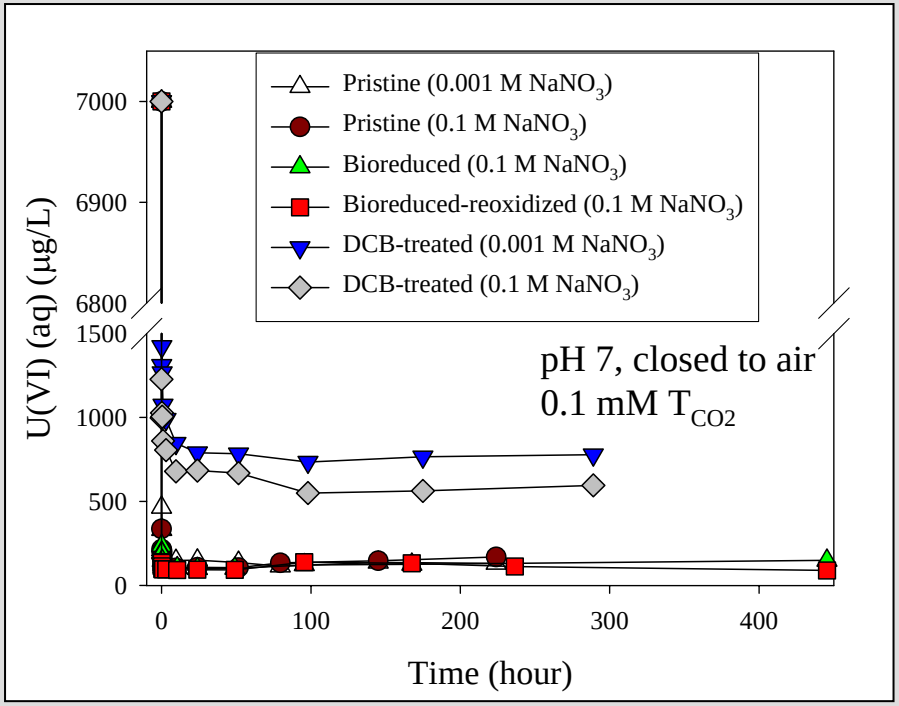
U (VI) Sorption to the Pristine, Bioreduced, and Bioreduced-Reoxidized FRC Sediments

Chongxuan Liu, Lirong Zhong, John Zachara,

Pacific Northwest National Laboratory

2004 DOE NABIR FRC Workshop at Oak Ridge, TN

U Sorption Kinetics



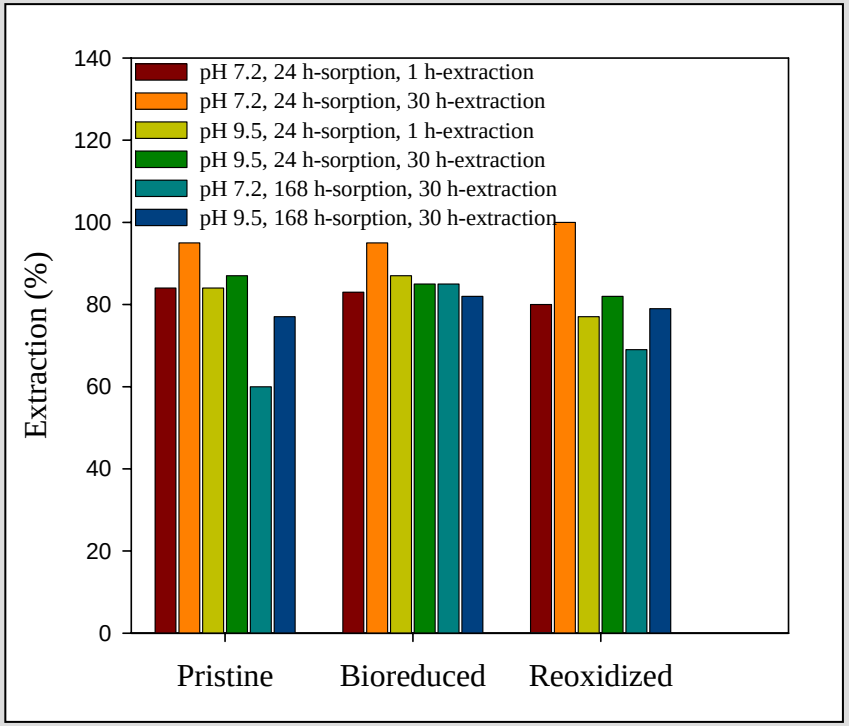
Pristine: FRC background sediment.

