A NEW SURFACE COMPLEXATION MODEL FOR CHROMATE ADSORPTION ON FERRIHYDRITE

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EXTENDED ABSTRACT

Surface complexation models (SCMs) provide a mechanistic and thermodynamically-based description of sorption reactions on mineral surfaces and can thus be used in geochemical modelling to predict contaminant sorption under a variety of geochemical conditions. In the last years, substantial effort has been put into obtaining multiple lines of evidence for the types of complexes formed on mineral surfaces and refining reactions and assumptions in SCMs using such information. A large number of studies have been performed to investigate the sorption behaviour of oxyanions (carbonate, sulphate, phosphate, arsenate and others) on iron oxides such as goethite, hematite and ferrihydrite. Surprisingly, there are very few studies conducted for chromate (CrO$_4^{2-}$), despite its prevalence as a soil and groundwater contaminant. Only two SCMS for chromate sorption on ferrihydrite were identified, dating back to the late 80s and early 90s, when no insight into mechanisms was available. A recent study that utilized spectroscopy and computational chemistry observed that chromate forms inner-sphere monodentate and bidentate complexes, the relative distribution of which depends on solution pH, surface loading and ionic strength. Accordingly, this study presents a new SCM that utilized the observed mechanisms for formulation and calibration of the sorption reactions. The Charge-Distribution Multisite Complexation (CD MUSIC) modelling framework was adopted and a recent analysis for the surface structure of ferrihydrite was considered. Specifically, only one type of singly-coordinated oxygens are thought capable of forming inner-sphere complexes with chromate, while both singly- and triply-coordinated oxygens can interact with electrolyte ions (Na$^+$, Cl$^-$, NO$_3^-$). Additionally, the influence of carbonate was considered, assuming an inner-sphere bidentate complex based on previous studies. The results showed that substantial improvement in the fit between model and experimental data was obtained using the new formulation compared to an older study that only considered outer-sphere complex formation for chromate. The fit was very good for a wide range of chromate concentrations (5 μM to 1 mM), pH (5-10) and ferrihydrite concentrations (0.077 to 2 g/L).

Modeling the effect of carbonate proved more challenging. The model under-predicted carbonate sorption at pH<6 and also under-predicted chromate sorption in the presence of carbonate at pH<7. It is considered that the two phenomena are related and that an improvement in the carbonate sorption model is necessary to improve modeling of chromate sorption on ferrihydrite in the presence of carbonate. Additional data on carbonate sorption of ferrihydrite are required to this end.

Keywords: chromate, ferrihydrite, sorption, surface complexation modeling
1. INTRODUCTION

Modeling metal sorption onto soil surfaces has traditionally been incorporated into transport using empirical distribution factor (Kd) values. However, this approach is extremely limited, because it cannot account for changes in groundwater chemistry (pH, ionic strength, competitive ions) and is restricted to the system for which the empirical Kd value was obtained. In the last 20 years, significant effort has been made to shift to a more mechanistic description of sorption reactions through the development of Surface Complexation Models (SCMs). SCMs are generally based on providing a thermodynamic description of the reaction between the surface ligands and the sorbed complexes, taking into account the charge associated with each. Major advantages of SCMs include the ability to incorporate these reactions in codes modeling aqueous chemistry and the ability to model sorption reactions across geochemical gradients (Goldberg et al., 2007). In exchange, the effort associated with obtaining the necessary parameters to adequately describe SCMs increases substantially; the more mechanistic a SCM is, the larger is the number of required parameters and the more difficult it is to obtain these parameters for field application.

A promising approach to developing complex SCMs is to obtain multiple lines of evidence for the types of surface complexes that a compound forms under different geochemical conditions. Various types of spectroscopy combined with quantum mechanical calculations can be used to narrow down the surface complexation reactions and constrain the number of parameters needed to adequately describe adsorption, as well as to validate the model predictions. An increasing number of studies utilize elements of this approach to describe sorption mechanisms of various contaminants to different types of surfaces and to improve SCM formulation and fits using this information. A large number of studies has been performed to investigate surface complexation mechanisms and develop SCMs for oxyanion sorption on iron oxides, e.g. phosphate, carbonate and arsenate sorption on goethite (Hiemstra et al., 2004; Rahnemaie et al., 2007; Salazar-Camacho and Villalobos, 2010).

Figure 1. Illustration of the potential surface species of Cr(VI).

Hexavalent chromium (Cr(VI)) also occurs as an anionic chromate (CrO$_4^{2-}$) and sorbs strongly on iron oxyhydroxides at acidic pH (Rai et al., 1989). Even though it is an important contaminant, e.g. it is the second most abundant heavy metal discharged to water from industrial facilities in the EU after Zn (EPRTR, 2013), there is surprisingly less information on its complexation behaviour and relatively few SCMs that have focused primarily on goethite ($\alpha$-FeOOH) as a sorbent (Fendorf et al., 1997; Van Beinum et al., 2006; Villalobos and Perez-Gallegos, 2008). However, ferrihydrite (Fe$_3$O$_3$H$_2$O$_{am}$) may
play an important role for chromate sorption in soil environments, given its prevalence and high surface area. Only one SCM was identified in the literature for chromate sorption on ferrihydrite (Zachara et al., 1987), which assumed outer-sphere chromate and bichromate \((\text{HCrO}_4^-)\) complexes forming on the surface (Fig. 1). Recently, Johnston and Chrysochoou (2012) reported that chromate forms both inner-sphere monodentate and bidentate complexes on ferrihydrite (Fig. 1), using Attenuated Total Reflectance – Fourier Transform Infrared (ATR-FTIR) spectroscopy and Density Functional Theory (DFT) calculations. Thus, the assumptions for the surface speciation of chromate of the only existing SCM for ferrihydrite were proved to be incorrect. Still, the fit between the experimental data and the modelled adsorption curve was satisfactory.

