Novel Adsorbent-Reactants for Treatment of Ash and Scrubber Pond Effluents

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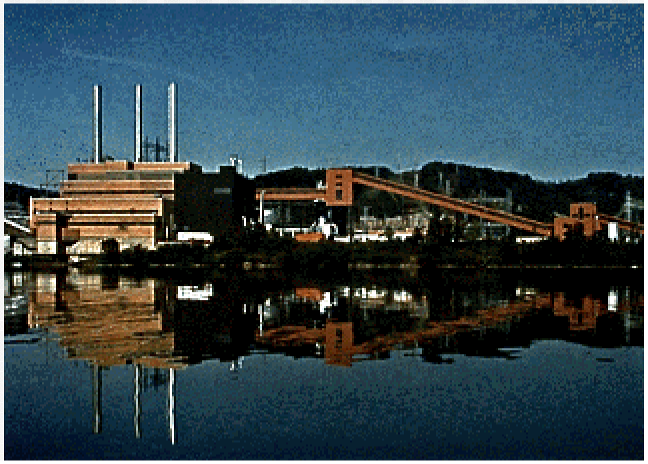
Overview

- Background
- Project Objectives
- Methods
- Results
- Summary



Background

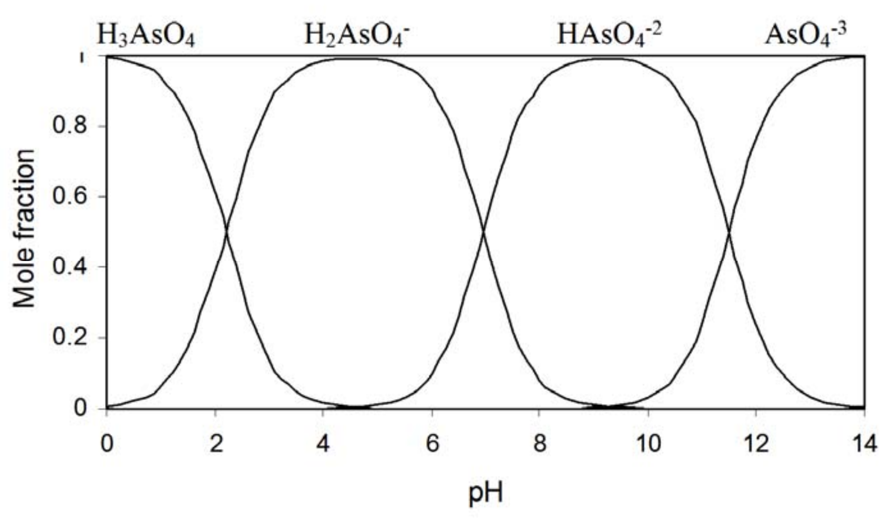
- Volatile Species
  - Arsenic
  - Mercury
  - Selenium
- Transfer to Water
  - FGD wastewater
  - Ash Pond water

Background (As)

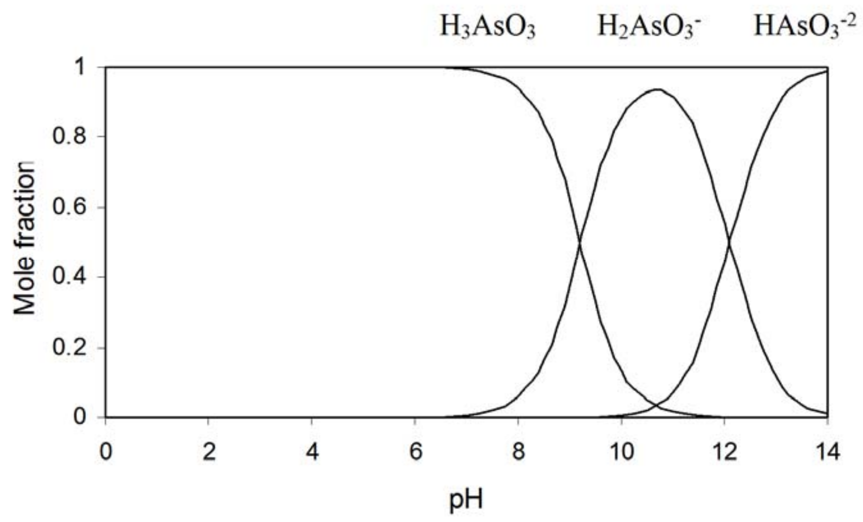
- Arsenic
  - Redox state
    - Arsenate, As(V)
    - Arsenite, As(III)
    - Elemental, As(0)
    - Arsenide, As(-III)

Background

- Arsenic
  - Acid/base
    - Arsenate



Arsenite



Background (As)

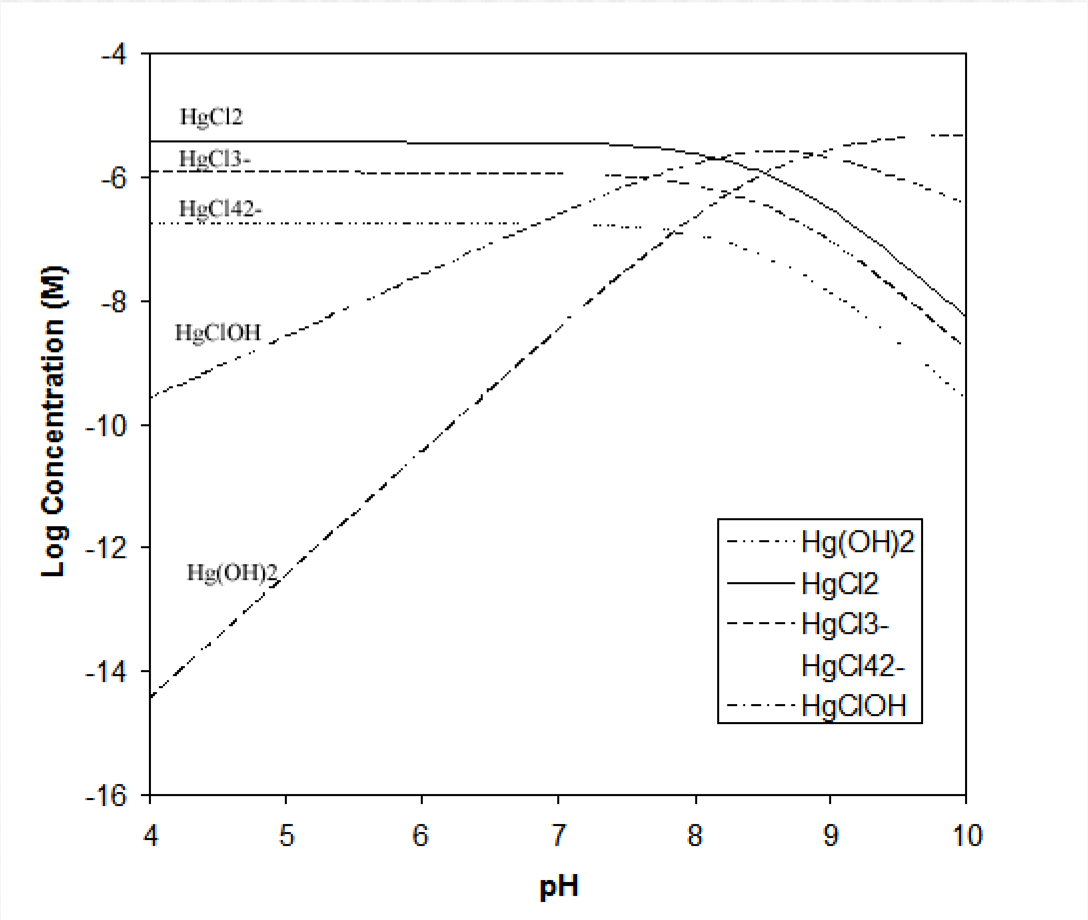
- Arsenic
  - Solid Phases
    - Arsenopyrite (As(0): FeAsS, $FeAs_xS_{2-x}$)
    - Arsenous sulfide (As(III): As_2S_3)
    - Calcium/Barium Arsenate (As(V))
    - Elemental (As^0)