Bioreduced: treated sediment through anaerobic incubation of the pristine sediment with CN32 for 60 days.

Bioreduced-reoxidized: treated sediment through bubbling O_2 in the suspension of the bioreduced sediment for 24 h and then air-dried for 7 days.

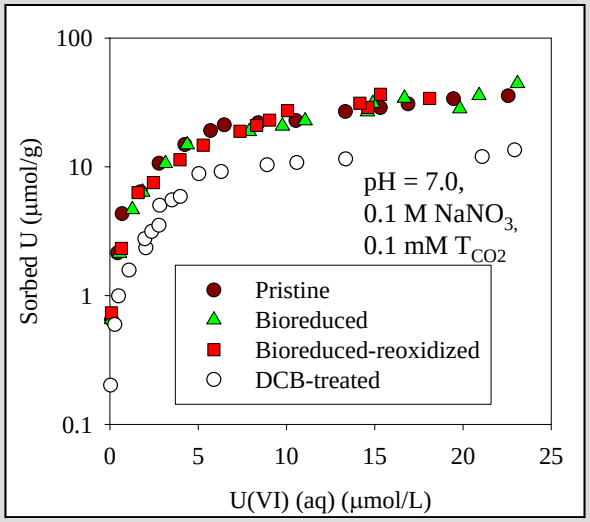
DCB-treated: treated sediment by reacting the pristine sediment with dithionite-citrate-bicarbonate (DCB) solution.

U(VI) Extraction with Bicarbonate (0.2 M)

