Surface complexation modelling of chromate adsorption on iron oxides

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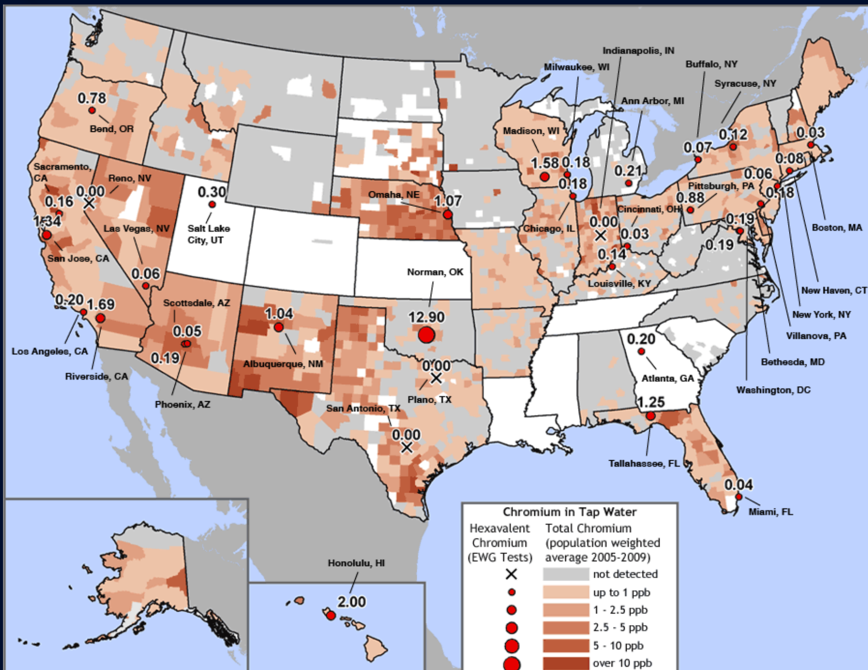
Chromium (Cr) in the environment

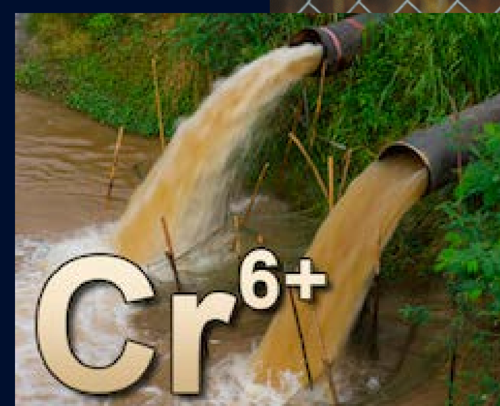


EWG analysis (2009) on in tap water from 35 US cities

Drinking water limit 0.1 ppm (100 ppb)
California limit 0.1 ppb

Sources of chromium are both natural and anthropogenic.

- Natural geochemical background (ultramafic and untrabasic rocks)
- It is used in the industry for metal plating, alloy production, dyes, paints, wood preservatives, and leather tanning.



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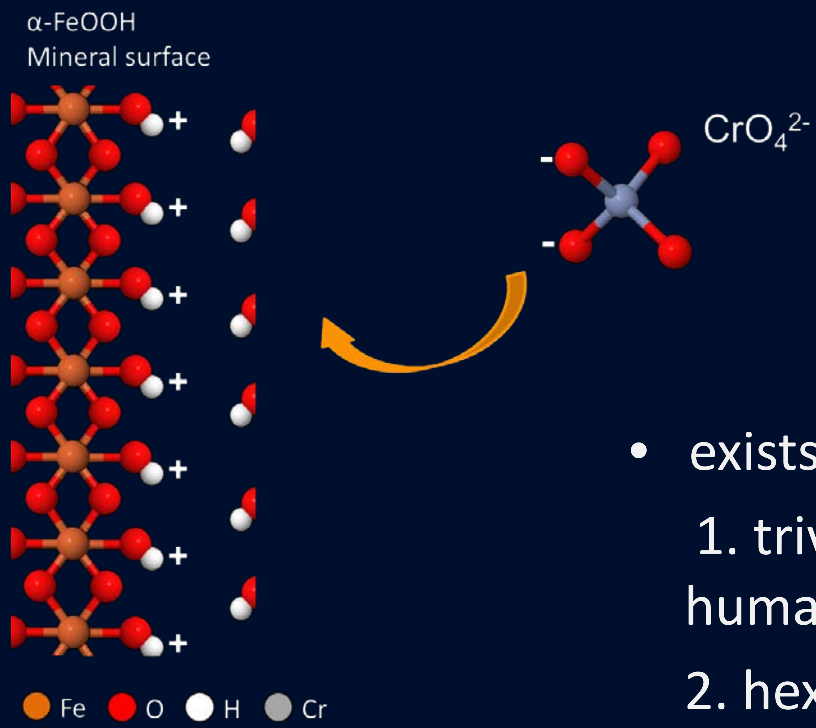
Chromium (Cr) speciation in the environment



Chromium (Cr)

- exists in the environment mostly in 2 states:

