Mechanisms for Arsenic Removal by Ferric Hydroxide Adsorbents

James Farrell & Dhananjay Mishra
Department of Chemical and Environmental Engineering
University of Arizona
Tucson, AZ 85721
Outline

- Arsenic removal technologies
- Ferric hydroxide structures
- As(III) & As(V) structures
- Chemical adsorption reactions
- Water chemistry effects on arsenic adsorption
Conventional Coagulation/Sedimentation

Cross-Section of Mixing Tank

Plan View of Settling Basin

FeCl₃ or Al(OH)₃
Arsenic Removal Technologies

• Chemical Precipitation
• Membrane Separations
• Fixed Bed Adsorption

  • ion exchange resins
  • activated alumina
  • granular ferric hydroxides
  • emerging technologies
    a) iron oxide coated: alumina, activated carbon, cloth fibers, aerogels, fly ash, membranes
    b) metal hydroxide mixtures containing: Fe, Ti, Zr, Cu, Mn, Mg
Best Available Technologies

Bayoxide E-33® (Bayer)
poorly crystalline goethite (\(\alpha\)-FeOOH)

GFH® (U.S. Filter)
poorly crystalline akaganeite (\(\beta\)-FeOOH)

Activated Alumina (\(\text{Al}_2\text{O}_3\))

- High surface area & porosity >> low mechanical strength.
- Media are used in packed bed configurations.
- Media are normally landfill disposed (no regeneration).
Fe(III) & Al(III) Hydroxides form Charged Octahedral Structures

$\alpha$-FeOOH (goethite)

$\gamma$-FeOOH (lepidocrocite)
Charge on Structures is pH Dependent

\[ \text{Fe} \quad \text{O} \quad \text{H} \]

![Diagram of FeOHx+ and FeO- concentration with pH scale from 2 to 12]

![Graph of pH vs. FeOHx+ and FeO- concentration]
Structures of As(III) and As(V)

Arsenic charge on arsenic species is pH dependent.
As(III) and As(V) Bind Strongly to Fe(III)-hydroxides

As(III) and As(V) species removed by mono- and bi-dentate complex formation with ferric hydroxides.

\[
2(\equiv FeOH) + HAsO_4^{2-} + 2H^+ \leftrightarrow Fe_2HAsO_4^{2-} + 2H_2O \quad K = 10^{26.2}
\]

Binding Energy \(=\Delta G = -RT \ln(K)\)
Isotherm Shapes and Arsenic Loadings

• Slope of the adsorption isotherms are indicative of the As-adsorbent binding energy

• Steep isotherm slopes at low concentrations indicate that there are some sites with very high binding energies

• Binding sites at high concentrations are different than those at low concentrations
Water Chemistry Effects

- pH
- ionic strength
- competing anions
- dissolved silica
- tap water versus NaCl electrolyte
Binding Energies are pH Dependent

- pH affects electrostatic charges on adsorbent and arsenic species
- pH affects the stoichiometry and binding energy of the chemical reactions

