Paper Presentation

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Simultaneous Oxidation and Reduction of Arsenic by Zero-Valent IronNanoparticles: Understanding the Significance of the Core-Shell Structure

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Introduction

- The principal forms of As in water are As (III) and As (V)
- As (V) exist in pH=2-12 as $H_2AsO_4^-$ or $HAsO_4^{2-}$
- As (III) remain as undissociated H₃AsO₃ below pH=9.2
- It is expected that both As (V) and As (III) are amenable to reduction by nzvi
- Prior studies indicate transformation of As (V) to As (III) is kinetically slow, and no clear evidence for As (0) has been published
- Several recent studies suggest that, instead of reduction, oxidation of As (III) is the prevalent reaction under oxic conditions through peroxide or radicals generated by Fenton reactions
- Iron nanoparticles obtained by ferric chloride reduction with sodium borohydride under nitrogen atmosphere



- (a) Bright field TEM micrograph of nZVI nanoparticles. The inset shows the electron diffraction pattern of the metallic core
- (b) HR-TEM micrograph of a single nZVI nanoparticle.
 - The lack of long-range periodic lattice fringes in the oxide layer suggests that it is amorphous in character.



Figure:1 As3d HR-XPS spectra of (a) fresh nZVI, (b) nZVI reacted with 100 mg/L As (V), and (c) nZVI reacted with 100 mg/L As (III). The nZVI loading in parts b and c was 5 g/L.

- Phase contrast TEM imaging reveals that oxide structure is disordered with a thickness of 10 to 20 nm, with composition of FeOOH.
- Thin dimension and disordered nature of shell, allows electron passage via tunneling effect or defect sites.
- The oxide layer is considered to be inherent part of nanoparticles.

Effect of As (III) concentrations:

- pH increasing due to $AsO_2^- + H_2O \longrightarrow H_3AsO_3/H_2AsO_3^- + OH^-$
- Due to high pH precipitation of iron occurred. (XPS evidence)
- Iron oxide precipitates supported by SEM images
- E_h potential rapidly changes at high concentrations
- Earlier reports also suggest the oxidation of As (III) whose mechanism is uncertain

- It is proposed that system may have more than one oxidizing species like peroxide or radical species (Fe (0) corrosion), hydroxide species and iron oxides.
- As (III) oxidation is due to hydroxide ions (from aqueous phase)
- Reattachment of As (V) from solution to nanoparticles at neutral to alkaline pH
- As (III) oxidation may also due to complexing with iron oxide
- The lack of distinct trend may also due to affinity of As (III) to iron oxides, available quantity for complexation, oxidation potential of iron oxides are affected by pH



Figure:3 As3d HR-XPS spectra from nZVI particles exposed to different initial concentrations of As (III). The nZVI loading was 5 g/L in all cases.



SEM images of a) a fresh nZVI sample, b) 5g/L nZVI reacted with 100 mg/L As (III) for 24 hr, and c) 5g/L nZVI reacted with 1000 mg/L As (III) for 24 hr.

| | Reaction conditions | pH (t=0 hr) | pH (t=24 hr) | E _h , mV (t=24 hr) |
|---------|---------------------|-------------|--------------|-------------------------------|
| Fig. 1b | As(V) 100 mg/L | 8.2 | 9.3 | 115 |
| Fig. 1c | As(III) 100 mg/L | 10.0 | 8.9 | -49 |
| Fig. 3a | As(III) 50 mg/L | 9.2 | 8.5 | -198 |
| Fig. 3b | As(III) 100 mg/L | 10.0 | 8.9 | -49 |
| Fig. 3c | As(III) 500 mg/L | 10.4 | 10.8 | 152 |
| Fig. 3d | As(III) 1000 mg/L | 10.4 | 11.0 | 158 |

Table S2. Solution pH and E_h before and after reactions*

* The amount of nZVI was 5g/L and the reaction time was 24 hr for each sample.



Figure S1. Solution pH for various initial As(III) concentrations. nZVI loading was fixed at 5 g/L. Initial pH was measured before nZVI loading. Equilibrium pH was obtained after a reaction time of 24 hours. The dashed line corresponds to the pK_a value of H_3AsO_3 , which dissociates to $H_2AsO_3^-$ at pH > pK_a.



O1s HR-XPS spectra obtained after different initial concentrations of As (III) (nZVI loading was fixed at 5 g/L). The prominent increase in OH- at the two highest As (III) concentrations indicates substantial iron hydroxide formation at the solid surface. The different forms of oxygen are indicated in the top spectrum: H2O at 531.8 eV, OH- at 530.7 eV, and O2- at 529.5 eV.



As3d HR-XPS spectra from nZVI Particles reacted with 100 mg/L As (III) for different reaction times. The nZVI loading was 5g/L in all cases. The proportions of the respective species as percentages of the total As detected are annotated on the spectra.

Conclusions:

- Simultaneous reduction and oxidation of As (III)
- Significance of core-shell structure

Future plan:

- As interaction with silver nanoparticles
- As (V) concentration dependent study

Thank You