  1. trivalent (Cr(III)): essential element of human metabolism

  2. hexavalent (Cr(VI) or CrO_4^{2-}): highly mobile, toxic and carcinogenic

- Cr(VI) adsorbs on iron oxide surfaces (≡FeOH) under favorable conditions

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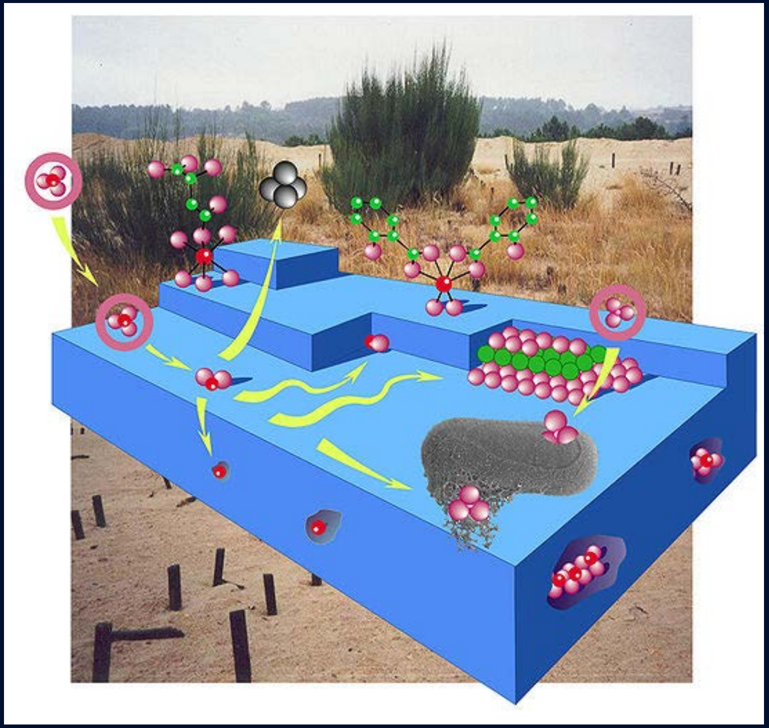
Fate and Transport of pollutants in the subsurface



Manceau et al. *Rev. Mineral. Geochem*. 2002, *49*, 341–428

Sorption is one of the most important processes affecting transport of contaminants in the environment.

Empirical distribution factor (K_d)

Surface Complexation Modeling (SCM)

Approaches to scale up SCMs in complex systems

Component Additivity

- Use of individual SCMs for pure minerals
- Characterization of soil for mineralogy and parameters for each mineral required

Generalized Composite

- Use of one or more generic surface sites to describe bulk soil
- Calibration for each ligand required

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Competing requirements for SCM application in transport modeling

Realistic description of sorption mechanisms and charge distribution

Site densities consistent with crystallography

Apply to all fields

Degree of complexity

High

Low

Difficulty to determine mineral-specific SSA in complex systems

High number of parameters for mineral assemblages / soils

Internal consistency of thermodynamic data

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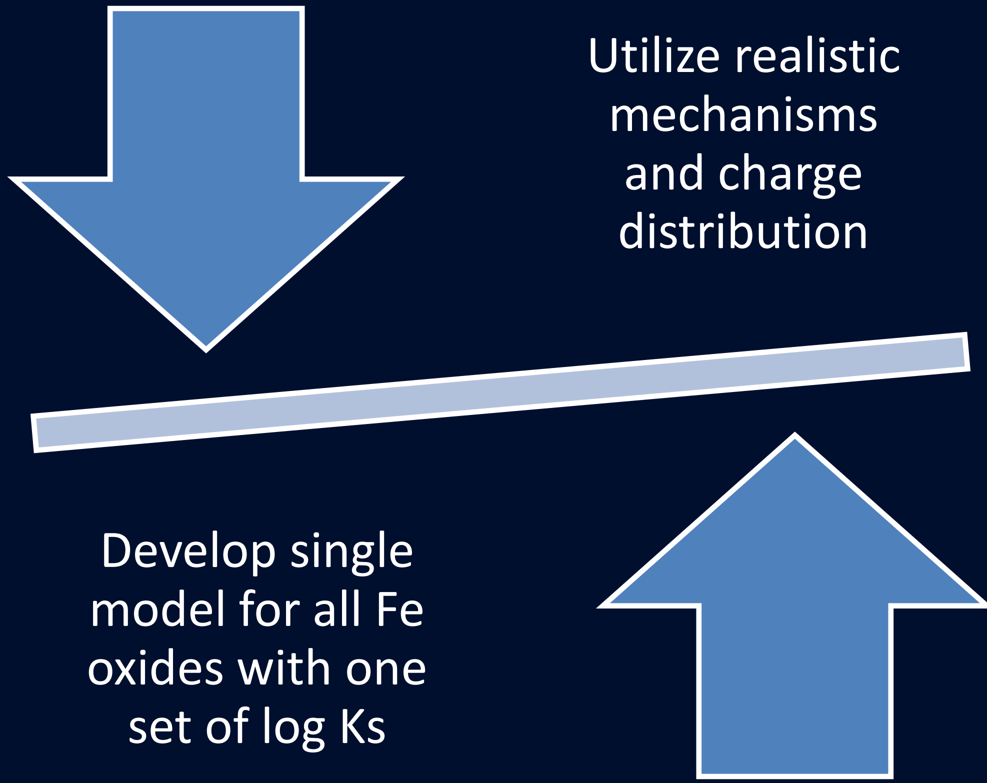
Proposed compromise



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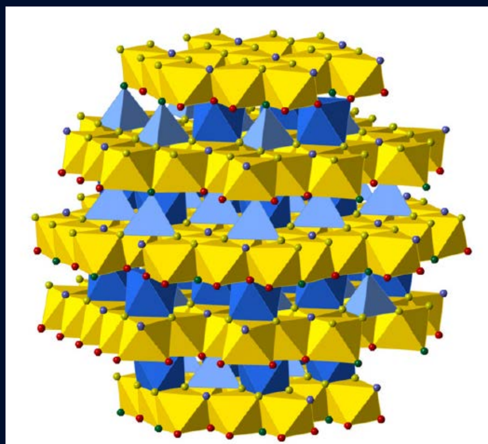
Surface structure