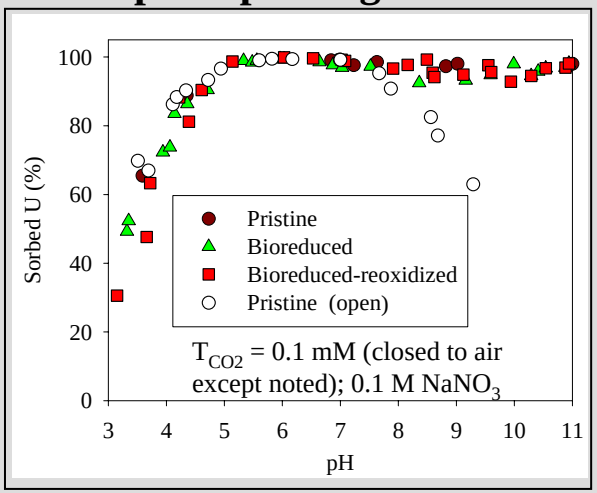


Effects of U(VI), pH, and Carbonate

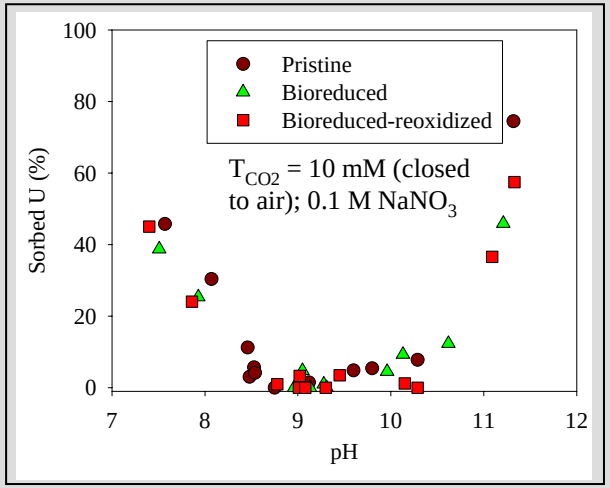
U Sorption Isotherms



U Sorption pH Edges



U Sorption pH Edges



Summary of Experimental Results and Modeling Approach

Summary

- U(VI) adsorption dominated the U(VI) interaction with the FRC sediments regardless of sediment bioreduction and reoxidation.
- U(VI) reduction by sorbed Fe(II) was either nonexistent or a minor process relative to U(VI) adsorption, implying that bioreduction is required to reduce U(VI) in the subsurface sediment.
- Fast U sorption kinetics indicated that local equilibrium models may be valid for modeling U(VI) adsorption.
- Similarity of U(VI) sorption isotherms and pH edges implied that the same adsorption model may be used for modeling U(VI) adsorption in the pristine, bioreduced, and bioreduced-reoxidized sediments.

Modeling Approach

- Component Additivity (CA) Approach
  - a) Goethite-based model.
  - b) Ferrihydrite-based model.
- Generic Composite (GC) Approach

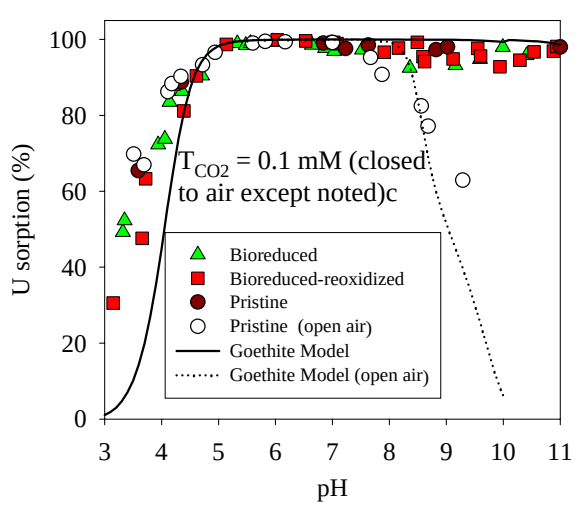
  Two-site non-electrostatic model.

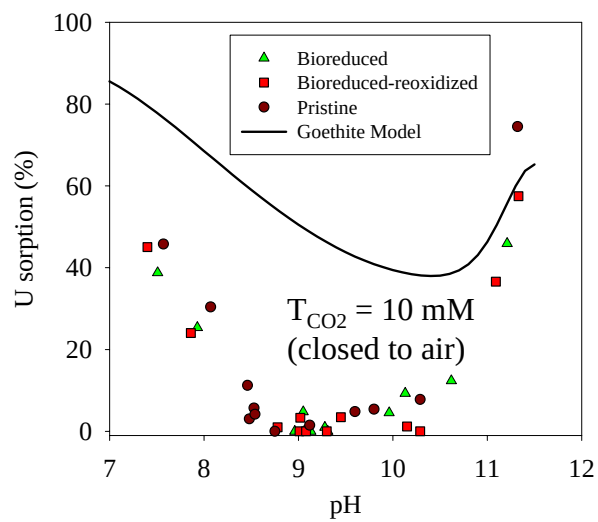
Goethite-Based Model

Surface Reactions (triple layer one-site model)	**log K (I = 0.1)**
$SOH = SO^- + H^+$	-11.2
$SOH + H^+ = SOH_2^+$	7.2
$SOH + Na^+ = SO^-\cdots Na^+ + H^+$	-10.37
$SOH + H^+ + NO_3^- = SOH_2^+\cdots NO_3^-$	8.35
$SOH + H_2CO_3 = SO^{-0.2}COO^{-0.8} + H_2O + H^+$	-4.28
$SOH + H_2CO_3 + Na^+ = SOCOONa + H_2O + H^+$	-4.71
$SOH + H_2CO_3 = SOCOOH + H_2O$	0.78
$2SOH + UO_2^{2+} = (SO)_2UO_2 + 2H^+$	-4.71
$2SOH + UO_2^{2+} + 2H_2CO_3 = (SO)_2^{2-}[UO_2(CO_3)_2]^{2-} + 6H^+$	-22.79

