Surface complexation modelling of chromate adsorption on iron oxides

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Chromium (Cr) in the environment

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.

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

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

- 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

- Utilize realistic mechanisms and charge distribution

- Develop single model for all Fe oxides with one set of log Ks
Surface structure

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

- FeOH\textsuperscript{a}, LogK= 10.4 and 1.3 nm\textsuperscript{-2}
- FeOH\textsuperscript{b}, LogK= 8 and 5.2 nm\textsuperscript{-2}
- Fe\textsubscript{3}O, LogK= 6.16 and 1.5 nm\textsuperscript{-2}
- Fe\textsubscript{3}O, LogK= 10.4 and 2.6 nm\textsuperscript{-2}

Ferrihydrite crystal structure (Hiemstra et al., 2013)
Surface Complexes

Inner-sphere monodentate complex
≡FeOH$^{-0.5}$ + H$^+$ +CrO$_4^{2-}$ $\leftrightarrow$ ≡FeOCrO$_3^{-1.5}$ + H$_2$O

Inner-sphere bidentate complex
≡2FeOH$^{-0.5}$ + 2H$^+$ +CrO$_4^{2-}$ $\leftrightarrow$ (≡FeO)$_2$CrO$_2^{-1}$ + 2H$_2$O
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 $C_s = 1.1$; $\log K_{Na} = -0.7$; $\log K_{NO_3} = -0.9$

Carbonate adsorption modeling (lines) and data by Zachara et al. (1989) (squares).
Carbonate complexation constant $\log K_{CO_3} = 21.3$
Complexation Reactions

**Surface Protonation reactions**
≡FeOH\(^{-0.5}\) + H\(^+\) ↔ ≡FeOH\(_2\)\(^{0.5}\)
≡Fe\(_3\)O\(^{-0.5}\) + H\(^+\) ↔ ≡Fe\(_3\)OH\(^{0.5}\)

**Electrolyte-Surface Reactions**
≡FeOH\(^{-0.5}\) + Na\(^+\) ↔ ≡FeOHNa\(^{+0.5}\)
≡FeOH\(^{-0.5}\) + H\(^+\) + Cl\(^-\) ↔ ≡FeOH\(_2\)Cl\(^{-0.5}\)
≡FeOH\(^{-0.5}\) + H\(^+\) + NO\(_3\)\(^-\) ↔ ≡FeOH\(_2\)NO\(_3\)\(^{-0.5}\)
≡FeOH\(^{-0.5}\) + H\(^+\) + ClO\(_4\)\(^-\) ↔ ≡FeOH\(_2\)ClO\(_4\)\(^{-0.5}\)

**Inner-sphere Surface Complexation Reactions**
≡FeOH\(^{-0.5}\) + H\(^+\) + CrO\(_4\)\(^{2-}\) ↔ ≡FeOCrO\(_3\)\(^{-1.5}\) + H\(_2\)O
≡2FeOH\(^{-0.5}\) + 2H\(^+\) + CrO\(_4\)\(^{2-}\) ↔ (≡FeO)\(_2\)CrO\(_2\)\(^{-1}\) + 2H\(_2\)O
≡2FeOH\(^{-0.5}\) + 2H\(^+\) + CO\(_3\)\(^{2-}\) ↔ (≡FeO)\(_2\)CO\(_2\)\(^{-1}\) + 2H\(_2\)O

LogKs
10.4 & 8.0\(^a\)
6.16 & 10.4\(^a\)
-0.7
-0.45\(^b\)
-0.9
-1.7\(^b\)

\(^a\) Hiemstra 2013
\(^b\) Hiemstra and Van Riemsdijk, 1996
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
Cr (VI) on Ferrihydrite

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

In various surface coverages

Data from this study and Hsia et al. (2015)
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
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.
Following steps for SCM in complex systems
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