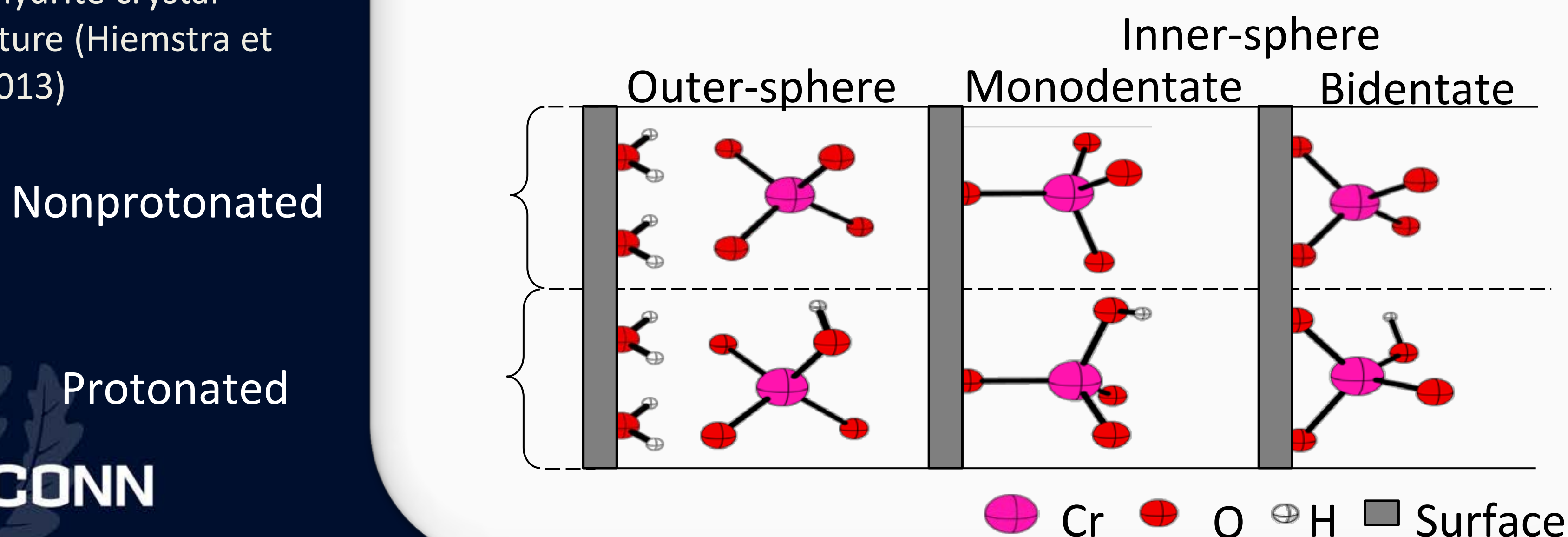


Ferrihydrite crystal structure (Hiemstra et al., 2013)

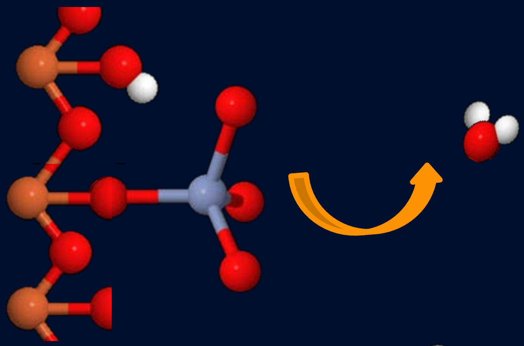
Based on ferrihydrite surface structure as proposed by Hiemstra (2013)

4 sites

- $FeOH^{a}$, LogK= 10.4 and 1.3 nm^{-2}
- $FeOH^{b}$, LogK= 8 and 5.2 nm^{-2}
- Fe_3O, LogK= 6.16 and 1.5 nm^{-2}
- Fe_3O, LogK= 10.4 and 2.6 nm^{-2}