(Villalbos et al., 2001 ES&T; total site density = 0.066 mol/ mol Fe)

Model Results





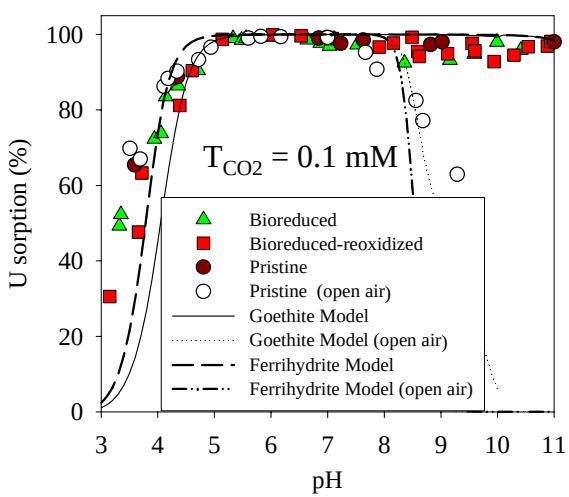
Ferrihydrite-Based Model

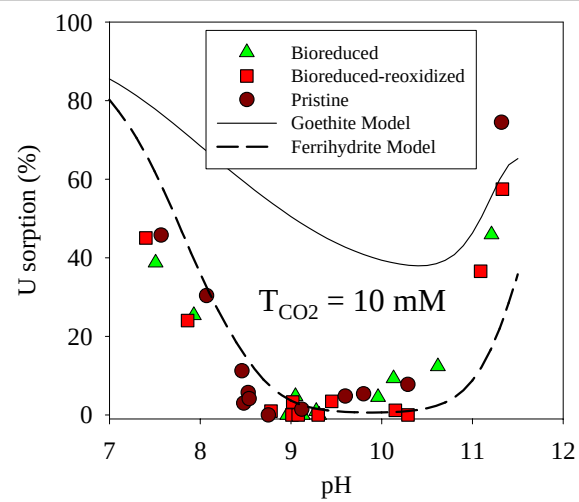
Surface Reactions (diffuse double layer two-site model) **log K (I = 0.1)**

$S(s,w)OH = S(s,w)O^- + H^+$	-9.13
$S(s,w)OH + H^+ = S(s,w)OH_2^+$	6.51
$S(s,w)OH + H_2CO_3 = S(s,w)CO_3H^0 + H_2O$	2.90
$S(s,w)OH + H_2CO_3 = S(s,w)CO_3^- + H_2O + H^+$	-5.09
$S(s)(OH)_2 + UO_2^{2+} = (S(s)O_2)\ UO_2^0 + 2H^+$	-2.57
$S(w)(OH)_2 + UO_2^{2+} = (S(w)O_2)\ UO_2^0 + 2H^+$	-6.28
$S(s)(OH)_2 + UO_2^{2+} + H_2CO_3 = (S(s)O_2)UO_2CO_3^{2-} + 4H^+$	-12.35
$S(w)(OH)_2 + UO_2^{2+} + H_2CO_3 = (S(w)O_2)\ UO_2CO_3^{2-} + 4H^+$	-16.44

(Waite et al., 1994 GCA and Davis, 2001 USGS report; total site density = 0.875 mol/mol Fe; strong site density: 0.0018 mol/mol Fe)

