 10^{-3} M^{-1}$ for Franklin County soil. The K values did not vary much among the soil samples. This was because the underlying principle behind the adsorption isotherms resulted from forms of bonding between As(V) and iron Fe(III) oxides in the soil. The minor variation was owing to the differences of the iron types in these soils.

Iron and Arsenic Reduction

With the oxidation of lactate, both Fe(II) and H$_3$AsO$_3$ were observed in the solution with H$_3$AsO$_3$ release dominated over Fe(II) release (**Fig. 2**). Metal-reducing bacteria which used solid substrates such as Fe(III) as the terminal electron acceptor for anaerobic respiration must be able to transport the electrons across the outer membrane between large particulate metal oxides (e.g., Fe$_2$O$_3$) and the electron transport chain in the cytoplasmic membrane (Newman *et al.*, 1997). Therefore, the bacterial strains that were responsible for iron reduction contained genes encoding cytosolic membrane proteins as well as periplasmic and outer membrane proteins (Ruebush *et al.*, 2006). These proteins were responsible for the inferred path of direct electron transfer from the cytoplasm to an insoluble extracellular substrate. As confirmed by PCR analysis, *S. putrefaciens* was the dominating iron reducing strains in the consortia, which had approximately 80% of the membrane-bound cytochromes localized in its outer membrane (Anderson & Cook, 2004; Sau *et al.*, 2008). Arsenic reducing bacterial strains were found to be dominated by *Shewanella* sp. The adsortpion of As(V) on Fe(III) oxide surfaces interfered with arsenic reduction since iron reduction was thermodynamically more fovorable as compared to arsenic reduction:

$$CH_3CHOHCOO^- + 4Fe_2O_3 + 7H^+ \rightarrow CH_3COO^-$$
$$+ HCO_3^- + 4Fe^{2+} + 4H_2O \qquad -265.9 \, kCal/mol$$

(4)

$$CH_3CHOHCOO^- + 2H_2AsO_4^- + H^+ \rightarrow 2H_3AsO_3$$
$$+ HCO_3^- + CH_3COO^- \qquad -216.7 \, kCal/mol$$

(5)

This was evidenced in this research by the fact that arsenic reduction was less pronounced as compared to that of iron reduction (**Fig. 2**). As shown in **Fig. 2**, iron reduction proceeded at much higher rate than that of arsenic reduction until 15 to 20 h, after which iron reduction and arsenic reduction had similar rates. With the iron reduction, adsorbed arsenate was released and arsenic reduction was further enhanced (Zhang *et al.*, 2008).
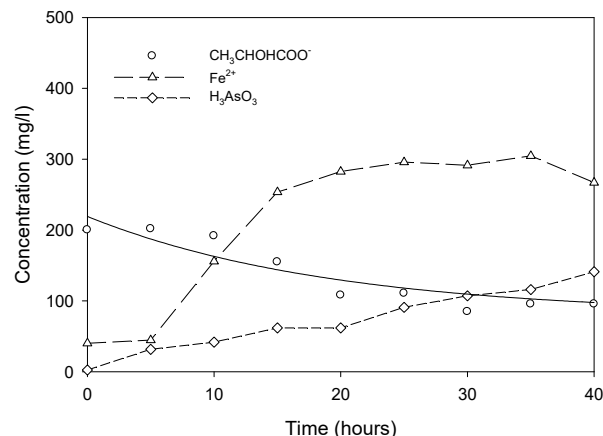

Fig. 2a Lactate Reduction and Fe(II) and As(III) Release in Franklin Landfill Soils.
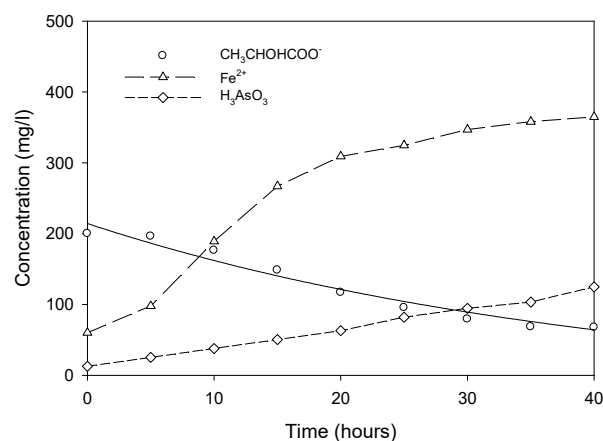