Background (Hg)

- Mercury
  - Redox State
    - Mercuric, Hg(II)
    - Mercurous, Hg(I)
    - Elemental, Hg(0)

Background (Hg)

- Acid/Base-Chloride Complexes



Background (Hg)

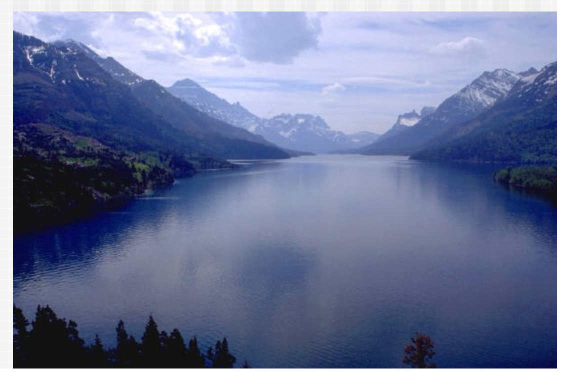
- Mercury
  - Solid Phases
    - HgS
    - HgO

Background

- Summary – As, Hg
  - Redox active; state important
  - Sulfide/Disulfide Solid phases

Background

- Removal/Disposal
  - Non-destructive
  - Residual Disposal
    - Regulatory Tests
    - Risk Assessment
  - Both Important
- Multiple Targets



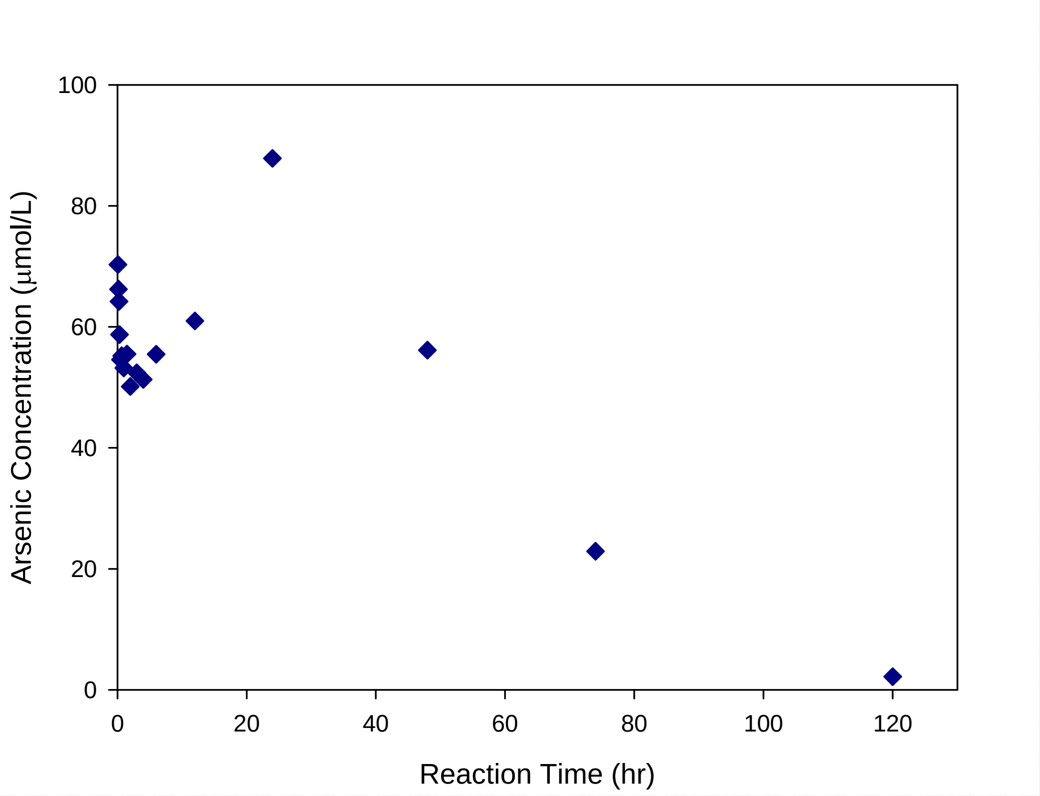
Background

- Approach
  - Adsorb target (As, Hg)
    - Pyrite (FeS_2)
    - Iron Sulfide (FeS)
  - Surface Reaction
    - Redox
      - Reduction; S(-II), Fe(II)
      - Oxidation; S(-I)
    - Surface Precipitation (FeAsS, HgS, As_2S_3)

Solution ⟶ Sorbed ⟶ Products

Background

- Approach
  - Anomalous behavior



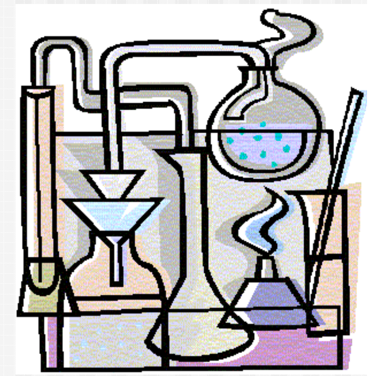
Project Objectives

- Evaluate Adsorbent-Reactants for Removal and Stability
  - Characterize Removal (pH, SO_4)
    (As(III), As(V), Hg, Se on FeS_2, FeS)
  - Characterize Surface Reactions
  - Develop Synthesis Techniques
    (FeS_2, FeS)

Methods

- Experimental Plan (Removal)
  - Batch System
    - Kinetic
    - Removal Characteristics
      - Vary target concentration
      - Constant sorbent-reactant dose
  - Effects
    - pH (7, 8, 9, 10)
    - Sulfate (0, 1, 10 mM)

Methods



- Analytical Methods
  - Arsenic
    - HGAAS (form AsH_3 with $NaBH_4$)
    - Speciation by pH (form AsH_3 with $NaBH_4$)
      - Total - Low pH reduction
      - As(III) - Moderate pH reduction
      - As(V) – Difference
  - Mercury
    - Cold Vapor AAS (reduction with $NaBH_4$)