Model Results





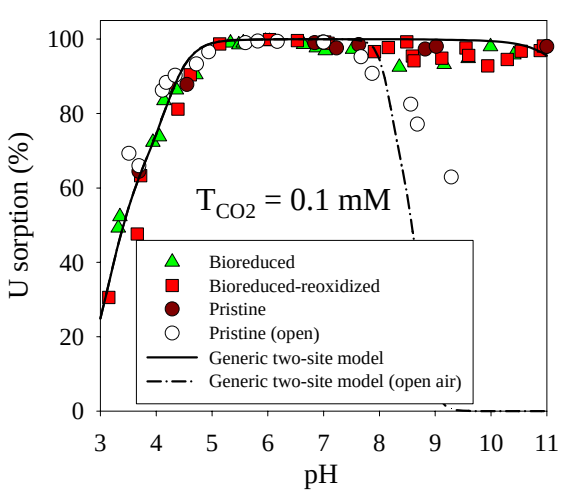
Generic Composite Model

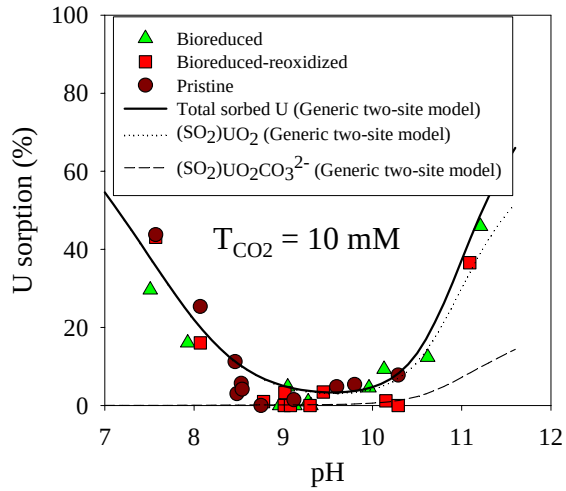
Surface Reactions (two-site non-electrostatic model) **log K (I = 0.1)**

$S(s)(OH)_2 + UO_2^{2+} = (S(s)O_2)\ UO_2^0 + 2H^+$	-1.81
$S(w)(OH)_2 + UO_2^{2+} = (S(w)O_2)\ UO_2^0 + 2H^+$	-5.89
$S(s)(OH)_2 + UO_2^{2+} + H_2CO_3 = (S(s)O_2)UO_2CO_3^{2-} + 4H^+$	-16.59
$S(w)(OH)_2 + UO_2^{2+} + H_2CO_3 = (S(w)O_2)UO_2CO_3^{2-} + 4H^+$	-20.48

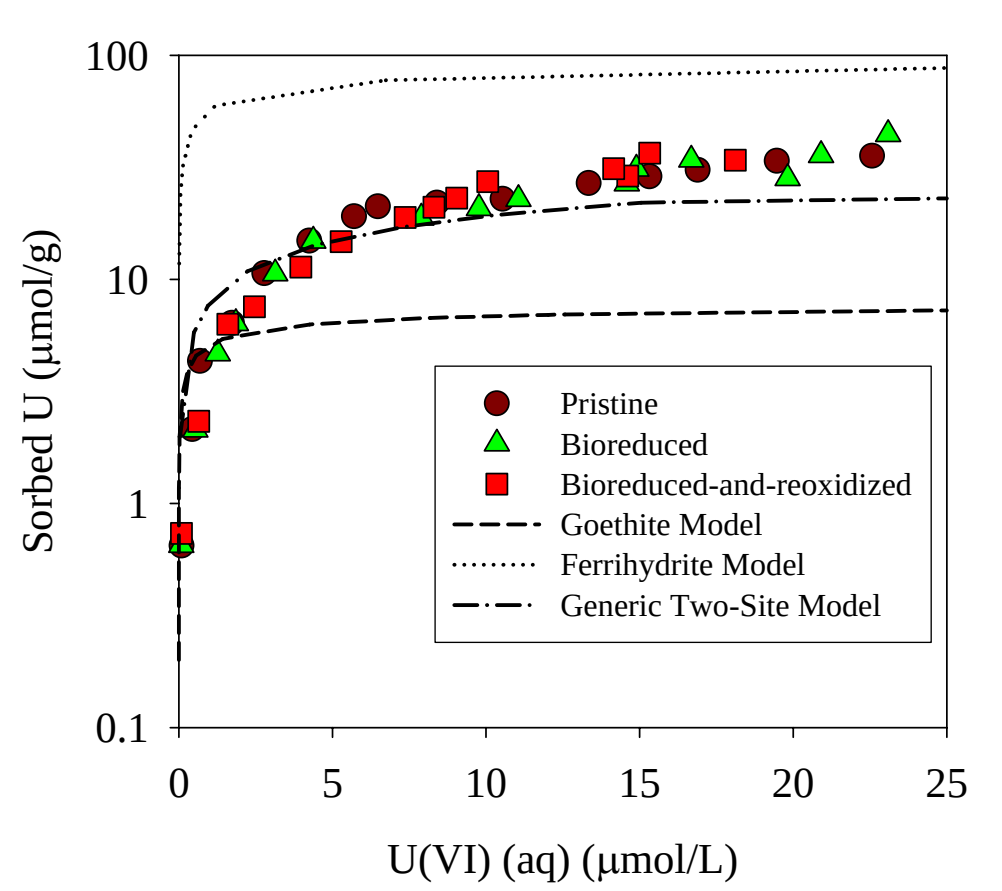
(total site density = 3.84 μmol/m^2; strong site density: 0.0506 μmol/m^2)