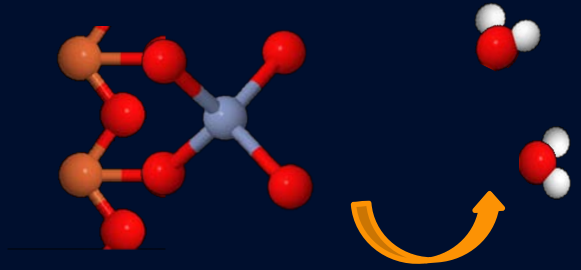


Surface Complexes



Inner-sphere monodentate complex

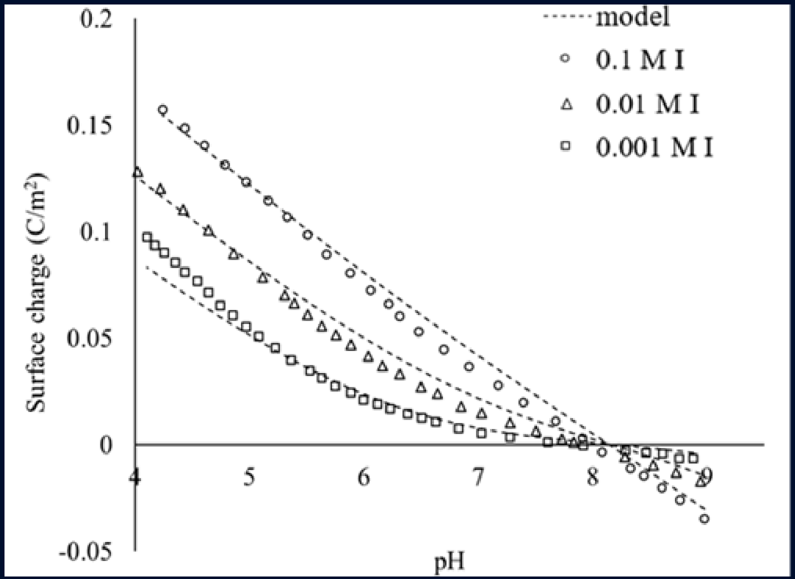
$\equiv FeOH^{-0.5} + H^{+} + CrO_4^{2-} \leftrightarrow \equiv FeOCrO_3^{-1.5} + H_2O$



Inner-sphere bidentate complex

$\equiv 2FeOH^{-0.5} + 2H^{+} + CrO_4^{2-} \leftrightarrow (\equiv FeO)_2CrO_2^{-1} + 2H_2O$

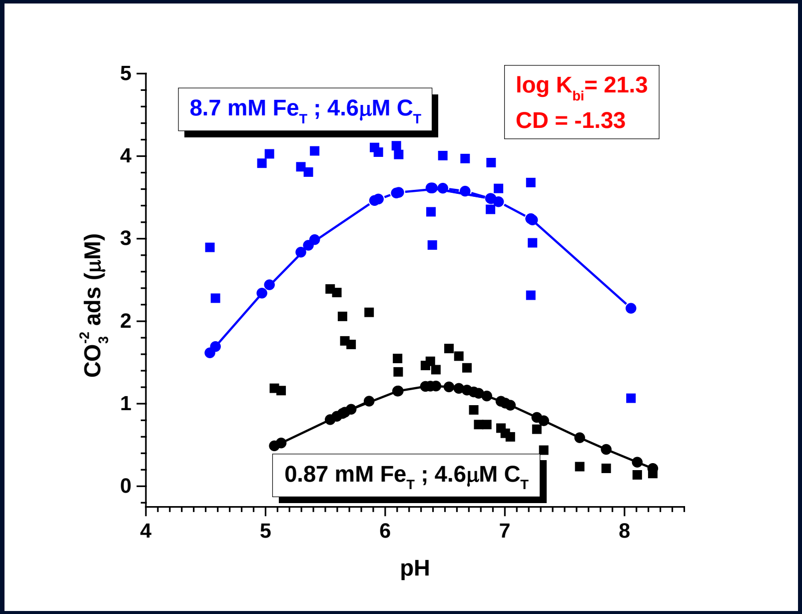
Model calibration utilizing ferrihydrite data



Surface charge modeling (line) and titration data by Girvin et al. (1991) on ferrihydrite (open schemes)

Basic Stern model fit with C_S = 1.1; $\log K_{Na}$ = -0.7; $\log K_{NO3}$ = -0.9

Carbonate adsorption modeling (lines) and data by Zachara et al. (1989) (squares).
Carbonate complexation constant $\log K_{CO3}$ = 21.3



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Complexation Reactions

Reaction	LogKs
Surface Protonation reactions	
$\equiv FeOH^{-0.5} + H^{+} \leftrightarrow \equiv FeOH_2^{0.5}$	10.4 & 8.0[a]
$\equiv Fe_3O^{-0.5} + H^{+} \leftrightarrow \equiv Fe_3OH^{0.5}$	6.16 & 10.4[a]
Electrolyte-Surface Reactions	
$\equiv FeOH^{-0.5} + Na^{+} \leftrightarrow \equiv FeOHNa^{+0.5}$	-0.7
$\equiv FeOH^{-0.5} + H^{+} + Cl^{-} \leftrightarrow \equiv FeOH_2Cl^{-0.5}$	-0.45[b]
$\equiv FeOH^{-0.5} + H^{+} + NO_3^{-} \leftrightarrow \equiv FeOH_2NO_3^{-0.5}$	-0.9
$\equiv FeOH^{-0.5} + H^{+} + ClO_4^{-} \leftrightarrow \equiv FeOH_2ClO_4^{-0.5}$	-1.7[b]
Inner-sphere Surface Complexation Reactions	
$\equiv FeOH^{-0.5} + H^{+} + CrO_4^{2-} \leftrightarrow \equiv FeOCrO_3^{-1.5} + H_2O$	11.2
$\equiv 2FeOH^{-0.5} + 2H^{+} + CrO_4^{2-} \leftrightarrow (\equiv FeO)_2CrO_2^{-1} + 2H_2O$	18.4
$\equiv 2FeOH^{-0.5} + 2H^{+} + CO_3^{2-} \leftrightarrow (\equiv FeO)_2CO_2^{-1} + 2H_2O$	21.3

[a] Hiemstra 2013

[b] Hiemstra and Van Riemsdijk, 1996

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Model Validation

Solid and initial Cr(VI) concentrations, SSA and ionic strength used as given in the respective study

Datasets used for the validation of the model:

Cr(VI) on ferrihydrite

- Benjamin et al., 1983
- Hsia et al., 2001
- This study

Cr(VI) on goethite

- Villalobos and Pérez-Gallegos, 2008
- VanGeen et al., 1994
- Mesuere and Fish, 2002