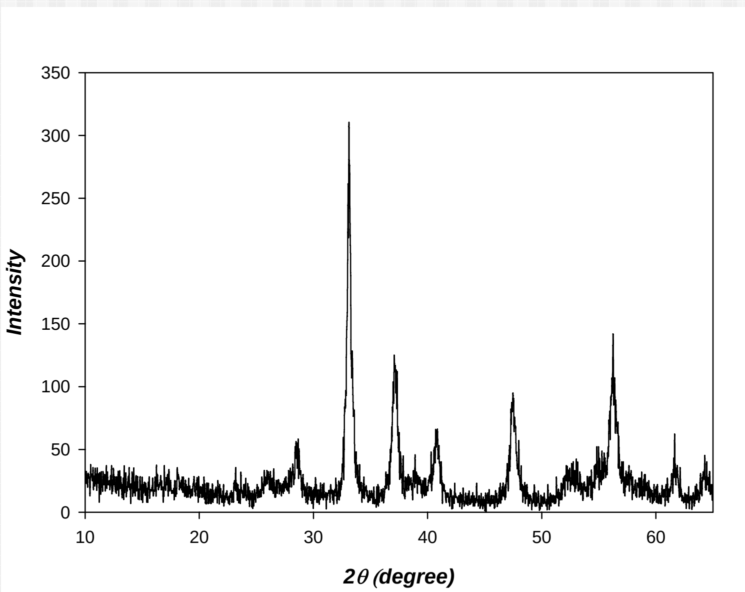
Methods (Analytical)

- Pyrite/Iron Sulfide
  - Differential dissolution/Fe analysis
  - Iron Sulfide – HCl
  - Pyrite – HNO_3

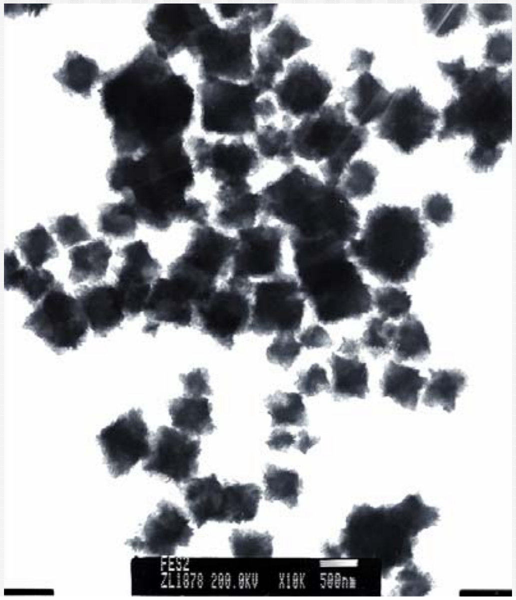
Methods (Synthesis)

- Pyrite Synthesis (Wei, et al. 1997, modified)
  - $2HS^{-} + 2\ Fe^{3+} = FeS_2 + 2H^{+} + Fe^{2+}$
  - 60 ºC