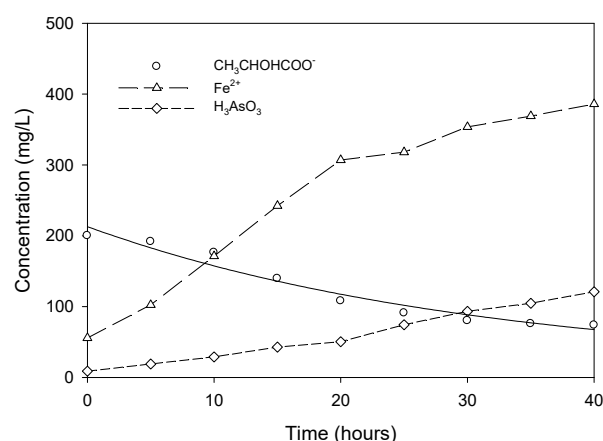**Fig. 2b** Lactate Reduction and Fe(II) and As(III) Release in Gadsden County Landfill Soils

Fig. 2c Lactate Reduction and Fe(II) and As(III) Release in Santa Rosa County Landfill Soils.
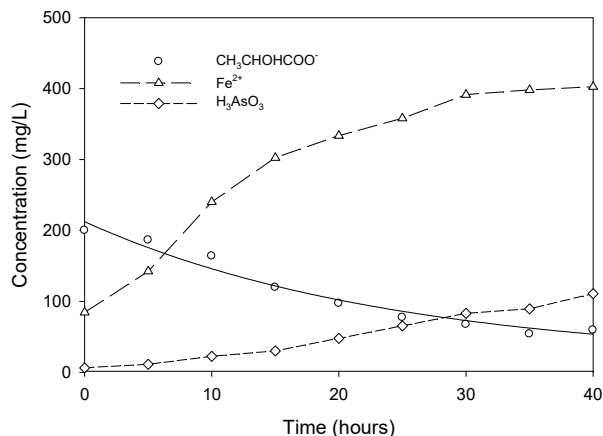
Fig. 2d Lactate Reduction and Fe(II) and As(III) Release in Okaloosa County Landfill Soils.

These bacterial strains can grow with lactate as the electron donor and carbon source while using Fe(III) and As(V) as the electron acceptors. By plotting Fe(II) release as a function of lactate consumed during the reduction experiments, it was discovered that all the four soil samples had similar Fe(II) production (**Fig. 3**). This indicated that there was no limitation for iron reduction in these four soil samples. However, for As(V) reduction, different observations were made for these four soil samples (**Fig. 4**). H_3AsO_3 release was most pronounced in Franklin county soil, followed by Gadsden county, Santa Rosa County and Okaloosa county. As(III) release increased after 20 h as indicated by the increased molar ratio of As(III)/Fe(II) (**Fig. 5**). This increase was attributed to the Fe(III) dissolution and subsequent As(V) release and reduction. If microbial growth is coupled with organic depletion, and Monod-type kinetics are assumed to describe microbial growth, the organic and biomass concentrations over time can be described by the following equations (Liu, 2006):

$$\frac{dX}{dt} = \frac{\mu_m SX}{K_s + S} - \frac{bX}{K_s + S} \qquad (6)$$

$$\frac{dS}{dt} = -\frac{1}{Y} \frac{\mu_m SX}{K_s + S} \qquad (7)$$

where X is the biomass concentration (mg/L); t is the elapsed time (h); μ_m is the maximum specific growth rate (h^{-1}); S is the organic concentration (mg/l); K_s is the half-saturation coefficient (mg/L); b is the microbial decay coefficient (h^{-1}) and Y is the growth yield coefficient (mg biomass per mg organic consumed). Ignoring microbial decay, Y can be used to estimate the biomass production based on organic depletion such that:

$$Y = -\frac{\Delta X}{\Delta S} \qquad (8)$$

$$X = X_0 + Y(S_0 - S) \qquad (9)$$

By substituting **Eq. (9)** into **Eq. (7)**, the organic depletion can be expressed as:

$$\frac{dS}{dt} = -\frac{1}{Y} \frac{\mu_m S[X_0 + Y(S_0 - S)]}{K_s + S} \qquad (10)$$