Cr(VI) on hematite

- Ajouyed et al., 2010

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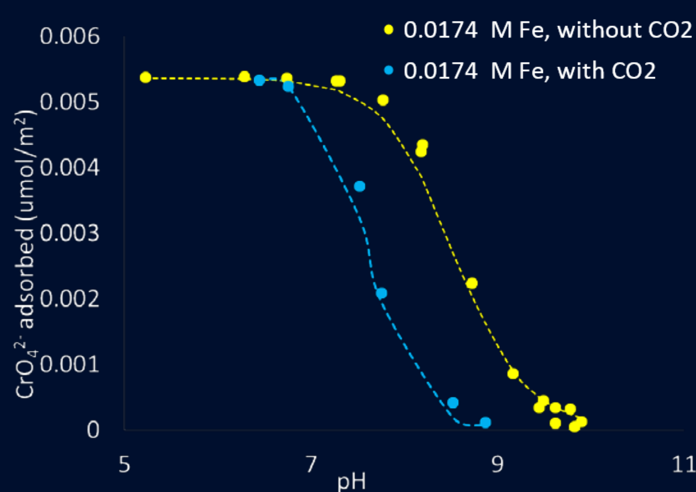
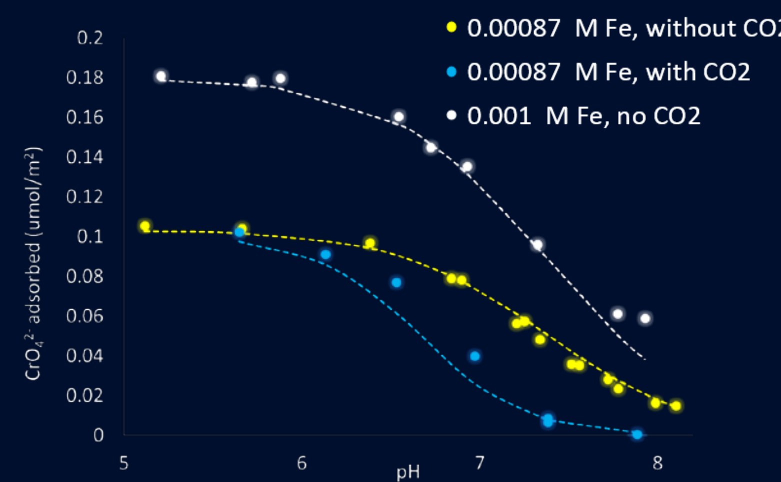
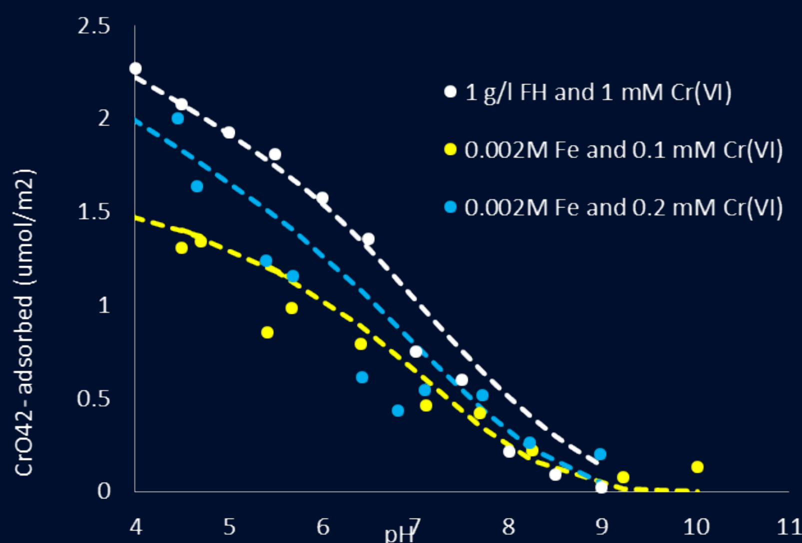
Cr (VI) on Ferrihydrite

In various surface coverages





Data from Zachara et al. (1989) and Benjamin (1983)



Data from this study and Hsia et al. (2015)