XRD



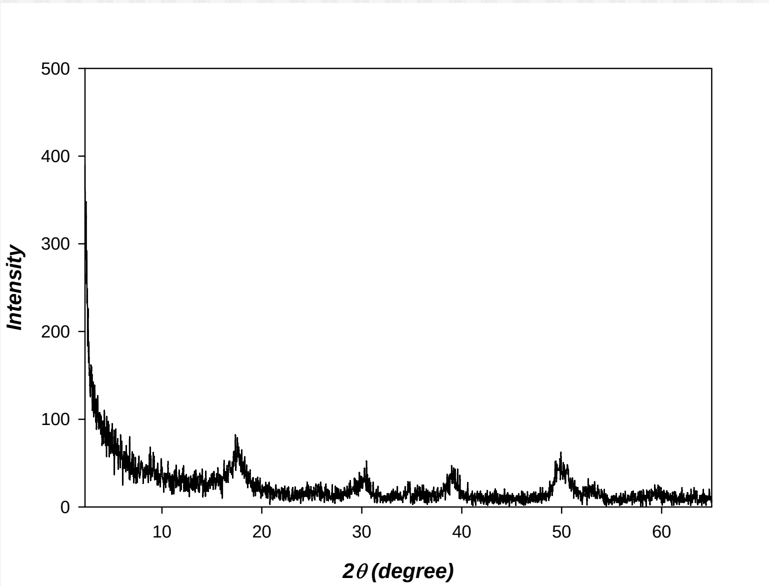
TEM



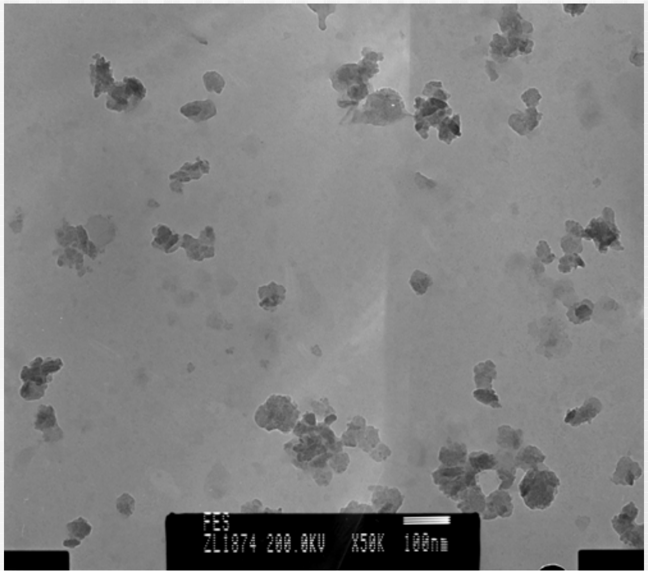
Iron Sulfide Synthesis

- $Na_2S + FeCl_2 = FeS + 2Na^+ + 2Cl^-$

XRD



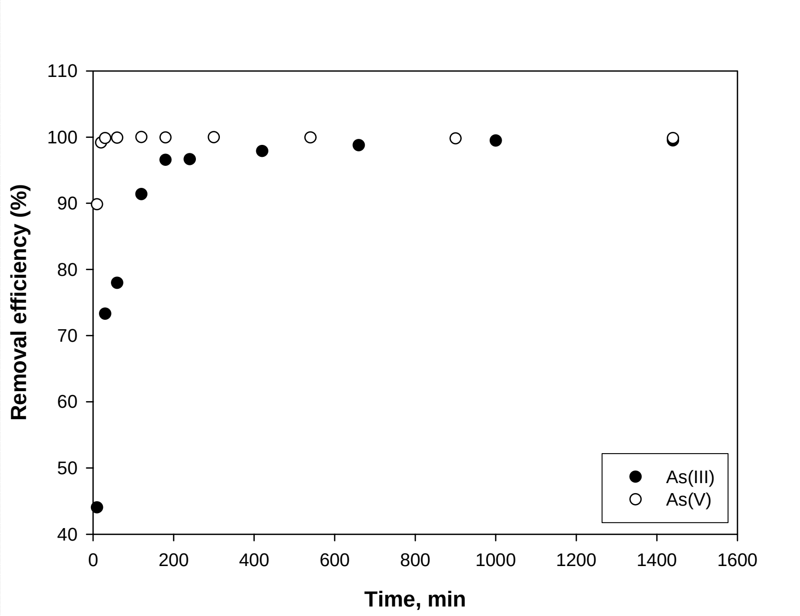
TEM



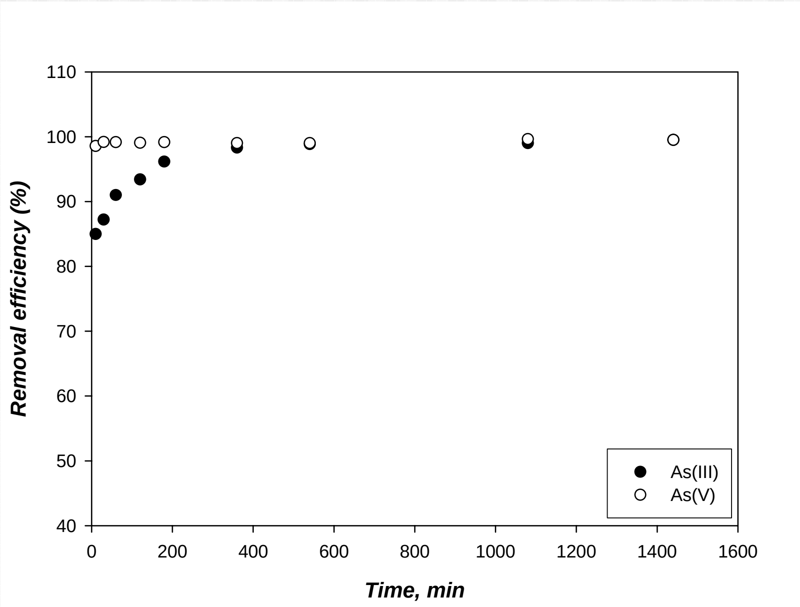
Results

❖ Arsenic Removal Kinetics

Pyrite

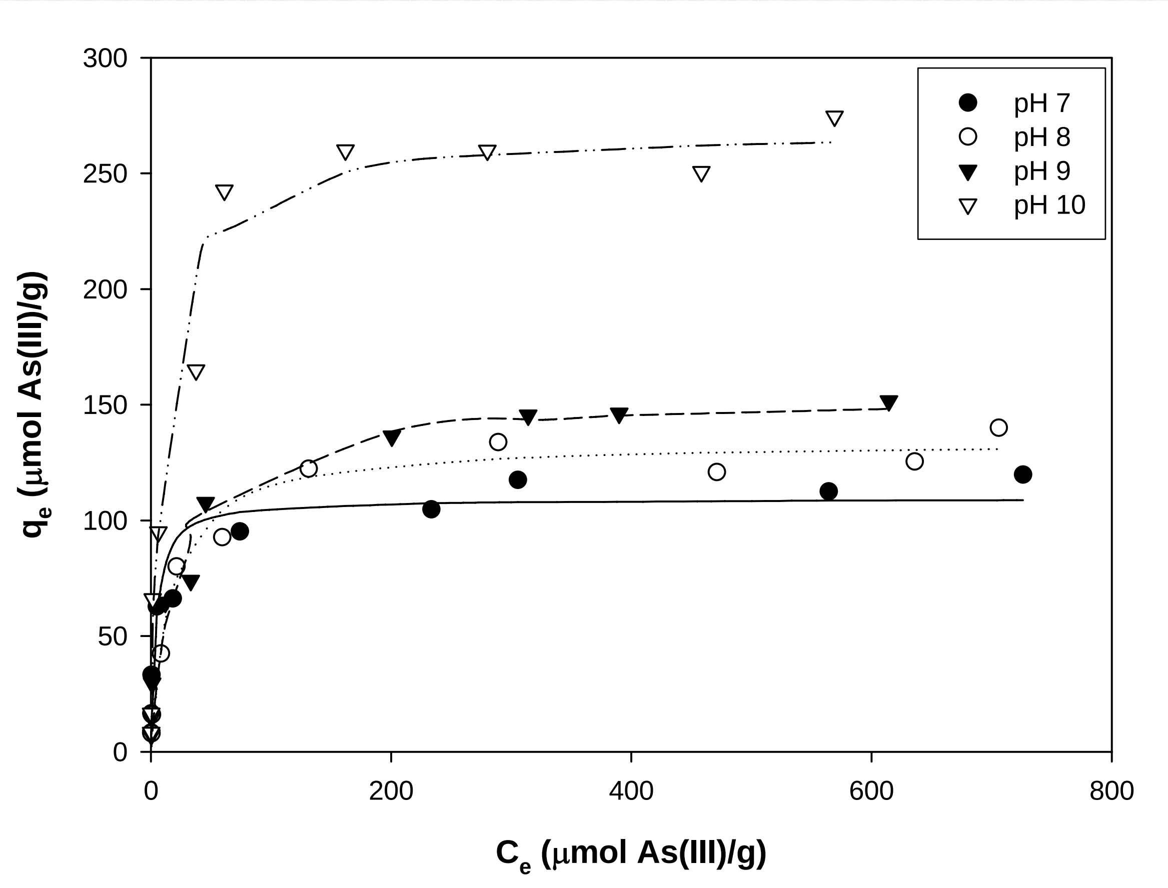