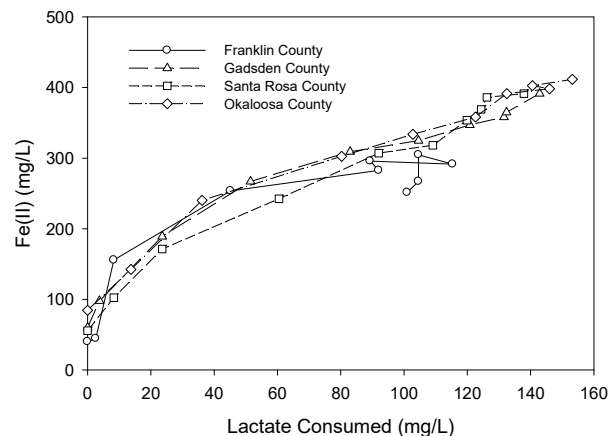where X_0 and S_0 refer to the initial biomass and organic concentration (mg/L).

Fig. 3 Fe(II) Release as a Function of Lactate Consumed during Fe(III) Reduction.

Lactate depletion was simulated by means of non-linear regression of simplex optimization of least squares against **Eq. (10)** to estimate their relevant Monod kinetic parameters (**Fig. 6**). The consortia had similar maximum half saturation coefficient values in all the four samples collected from different landfills and the average half saturation coefficient was 232.8 mg/L (214.9 mg/L in Franklin county soil, 252.4 mg/L in Gadsden county soil, 236.5 mg/L in Santa Rosa County soil and 227.4 mg/L in and Okaloosa county soil). The similar half saturation coefficient values indicated that the consortia had similar affinity to the organic components in these four sample soils. Similarly, growth yield coefficient values were also in a similar range and the average yield coefficient was 0.276 mg/g. For maximum specific growth rate, Okaloosa county soil had the greatest maximum specific growth rate of 0.0087 h^{-1} and Franklin county had the least one of 0.0048 h^{-1}. Gadsden county and Santa Rosa County were in between with values of 0.0071 h^{-1} and 0.0059 h^{-1}. The variation in maximum specific growth rate among different soil samples was attributed to variations of consortia in the soil. Based on the speciation analysis, Fe(II) did not precipitate in the pH range of 5 to 9. Therefore, the effect of precipitation of ferrous iron on As(V) reduction was minimal. By plotting H_3AsO_3 release as a function of α, the mass of As(V) required to completely cover a unit mass of soil, it was found that the molar ratio of As(III)/Fe(II) exponentially decreased with the

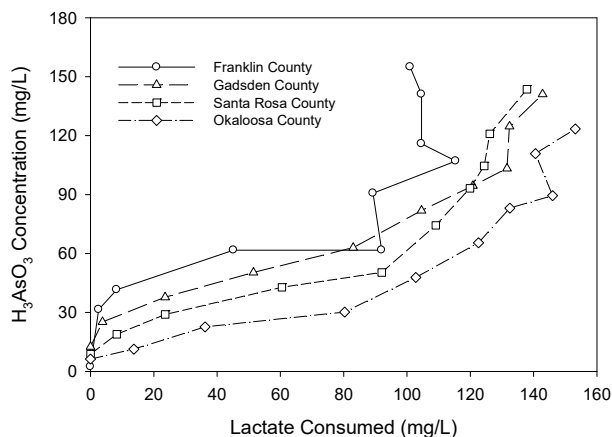increase of α, indicating that As(V) reduction was limited by the As(V) adsorption in the soil (**Fig. 7**).

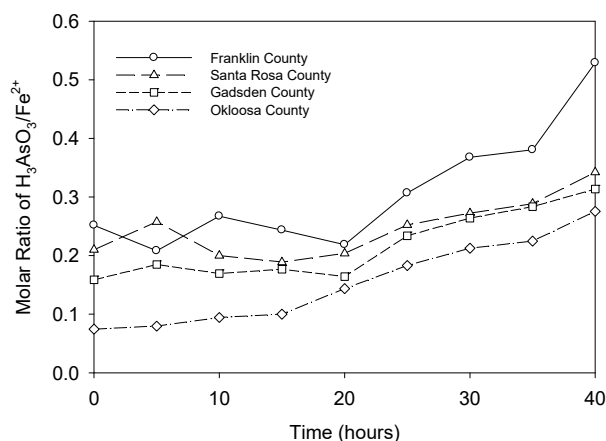**Fig. 4** As(III) Release as a Function of Lactate Consumed during As(V) Reduction.