Model Results (fitted)





Prediction of U Sorption Isotherms



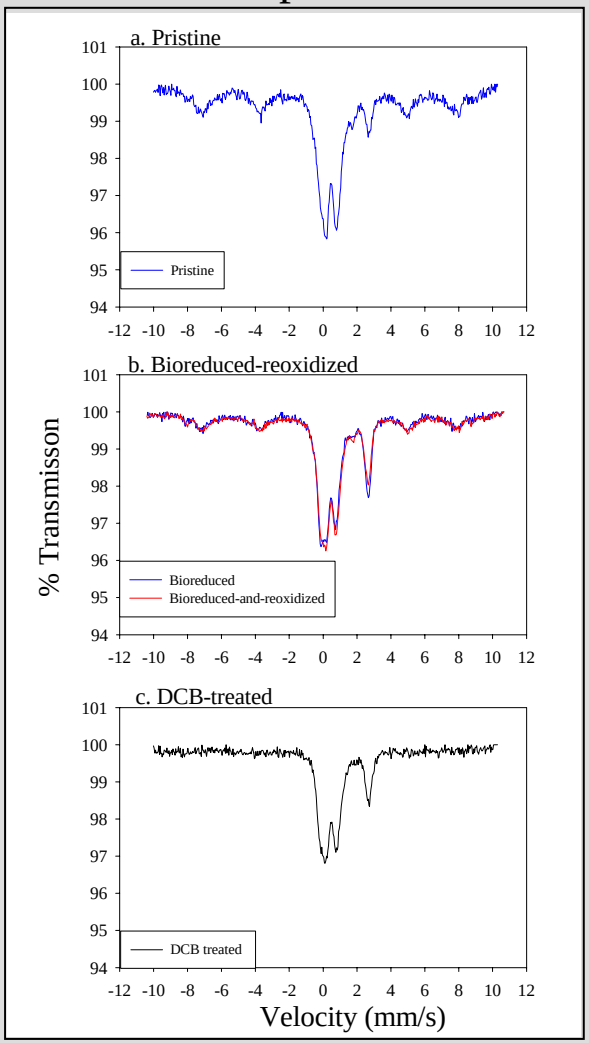
Modeling Summary

- U(VI) sorption to the pristine, bioreduced, and bioreduced-reoxidized FRC sediments was best described by a generic two-site non-electrostatic model.