**Adsorption Reaction**

<table>
<thead>
<tr>
<th>Adsorption Reaction</th>
<th>B.E. (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$+4 : H_3AsO_4^{+} + Fe(OH)_2(OH)_4(H_2O)_4^{2-} \Leftrightarrow H_3AsO_4 = Fe(OH)_2(OH)_4^{2+} + 2H_2O^0$</td>
<td>34.15</td>
</tr>
<tr>
<td>$+2 : H_3AsO_4^{+} + Fe(OH)_2(OH)_4(H_2O)_4^{2-} \Leftrightarrow HAsO_3 = Fe(OH)_2(H_2O)_6^{4+} + 2H_2O^0$</td>
<td>-5.50</td>
</tr>
<tr>
<td>$0 : H_3AsO_4^{+} + Fe(OH)_2(OH)_4(H_2O)_4^{2-} \Leftrightarrow HAsO_3 = Fe(OH)_4(H_2O)_6^{6+} + 2H_2O^0$</td>
<td>-19.31</td>
</tr>
<tr>
<td>$0 : H_3AsO_4^{+} + Fe(OH)_2(OH)_4(H_2O)_4^{2-} \Leftrightarrow HAsO_3 = Fe(OH)_4(H_2O)_6^{6+} + 2H_2O^0$</td>
<td>-65.25</td>
</tr>
<tr>
<td>$-2 : H_3AsO_4^{+} + Fe(OH)_2(OH)_4(H_2O)_4^{2-} \Leftrightarrow AsO_3 = Fe(OH)_4(H_2O)_6^{6+} + H_2O^0 + OH^{-}$</td>
<td>-52.43</td>
</tr>
<tr>
<td>$-2 : H_2AsO_4^{+} + Fe(OH)_4(H_2O)_4^{2+} \Leftrightarrow AsO_3 = Fe(OH)_4(H_2O)_6^{6+} + 2OH^{-}$</td>
<td>13.15</td>
</tr>
<tr>
<td>$-2 : H_2AsO_4^{+} + Fe(OH)_4(H_2O)_4^{2+} \Leftrightarrow AsO_3 = Fe(OH)_4(H_2O)_6^{6+} + H_2O^0 + OH^{-}$</td>
<td>-284.03</td>
</tr>
<tr>
<td>$-2 : H_2AsO_4^{+} + Fe(OH)_4(H_2O)_4^{2+} \Leftrightarrow AsO_3 = Fe(OH)_4(H_2O)_6^{6+} + 2OH^{-}$</td>
<td>-218.44</td>
</tr>
<tr>
<td>$-4 : H_2AsO_4^{+} + Fe(OH)_4(H_2O)_4^{2+} \Leftrightarrow AsO_3 = Fe(OH)_4(H_2O)_6^{6+} + O_2 + OH^{-}$</td>
<td>-284.46</td>
</tr>
<tr>
<td>$-4 : H_2AsO_4^{+} + Fe(OH)_4(H_2O)_4^{2+} \Leftrightarrow AsO_3 = Fe(OH)_4(H_2O)_6^{6+} + 2O_2$</td>
<td>-23.38</td>
</tr>
</tbody>
</table>
pH Effects

As(III) & As(V) adsorption on hydrous ferric oxide at two different initial arsenic concentrations.

As(V) adsorption on amorphous ferric hydroxide media.

- Solution pH values have a smaller effect on As(III) adsorption as compared to As(V).

• Increasing ionic strength increases adsorption of $\text{H}_2\text{AsO}_4^-$.
• Ions in solution neutralize electrostatic repulsions between negatively charged surface species.
Other Oxyanions also Bind to Fe(III) Hydroxides

- $\text{H}_2\text{SiO}_4^{2-}$
- $\text{SO}_4^{2-}$
- $\text{HPO}_4^{2-}$
- $\text{HCO}_3^-$
Dissolved Silica Effect

- Typical drinking waters in Arizona have 15 to 30 mg/L of dissolved silica (as SiO₂).
- Because of its high concentrations, silica is the primary species that competes with arsenic for adsorption sites.
Tap Water versus NaCl Electrolyte

Effluent As(V) concentrations for column packed with Bayoxide E-33 with a feed concentration of 50 µg-As(V)/L.

Ratios of As(V) to Fe(III) in spent PEL media from column experiments.

- Ions (SiO₂ @ 30 mg/L) in Tucson tap water compete with As(V) for adsorption sites.
- Different iron oxide media show similar competitive adsorption effects.
Column versus Batch As Loadings

Column data for Bayoxide E-33 media for 50 µg/L feed concentration in 15 mM NaCl.

Equilibrium loading for Bayoxide E-33 media in 15 mM NaCl. Isotherm points equilibrated for 30 days.

- Time scales affect the amount of arsenic adsorbed.
- Long time scales allow media dissolution & reprecipitation which may increase the number of adsorption sites.
- Testing of adsorbents must be performed under conditions as close to those in the desired application.
Acknowledgements

• Superfund Basic Research Program: NIEHS Grant # 2P42ES04940-11
• PEL Technologies, Canton, OH