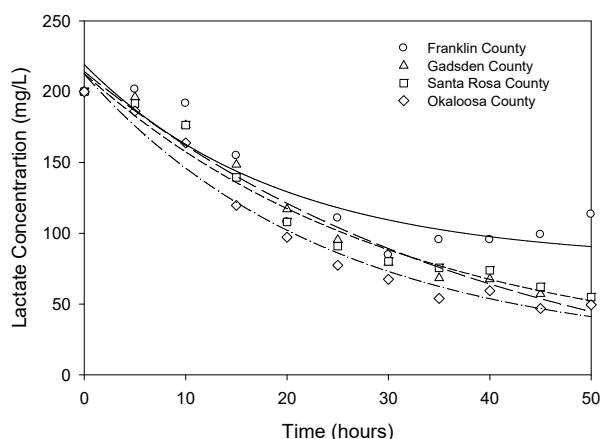**Fig. 5** Molar Ratio of As(III)/Fe(II) for Different Landfill Soils.

Fig. 6 Lactate Consumption and Simulation based on Monod-Type Microbial Growth Kinetics.
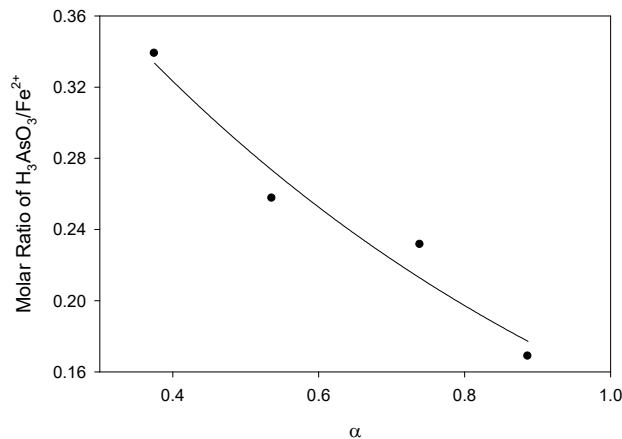

Fig. 7 Molar Ratio of As(III)/Fe(II) as a Function of α, Mass of As(V) Required to Completely Cover Unit Mass of Soil.

Arsenate Adsorption and Reduction

In this research, Fe(II) and As(III) release was observed with the depletion of lactate, which increased with the proceeding of the experiments, although Fe(II) release was more pronounced. Before Fe(III) oxide dissolution, As(V) and Fe(III) in the solution were able to be reduced simultaneously based on the thermodynamic analysis. However, the amount of Fe(III) and As(V) in solution was dependent not only on the extent of reduction of each element but also the extent to which they were adsorbed in the soil. Since Fe(III) reduction was thermodynamically more fovorable as compared to As(V) reduction, Fe(III) reduction preceded As(V) reduction. Owing to the strong adsorption of As(V) to Fe(III), it was proposed that iron reduction and associated dissolution eventually led to continued As(III) release and elution. Therefore, As(V) adsorption on Fe(III) oxides played an important role in controlling arsenic mobility. As demonstrated in this research, Fe(III) oxide dissolution-induced As(V) was more pronounced after 15 to 20 h (**Fig. 2**).

This research demonstrated that arsenic dissolution can be driven by Fe(III) oxide reduction, which was consistent with the previously described arsenic mobilization mechanisms by dissimilatory iron reducers. In essence, since both dissimilatory arsenate reducer and iron reducer can effectively grow with lactate as the electron donor, the following processes occurring simultaneously: (1) Desorption promoted by chemical disequilibrium during pore water replacement; (2) Reduction of Fe(III) oxide by iron reducers; and (3) Reduction of As(V) released from iron reduction by arsenate reducers. It should be noted that although As(V) may be released from Fe(III) reduction, owing to its high adsorption capacity, the released As(V) would still be severely constrained by re-adsorption and cannot be mobile until it was reduced. Arsenic mobilization was only possible after As(V) was reduced to As(III) as

facilitated by reductive dissolution of Fe (III) oxides in the iron-rich soil.

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