FeS



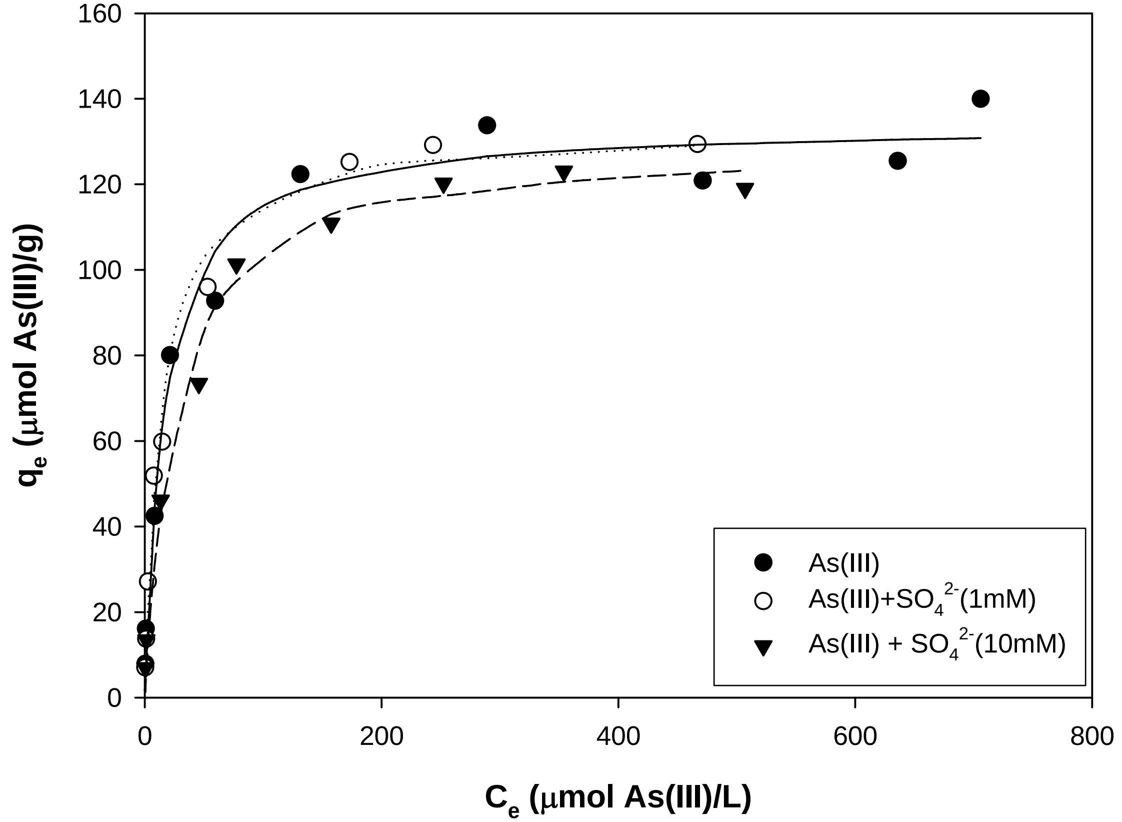
Results

❖ Arsenic (III) – Pyrite/pH



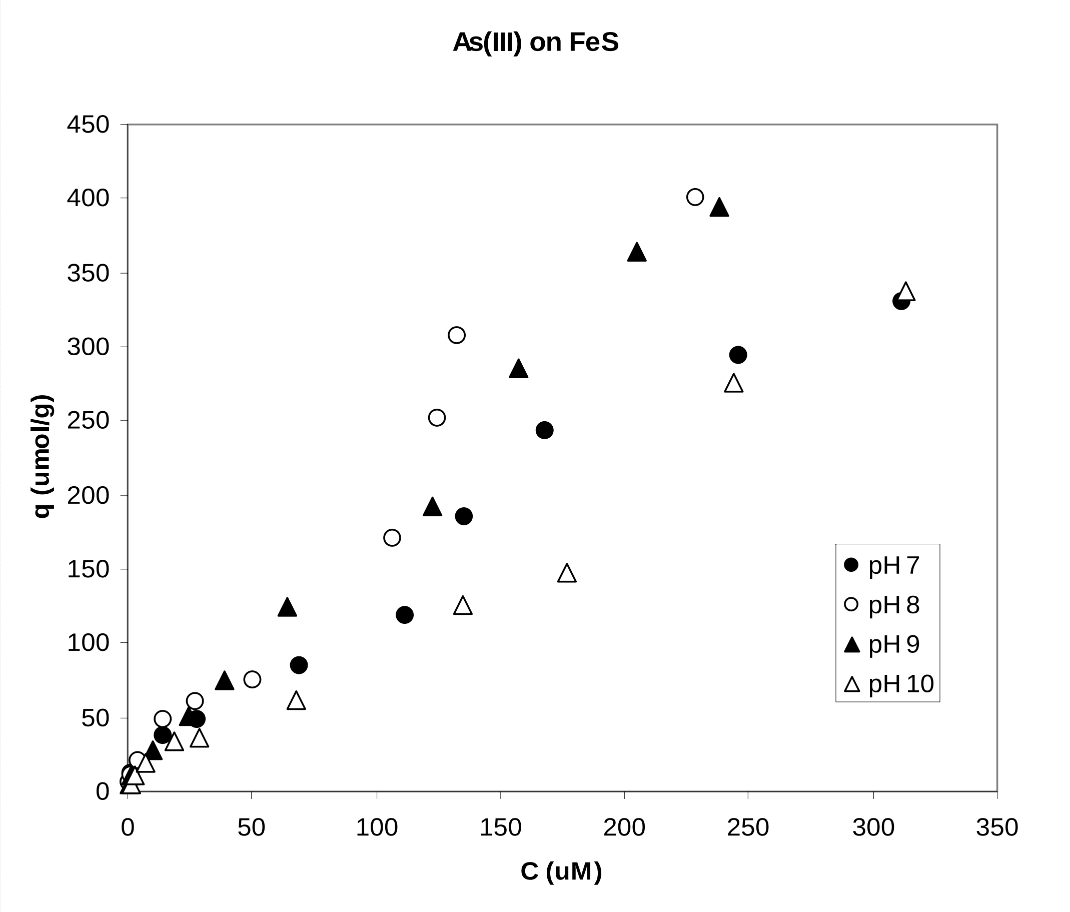
Results

- Arsenic (III) – Pyrite/SO_4



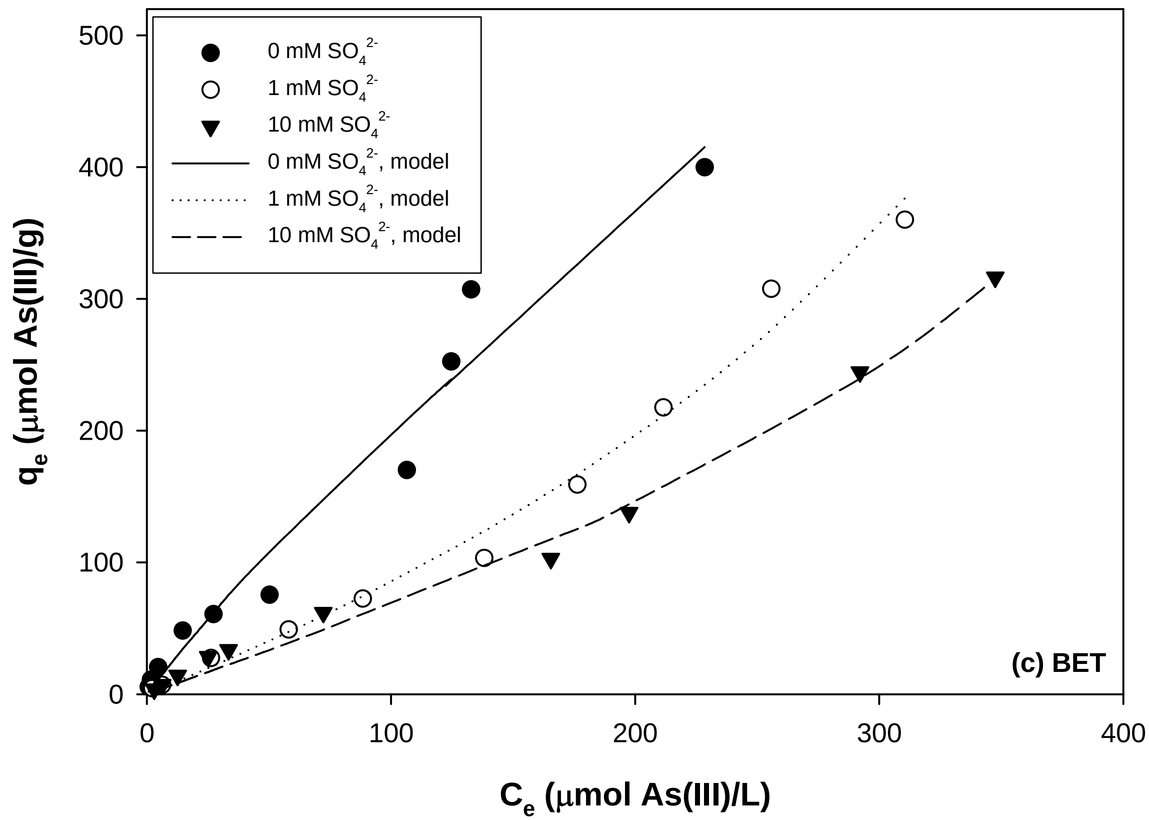
Results

- Arsenic (III) – FeS/pH



Results

- Arsenic (III) – FeS/SO_4

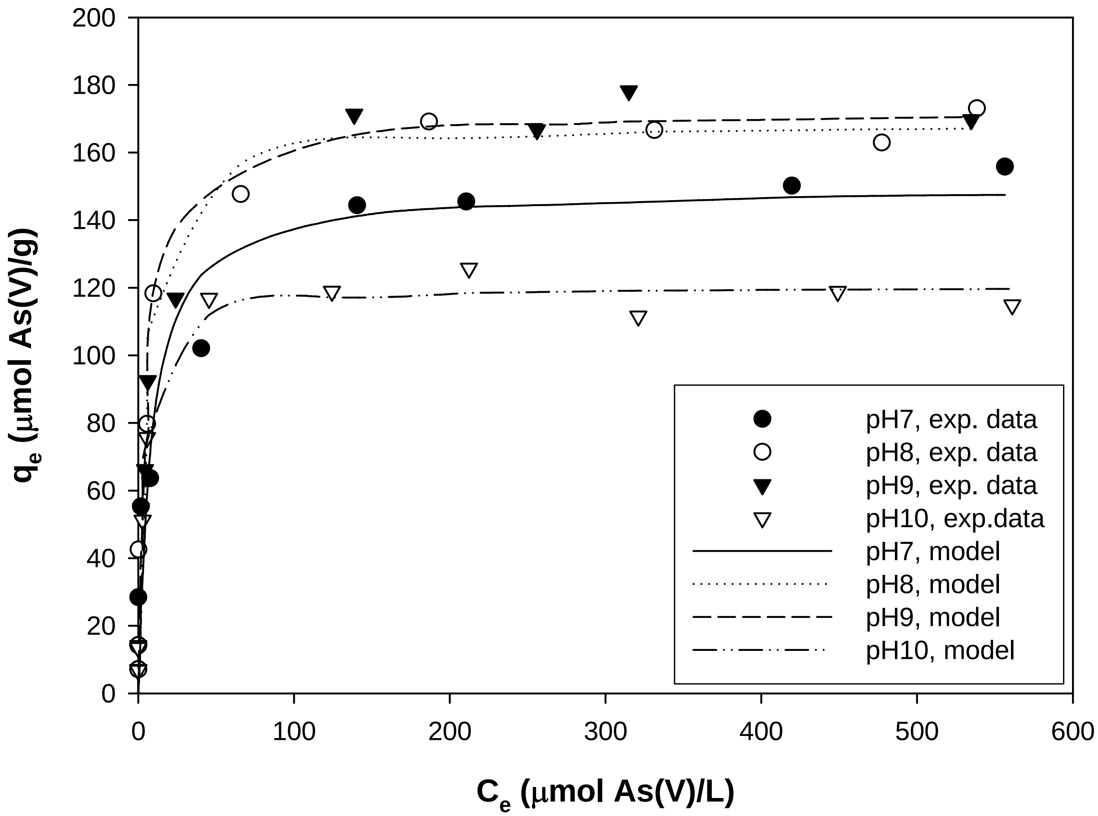