This study presents a new SCM for chromate on ferrihydrite that utilizes these findings and insights on surface speciation and adopts a more recent modelling formulation, i.e. Charge Distribution – Multisite Complexation (CD-MUSIC) model (Hiemstra and van Riemsdijk, 1996; Hiemstra et al., 1996). The model also incorporates recent insights into ferrihydrite surface structure (Hiemstra, 2013).

2. METHODS AND MODEL DESCRIPTION

2.1 Experimental data and methods

Experimental data for chromate sorption on ferrihydrite (FH) were obtained from Zachara et al. [10] for the following conditions: 5 \(\mu\)M initial Cr(VI) concentration sorbed on \(0.87 \cdot 10^{-3} M\) and \(17.4 \cdot 10^{-3} M\) FH as total Fe in both a \(\text{N}_2\) atmosphere and in air with a \(\text{CO}_2\) partial pressure of \(10^{-2.16} \text{ atm}\); pH varied between 5 and 8 at an ionic strength of 0.1M NaNO\(_3\). Proton adsorption data for FH for three ionic strengths (0.1M, 0.01M and 0.001M) in NaNO\(_3\) were obtained from Girvin et al. (1991).

In addition, two pH edges for chromate sorbed on FH were obtained at an initial Cr(VI) concentration of 1 mM and an FH concentration of 2 g/L for ionic strengths of 0.1M and 0.01M \(\text{NaCl}\); all experiments were conducted in an \(\text{N}_2\)-purged glove bag. The pH was varied between 4 and 10 using concentrated \(\text{HCl}\) and \(\text{NaOH}\). The FH suspension was prepared according to the method of Schwertmann and Cornell (2003): A 0.2 M \(\text{FeCl}_3\cdot6\text{H}_2\text{O}\) solution was mixed with 1 M KOH and continuously stirred to raise the pH to 7-8 within a 10-20 min period. The dark brown precipitate was then dialyzed until the conductivity was less than \(~20\ \mu\text{S/cm}\) and stored as a concentrated suspension. All chemicals used for the study were ACS grade or higher.

2.2 Model Description

The SCM was based on the CD MUSIC framework, considering the following reactions:

\[
> \text{FeOH}^{\frac{1}{2}} + \text{H}^+ + \text{CrO}_4^{2-} \rightarrow \text{FeOCrO}_3^{\frac{3}{2}} + \text{H}_2\text{O} \quad (1)
\]

\[
2 > \text{FeOH}^{\frac{1}{2}} + 2\text{H}^+ + \text{CrO}_4^{2-} \rightarrow (\text{FeO})_2\text{CrO}_2^{-1} + 2\text{H}_2\text{O} \quad (2)
\]

where reaction (1) corresponds to an inner-sphere monodentate species and reaction (2) to an inner-sphere bidentate species. Table 1 presents an overview of the species considered in the model, along with the charge distribution (CD) factors assuming a Basic Stern plane with a capacitance of \(C_s=1.1\) as obtained by fitting the Girvin et al. (1991)
proton adsorption data. The FH surface area was assumed to be 600 m$^2$/g following both Girvin et al. (1991) and Davis and Leckie (1978).

### Table 1. Overview of surface complexation species and charge distribution (CD) factors and thermodynamic constants

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta z_0$</th>
<th>$\Delta z_d$</th>
<th>Log $K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{&gt;FeOH}_2^{1/2}$</td>
<td>1</td>
<td>0</td>
<td>8.0$^a$</td>
</tr>
<tr>
<td>$\text{&gt;FeOH}^{1/2} - \text{Na}^+$</td>
<td>0</td>
<td>1</td>
<td>-0.7$^b$</td>
</tr>
<tr>
<td>$\text{&gt;FeOH}^{1/2} - \text{NO}_3^-$</td>
<td>0</td>
<td>-1</td>
<td>Log $K_{\text{H}^+} + \log K_{\text{NO}_3^-}$ = 7.1$^b$</td>
</tr>
<tr>
<td>$\text{&gt;FeOCrO}_3^{-1.5}$</td>
<td>0.5</td>
<td>-1.5</td>
<td>11.4</td>
</tr>
<tr>
<td>$\text{(FeO)}_2\text{CrO}_2^-$</td>
<td>1</td>
<td>-1</td>
<td>18.9</td>
</tr>
<tr>
<td>$\text{(FeO)}_2\text{CO}$</td>
<td>1.25</td>
<td>-1.25</td>
<td>21.3</td>
</tr>
</tbody>
</table>