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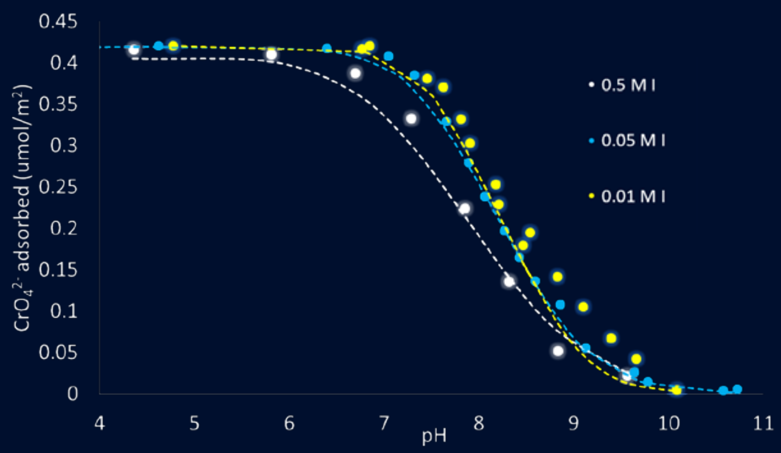
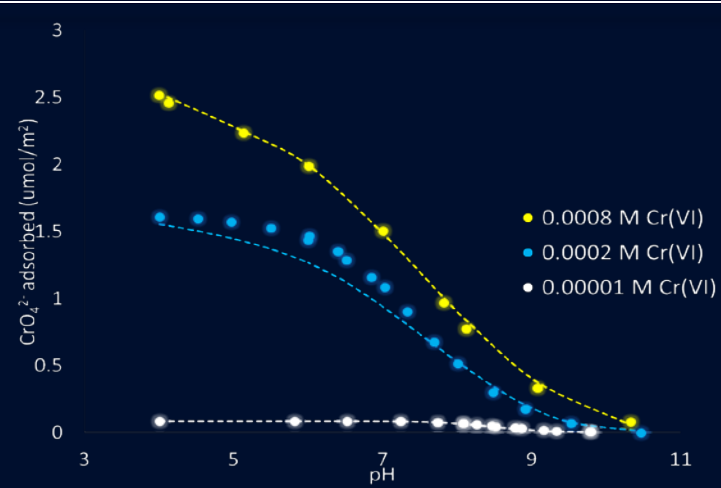
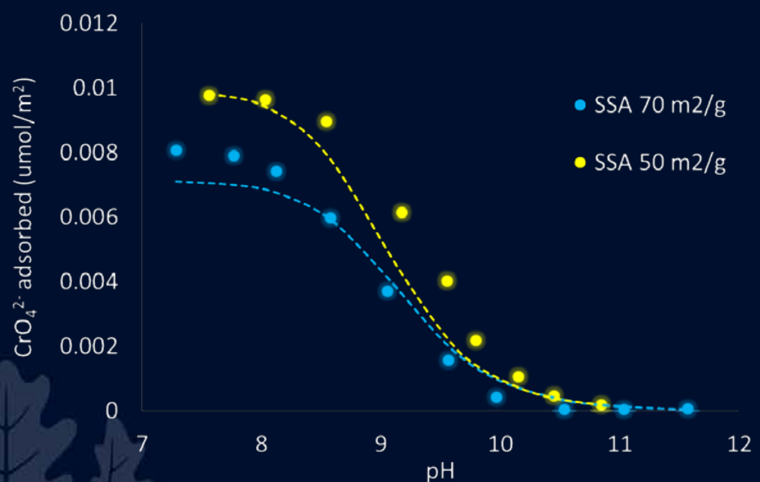
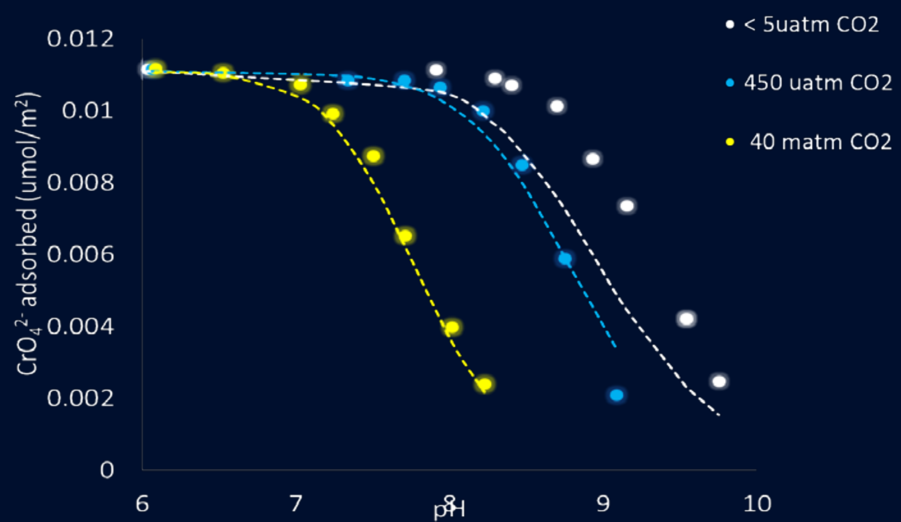
Cr(VI) on Goethite





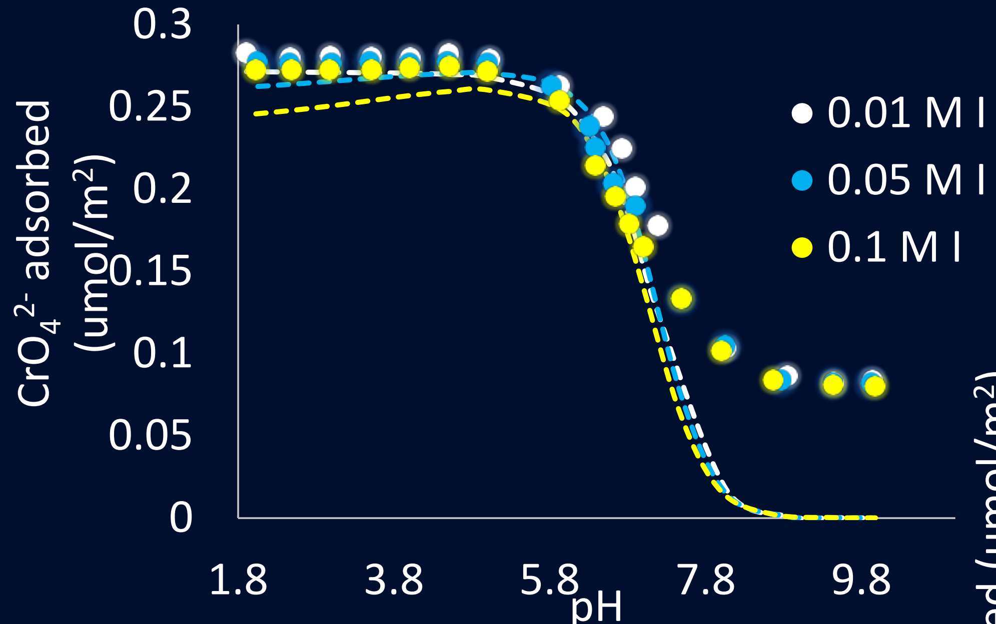
Data from Mesuere and Fish (1992)

