Selective Dissolution of Co or Cd Doped Hydrous Ferric Oxide

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Intention / Context

- RELEVANCE: The model Fe(III) reducing bacteria Shewanella putrefaciens is thought to reduce Fe(III) to Fe(II) which in turn is reduced to Fe(0). Elements such as Co and Cd are preferentially reduced by Shewanella. Dissolution rates of Fe(III) oxides depend on the reactivity of the Fe(III) oxide, the speciation of Co and Cd, and the pH. The potential for Co and Cd to coprecipitate with other solids and become a contaminant is only partly quantified in the current literature. Understanding microbial redox behavior is necessary for improving the efficiency of the microbial reduction of Fe(III) oxides, which could be useful in bioremediation applications.

- EXPERIMENTAL PROCEDURES:
  - DETAILS OF SYNTHESIS:
    - To address this question, future work includes: (1) completion of extractions on HFO with surface bound Co and Cd only, at conditions well below saturation with respect to hydroxide or carbonate (by mass). (2) Co and Cd concentration experiments in under 60 min as expected (Kostka and Luther, 1994). Consequently, maximum concentrations (by mass) are achieved for Co and Cd in 10% (by mass) HFO coprecipitates in 10% Cd (by mass), (3) HFO coprecipitated in 1% Co (by mass), (4) HFO coprecipitated in 1% Cd (by mass), and (5) HFO coprecipitated with other solids (by mass) hinder current efforts to quantify adsorbed or coprecipitated with Fe(Ox) into solution.
  - EXPERIMENTAL RESULTS:
    - All extractions of HFO: Initial results indicate that the 2M HCl completely dissolves HFO and all of the HFO reactivity is used up in under 6 days. However, the maximum concentrations of Co and Cd release in this experiment do not exceed 5% of the initial concentration after 6 days.
  - CONCLUSIONS / FUTURE WORK:
    - With Co release, the Fe fraction released into solution never exceeds 5% of total concentration after ~6 hrs.
    - The Cd fraction peaks at ~80% observed release after ~120 min, but decreases to ~25% observed release after ~6 hrs. Likewise, the Co fraction peaks at ~50% observed release after ~120 min but decreases to ~35% observed release after ~6 hrs. Fe release is consistent with the results for the plain HFO experiment; ~10% of the total Fe fraction was released after ~6 hrs. The Cd fraction appears to converge around ~40% of the total concentration. Fe release is nearly identical to the plain HFO and 1% Cd - HFO experiments with slightly greater than 50% of the total fraction was released.
  - Methods / Materials
    - Selective Dissolution of Co or Cd Doped Hydrous Ferric Oxide
    - Experimental Data
    - Discussion / Conclusions

- CONCLUSIONS / FUTURE WORK:
  - As expected from Tessier et al. (1979, 1982) only hydroxylamine HCl significantly dissolves ferrihydrite. The time suggested by Tessier et al. to completion of Fe release from 0.04M NH\textsubscript{3}OH is consistent with the plain HFO experiment; ~10% of the total Fe fraction was released after ~6 hrs. The Cd fraction appears to converge around ~40% of the total concentration. Fe release is nearly identical to the plain HFO and 1% Cd - HFO experiments with slightly greater than 50% of the total fraction was released.
  - Experimental Data
    - EXPERIMENTAL PROCEDURES:
      - Plain HFO: Fe release did not exceed 5% after ~6 hrs.
      - (1) Fe(OH)\textsubscript{3} - 80% of the total Fe fraction was released after ~6 hrs. Fe release does not exceed 70%.
      - (2) 1M NaAcetate: ~50% of the total Fe fraction was released after ~6 hrs; ~50% of the total Cd fraction was released after ~6 hrs. 30% H\textsubscript{2}O\textsubscript{2} was added after the initial 2 hrs, and allowed to remain at 65˚ C under continuous agitation for an additional 3 hrs. The results were compared against those shown here for 65˚ C. All samples were centrifuged at 13,000 rpm and washed three times.
      - Analysis of the centrifuged HFO powder revealed a significant increase in the concentration of Fe(II) to Fe(0).
      - All other extractions were performed under pH 2 to 3. Fe(II) concentrations slowly, but steadily increased throughout both experiments with no indication of a plateau.
      - 40 g of ferric nitrate was dissolved in 500 mL of 18 Ω DDI water, and (5) HFO coprecipitated in 10% Cd (by mass), (4) HFO coprecipitated in 1% Cd (by mass), (3) HFO coprecipitated in 1% Co (by mass), (2) HFO coprecipitated in 30% H\textsubscript{2}O\textsubscript{2} (by mass) followed the same procedure described above but with an indication of two component aqueous systems. (by mass).
      - All samples were centrifuged to isolate the supernatant.
      - Selective Dissolution of Co or Cd Doped Hydrous Ferric Oxide
      - A mixture of 3 mL of 0.02M HNO\textsubscript{3} and 1 g/L HFO (undoped and doped) was slowly titrated to a pH of ~2.0 using HNO\textsubscript{3} to pH of 7.8. The resulting precipitate was washed, followed by washing in DI water until free of electricity, and then dried prior to use. Doped HFO allows the same procedure described above but with ~40% of ferric nitrate dissolved in 10% (by mass) H\textsubscript{2}O\textsubscript{2} (by mass) under constant agitation.
  - Resources

- Methods / Materials
  - PALETTE OF 2-LINE FERRHYDRITE:
    - • FILE: A mixture of 20% H\textsubscript{2}O\textsubscript{2} and 200 mL of 18 Ω DDI water was slowly titrated to a pH of ~2.0 using HNO\textsubscript{3} to pH of 7.8.
    - The resulting precipitate was washed, followed by washing in DI water until free of electricity, and then dried prior to use. Doped HFO allows the same procedure described above but with ~40% of ferric nitrate dissolved in 10% (by mass) H\textsubscript{2}O\textsubscript{2} (by mass) under constant agitation.

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