Results

- Arsenic
  - As(III)
    - pH
      - Pyrite – higher pH increases loading
      - FeS – optimum pH 8-9
    - SO_4
      - Small effect on pyrite
      - Moderate effect on FeS
    - Pyrite/FeS
      - Loadings similar
      - More surface reaction on FeS

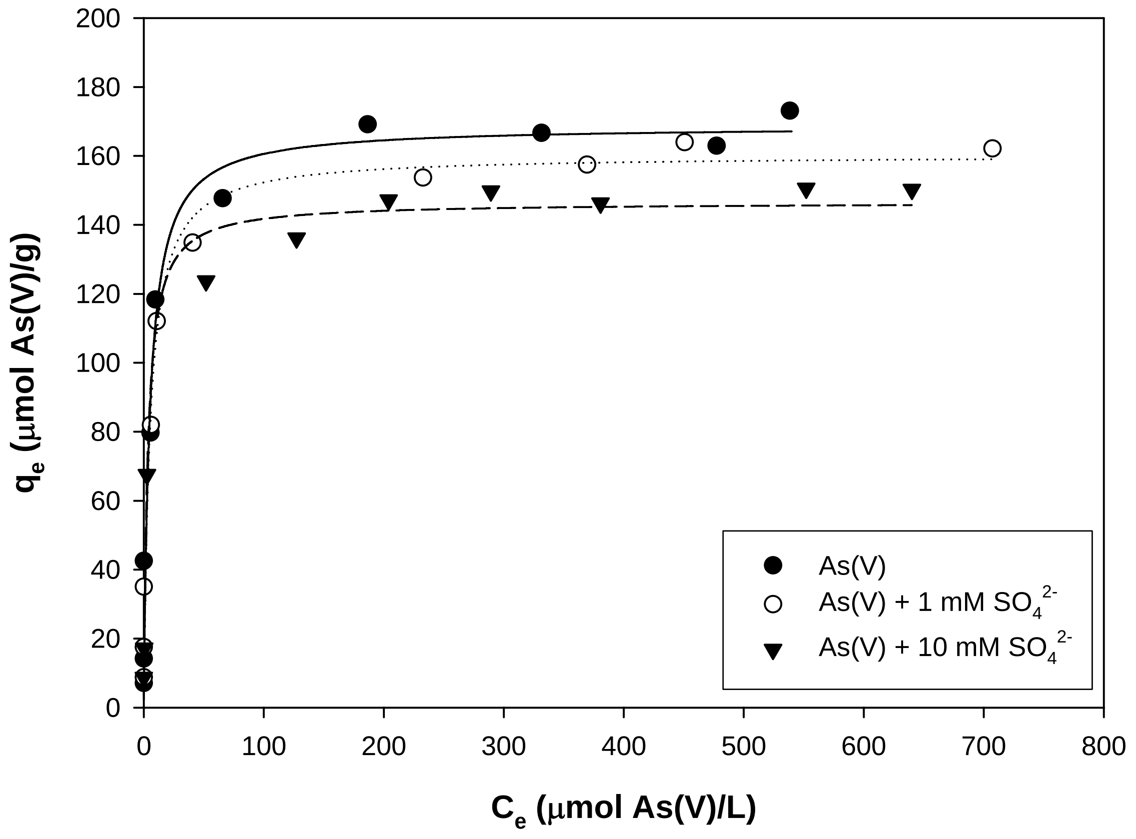
Results – As(V)