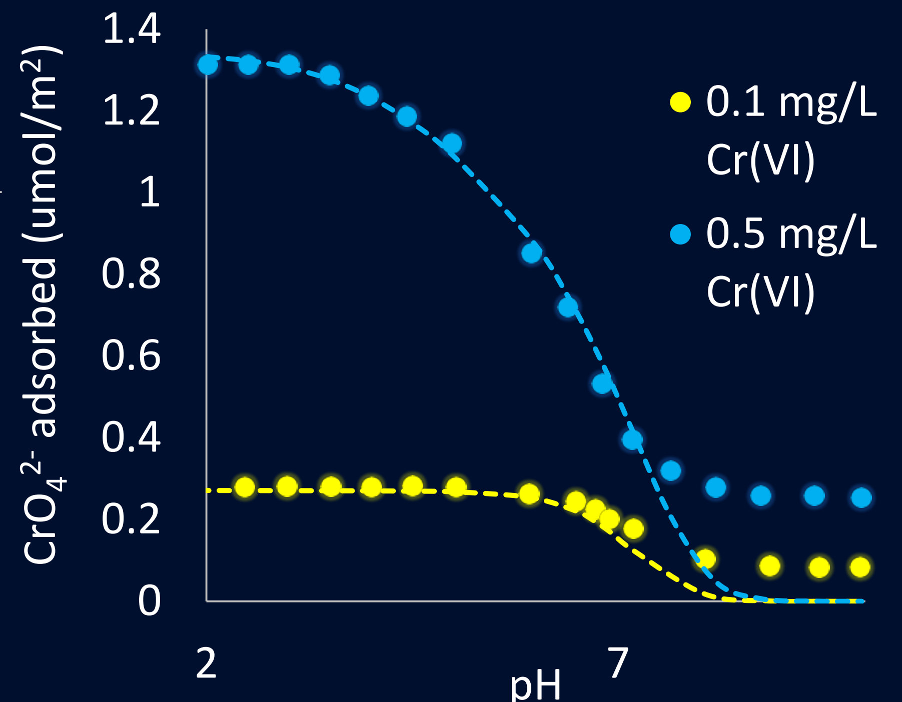




Data from Villalobos and Pérez-Gallegos (2008) and Van Geen et al. (1994)