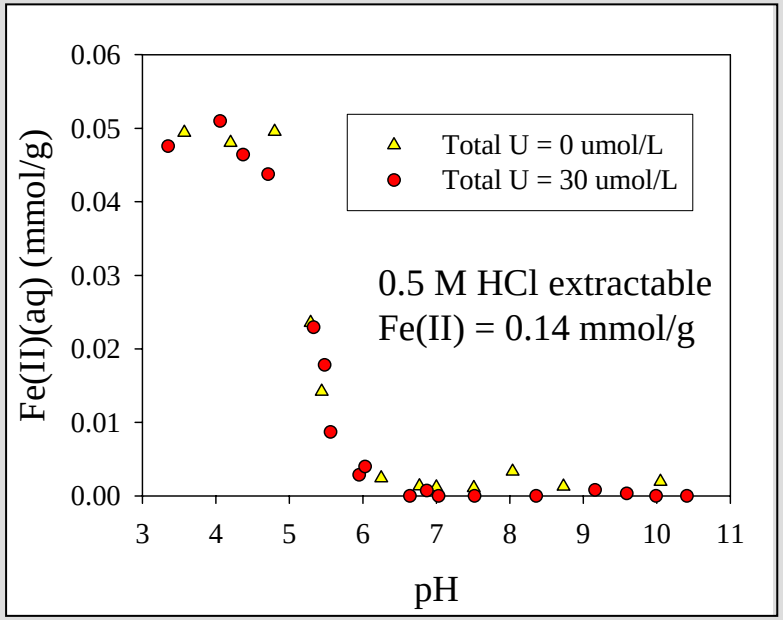
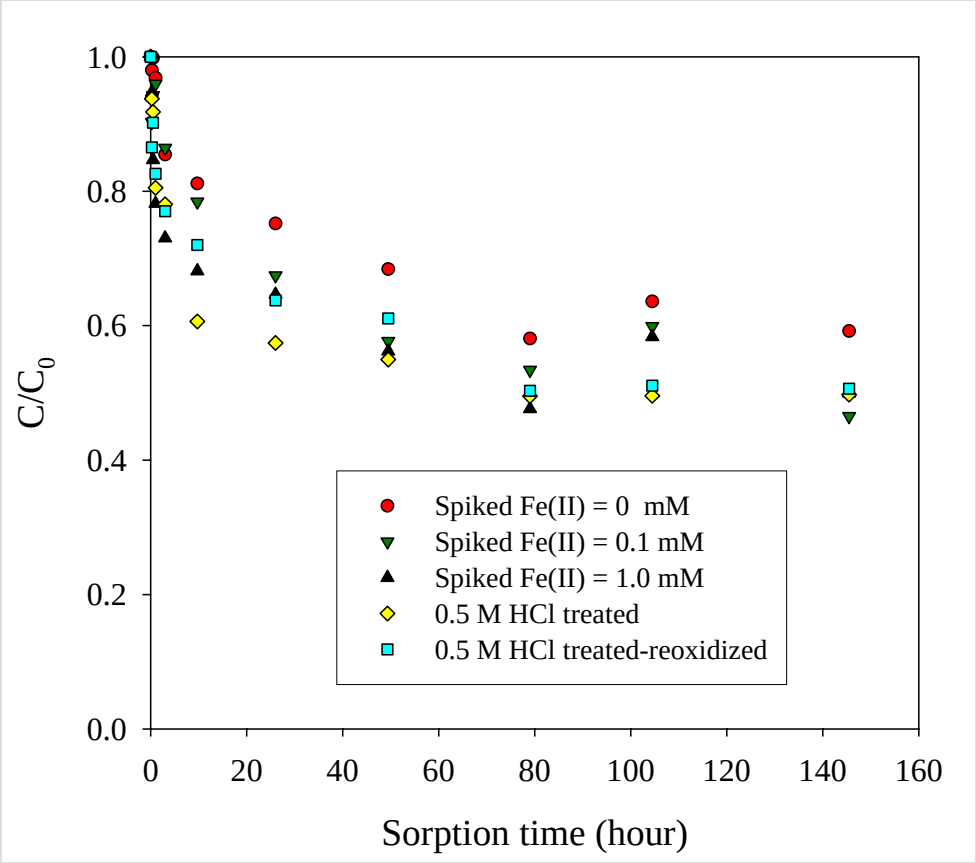
- The ferrihydrite-based model without parameterization predicted the U(VI) sorption better than goethite-based model although goethite was a dominant iron oxide in the FRC sediment.

Sediment Properties

Mössbauer spectra



Fe(II) in the bioreduced sediment



U(VI) extraction from DCB-treated sediment