Facters Affecting Arsenic Retetion Under Anaerobic Conditions

Factors Affecting Arsenic Retention Under Anaerobic Conditions

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Introduction

Iron (hydr)oxides such as ferrihydrite exert a dominant influence on arsenic retention within soils and sediments. Under anaerobic conditions, reductive transformation of ferrihydrite, or other ferric oxides, may release arsenic to the aqueous phase. However, reductive biomineralization may limit the release of arsenic through its incorporation in (or on) secondary solids. We have recently observed a promotion of arsenic attenuation during Fe(III) reduction of ferrihydrite by the model iron reducing bacterium *Shewanella putrefaciens*. In this study, we examine the extent and means by which arsenic is sequestered during active Fe(II) generation. In accordance with arsenic retention being modified by iron reduction, biomineralization of ferrihydrite should likewise be impacted by arsenic (or other oxyanions). We therefore examined the extent, rate, and production of ferrihydrite reductive biomineralization induced by *S. putrefaciens*. We explored how the strength versus extent of oxyanion retention modified the biomineralization process by examining arsenate (strong but less extensive adsorption) and arsenite (extensive but weaker binding) loaded ferrihydrite.

Methods

Formation and Characterization of Ferrous-Arsenite Solid. Sodium arsenite and ferrous chloride were reacted at 10:1 [10 mM Fe(II) and 1 mM As(III)], 1:1 [10 mM Fe(II) and 10 mM As(III)], and 1:10 [1 mM Fe(II) and 10 mM As(III)] Fe:As molar ratios under anaerobic condition at pH 7.2 in 10 mM PIPES or 5 mM bicarbonate buffer. The resulting solid was digested in 0.3 N HCl and analyzed by ICP to determine its stoichiometry. The solid was further examined using XRD and EXAFS spectroscopy.

Effect of Surface Modification on Ferrihydrite Biomineralization. Arsenate or arsenite was adsorbed onto 2-line ferrihydrite coated quartz sand at pH 7.2 for 48 hours. On the basis of adsorption maxima, ferrihydrite was loaded with 100% As(V) or As(III). The solid phase was then reacted with *Shewanella putrefaciens* CN32 (cell density ~10^8 cells mL^{-1} with 3 mM lactate). The systems were allowed to react for 17 days in columns with a flow rate at 0.6 m d^{-1}. The solid phase was identified using EXAFS spectroscopy.

Results

Formation and Characterization of Ferrous-Arsenite Solid. Mixing ferrous chloride and sodium arsenite at pH 7.2 in PIPES and bicarbonate buffers, resulted in poorly crystalline solid (Figure 1). Stoichiometry of the Fe(II)-As(III) solid was approximately 0.85 Fe/As molar ratio. EXAFS data indicated Fe(II)-As(III) precipitate as a disordered sheet-like structure in which arsenic is coordinate to double-corner and edge-sharing Fe octahedral (Figure 2).

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Figure 1. XRD diffraction patterns of Fe(II)-As(III) precipitate at pH 7.2 in (a) PIPES buffer and (b) in bicarbonate buffer.

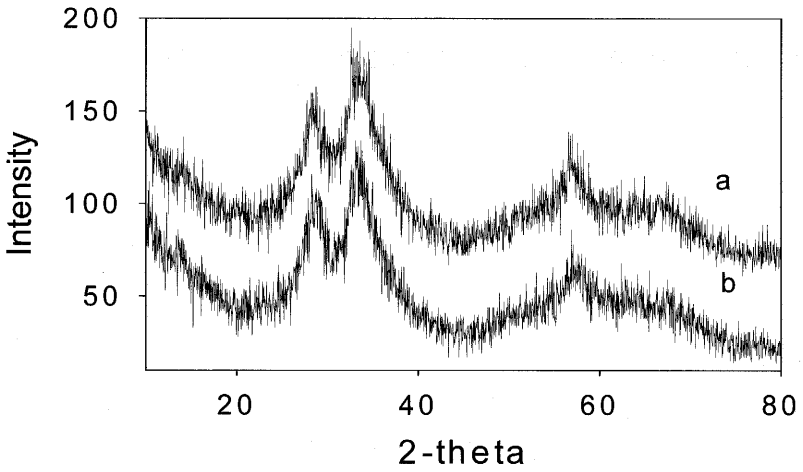
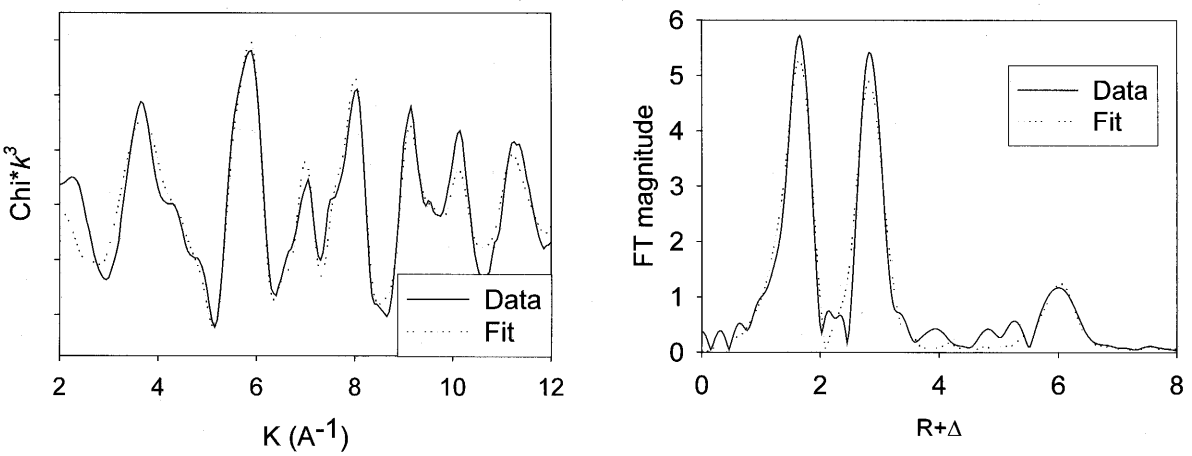


Figure 2. k^3-weighted Fe EXAFS spectra (a) and Fortier transformed spectra (b) of Fe(II)-As(III) precipitate .



Effect of Surface Modification on Ferrihydrite Biomineralization. After 17 days reaction under dynamic flow, greater oxidation of lactate to acetate and concomitant Fe(II) generation resulted from lower surface coverage of arsenate relative to arsenite. Ferrihydrite, magnetite and a green rust-like phase resulted from the biomineralization of arsenite- and arsenate-loaded ferrihydrite induced by *S. putrefaciens*.

Conclusion

Formation of Fe(II)-As(III) solid may attenuate arsenite transport (pronounced iron reduction my limit rather than promote arsenic migration).

Microbial respiration rate on ferrihydrite changes depending on arsenic species and loading, thus altering the biomineralization pathway.