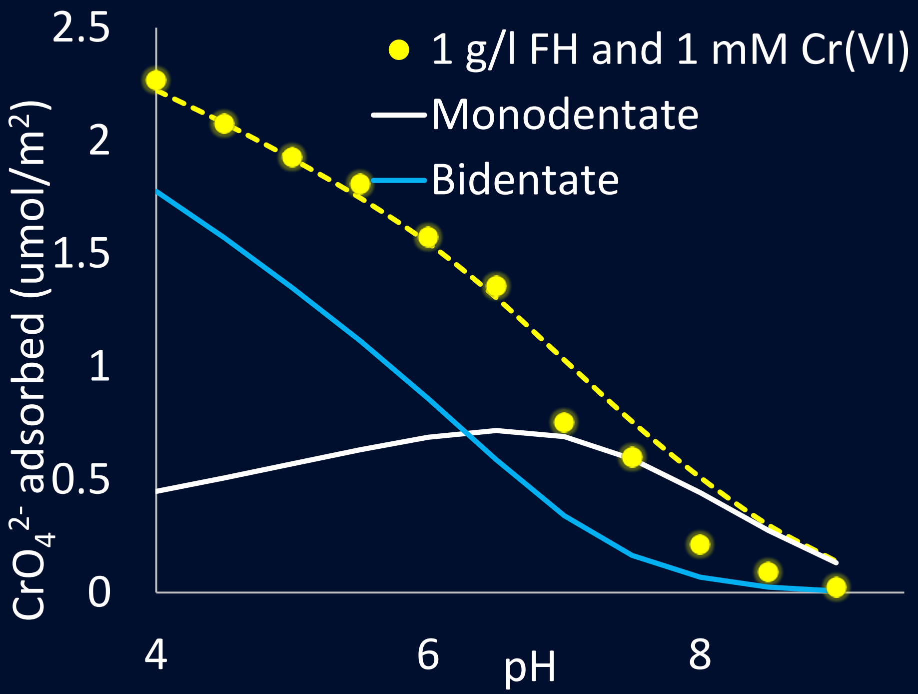
Cr(VI) on Hematite



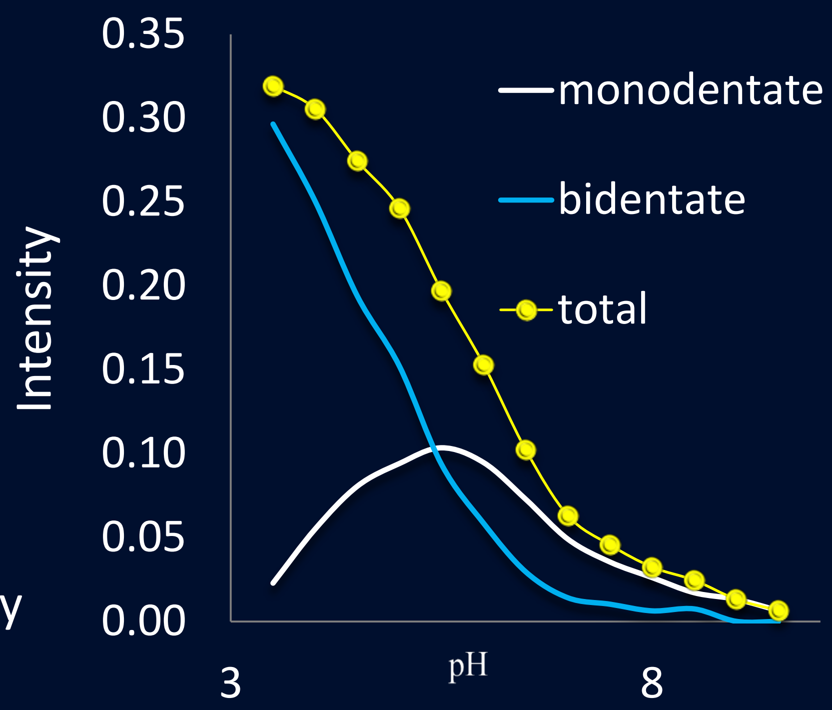


Batch data from Ajouyed at al. (2010)

Inner - sphere species distribution



Data from spectroscopy



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Conclusions

- The SCM based on FH surface structure described well enough the Cr(VI) adsorption on FH and GH.
- For HT, the model underestimated the adsorption at high pH.
- Inner – sphere speciation in accordance with spectroscopic evidence.

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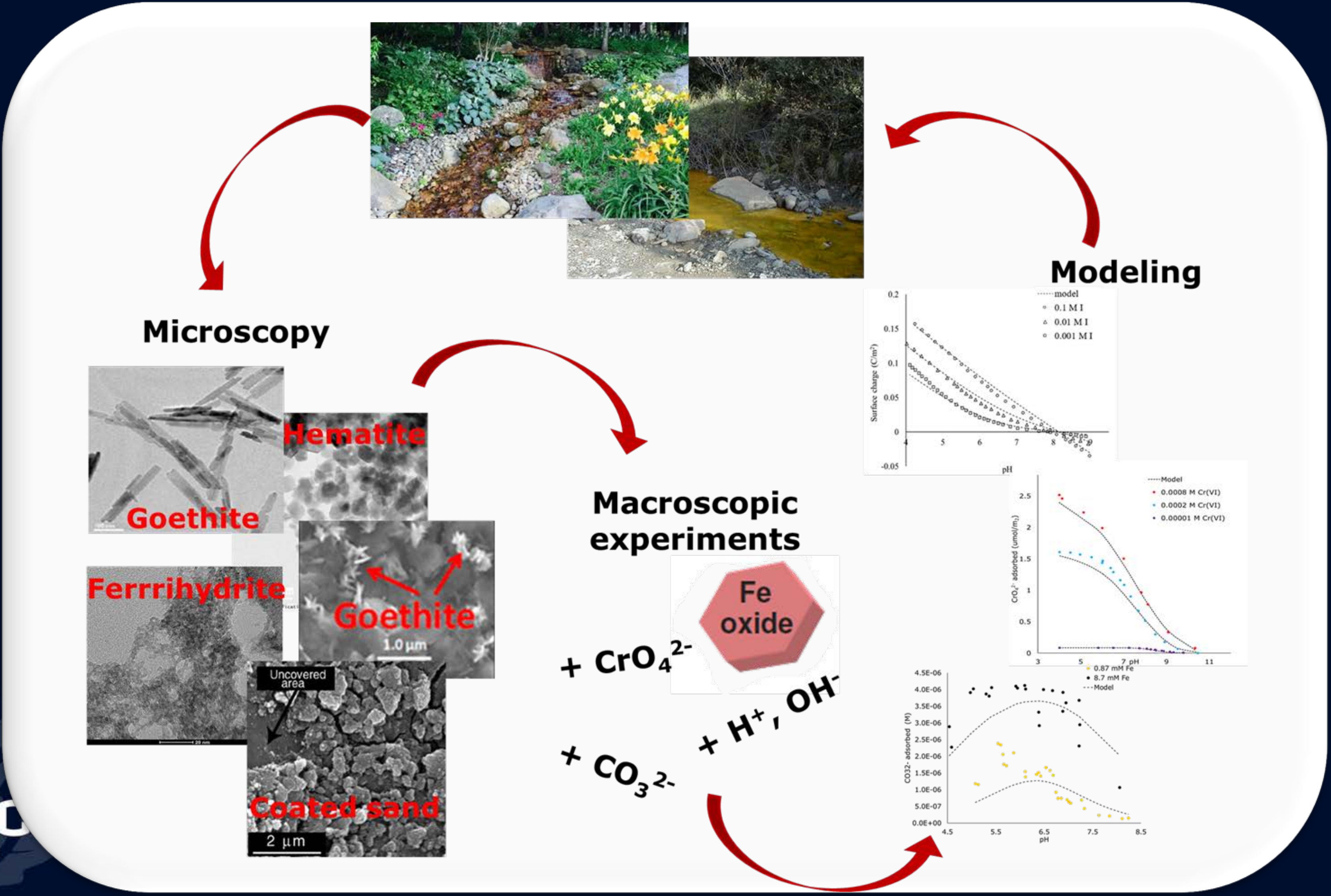
Following steps for SCM in complex systems



Acknowledgments

NSF project 1404633

Collaborative Research: Toward a unified model for ferrihydrite nanoparticles behavior in the environment: a multipronged investigation of surface structure and reactivity

FEI fellowship in relation to the new UCONN FEI Center of Excellence in Microscopy (UFCEM) for "Investigating soil surfaces utilizing electron microscopy".

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