❖ Arsenic (V) – Pyrite/pH



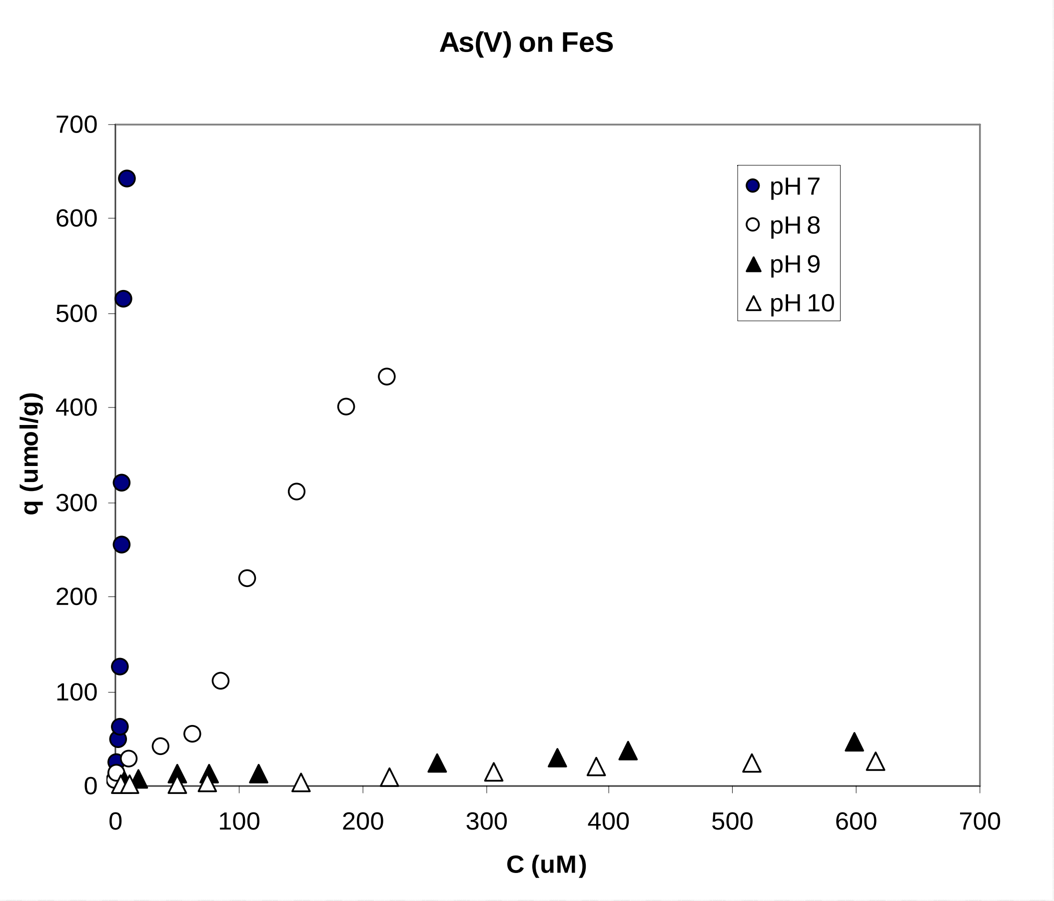
Results - As(V)

- Arsenic (V) – Pyrite/SO_4



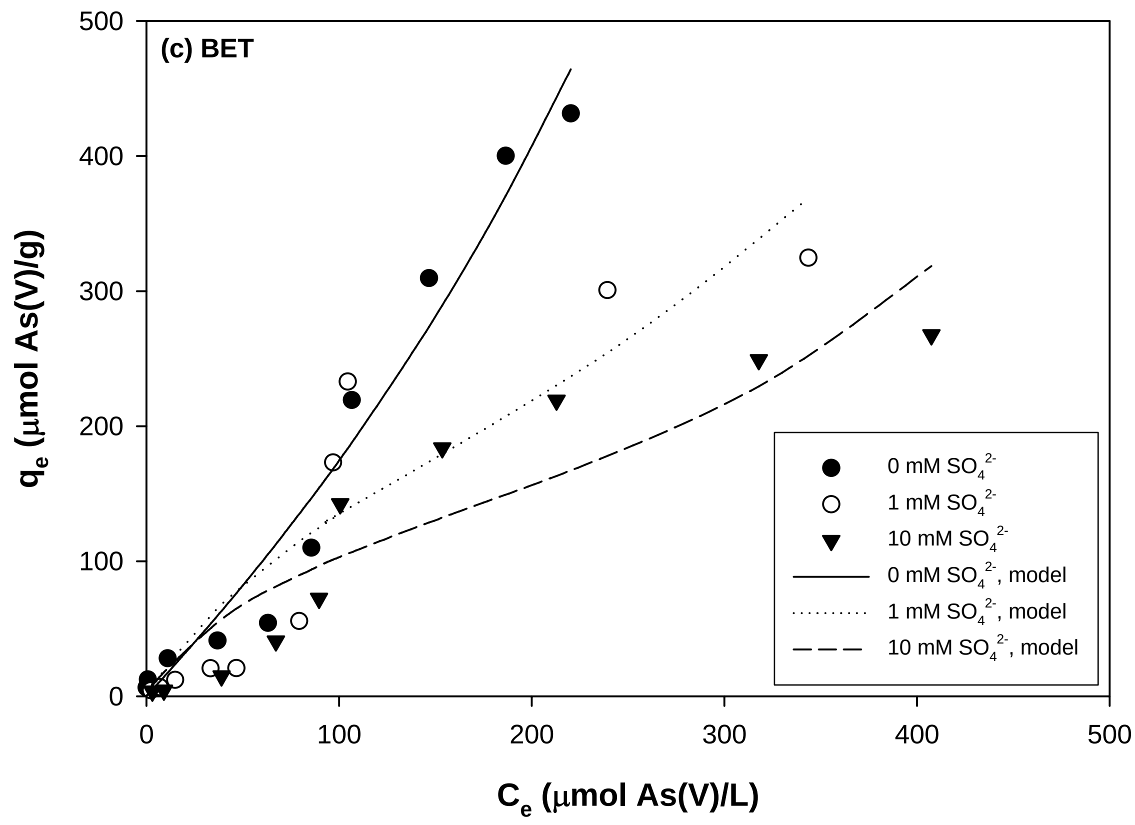
Results – As(V)

- Arsenic (V) – FeS/pH



Results – As(V)

- Arsenic (V) – FeS/SO_4

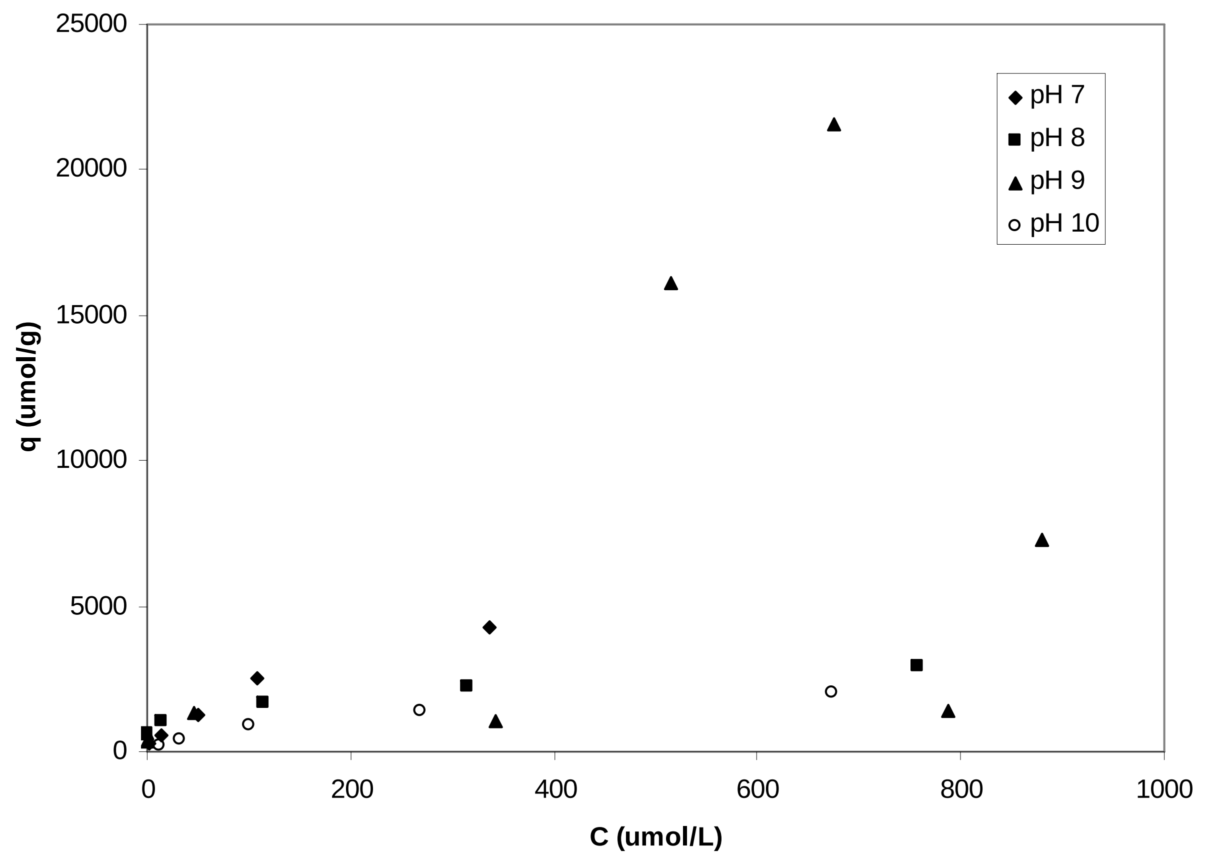


Results

- Arsenic
  - As(V)
    - pH
      - Pyrite – optimum pH 8-9
      - FeS – strong effect, higher loading at lower pH
    - SO_4
      - Pyrite – small effect
      - FeS – moderate effect
    - Pyrite/FeS
      - pH response different
      - FeS higher loading at low pH
      - FeS more surface reaction

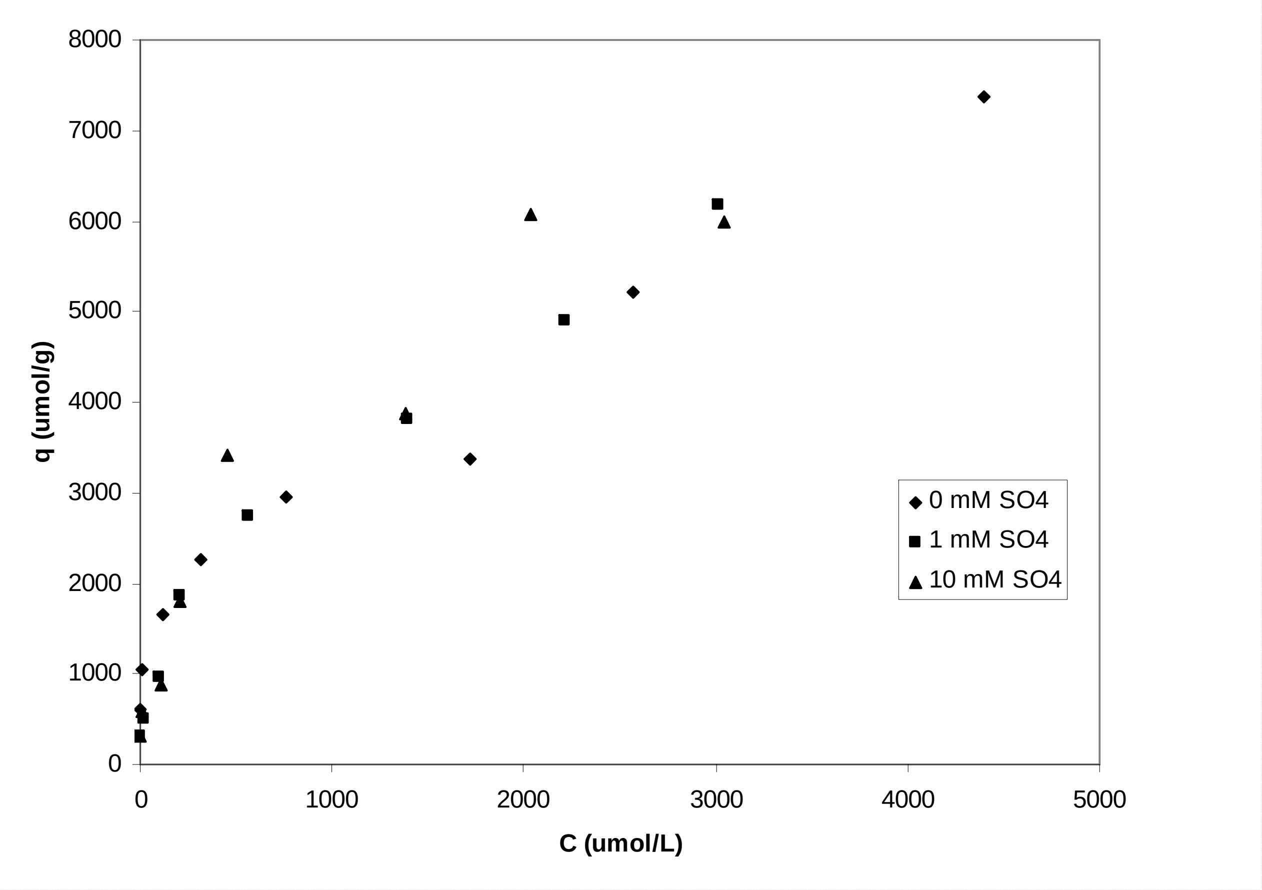
Results - Hg

❖ Mercury – Pyrite/pH



Results – Hg

❖ Mercury – Pyrite/SO_4



Results

- Mercury
  - Hg
    - pH – no strong effect
    - High variability – surface reactions
    - SO_4 – little effect
    - As(III)/As(V) – much higher loading (10x)

Summary

- Characteristics of Removal

	As(III)		As(V)		Hg
	FeS_2	*FeS*	*FeS_2*	*FeS*	*FeS_2*
Opt. pH	high	8-9	8-9	low pH	weak
SO_4 effect	small	moderate	small	moderate	small
Surface Rxn.	less	more	less	more	moderate
Loading	moderate	moderate	moderate	moderate	high

Summary

- Adsorbent-Reactants Effective
  - Removal
  - Stability (?)
- Sorption and Reaction
- Multiple Targets (As(III), As(V), Hg)

Questions