$^a$Adopted from Hiemstra [14]  
$^b$This study

The estimation of the site density was done following the analysis of the FH structure recently presented by Hiemstra (2013). Three types of reactive sites were considered for electrolyte binding via outer-sphere complex formation, with a 37.5% contribution from the (1-10) face of the FH crystal, 37.5% from the (1-11) face and 25% contribution from the (001) and (00-1) faces. Type "a" singly-coordinated $\text{>FeOH}^{1/2}$ with a site density of 2.18 $\mu$mol/s/m$^2$, type "b" singly-coordinated $\text{>FeOH}^{1/2}$ with a site density of 8.63 $\mu$mol/s/m$^2$ and triply coordinated $\text{>Fe}_2\text{O}_1^{1/2}$ with a site density of 1.37 $\mu$mol/s/m$^2$. Only type "b" singly-coordinated sites were considered to form inner-sphere complexes with chromate.

For consideration of the influence of carbonate species, it was considered that carbonate forms bidentate complexes on type "b" $\text{>FeOH}^{1/2}$ sites according to spectroscopic observations on hematite ($\alpha$-$\text{Fe}_2\text{O}_3$) and goethite ($\alpha$-$\text{FeOOH}$) (Bargar et al., 2005; Hiemstra et al., 2004). Carbonate adsorption data on FH were obtained from Zachara et al. (1987).

All adsorption data for each set of experimental conditions were fit simultaneously using Mathematica™ software.

### 3. RESULTS AND DISCUSSION

Figure 2 shows the fit between the modelled and experimental data for the three titration curves, showing an excellent agreement with the exception of the low ionic strength and pH data, which may also be attributed to experimental error. The fit resulted in the thermodynamic constants for Na$^+$ and NO$_3^-$ binding to the FH surface shown in Table 2, which are very close to the constants determined by Hiemstra and van Riemsdijk (2009) using other datasets and an Extended Stern layer model; they are also very close to the Triple Layer Model constants determined by the original authors (Girvin et al., 1991). The Cl$^-$ binding constant was assumed to equal that fit for NO$_3^-$ for the Cr(VI) adsorption data obtained in NaCl.
Figure 2. Model fit (red) of ferrihydrite titration data obtained from Girvin et al. (1991). From bottom to top: I=0.001M, 0.01M and 0.1M NaNO₃.

Figure 3. pH edges of CO₂ adsorption on ferrihydrite [10] and model fits. Figure 3 shows the model fit to the carbonate adsorption data from Zachara et al. [10]. The model provides improved results compared to the TLM model of the original study, which did not predict the decreased sorption below pH 5. The fit was slightly worse compared to the model of Hiemstra et al. (2009), which used similar assumptions, but a higher surface area of 650 m²/g. We chose to maintain 600 m²/g to be consistent in fitting the entire dataset provided by Zachara et al. (1987), who also utilized 600 m²/g. The uncertainty in the FH surface area is a limiting factor, rendering it essentially a fitting parameter instead of an experimentally determined one.
For both high and low FH concentrations our model under-predicts carbonate sorption at pH<6 (even considering the considerable scatter), which was also the case in the model produced by Hiemstra et al. (2009), whereas the TLM of Zachara et al. (1987) plateaued below pH 6. Since both Hiemstra et al. (2009) and this study used a single bidentate complex, while Zachara et al. (1987) used two outer-sphere species, it may be that the discrepancy at low pH is due to inaccurate assumptions about the surface speciation. Regardless, given the abundance of carbonate in many natural environments, additional experimental studies of carbonate adsorption by FH are warranted.

**Figure 4.** pH adsorption edges of chromate in N<sub>2</sub> (a) and CO<sub>2</sub> (b). Dashed lines represent model fits without CO<sub>2</sub> and solid lines model fits with CO<sub>2</sub>. Red and green datasets are from Zachara et al. (1987) and purple dataset from this study. The ionic strength was 0.1M in all datasets.

Figure 4 shows the fits obtained between the Cr(VI) adsorption data and the model. There is excellent agreement between the Zachara et al. [10] data under N<sub>2</sub> and the modelled pH edge and the fits appear to be improved compared to the TLM model presented in the original study. The fit between the model and data was less satisfactory for our dataset (1 mM, 2 g/L FH), with the model over-predicting adsorption at pH values greater than 7. However, when CO<sub>2</sub> adsorption was incorporated into the model at atmospheric partial pressure (P<sub>CO2</sub>=0.00038 atm), the fit was much improved (Fig. 4a), which may be an indication that purging of CO<sub>2</sub> from the surface may have been incomplete for our experiments.

With CO<sub>2</sub> present the fit between the experimental data and the model was less satisfactory (Fig. 4b), with adsorption greatly under-predicted for 0.077 g/L, and somewhat under-predicted at pH<8 for 1.5 g/L FH. Conversely, the TLM model presented by Zachara et al. [10] over-predicted chromate adsorption in the presence of carbonate especially for 1.5 g/L FH. Our model is clearly deficient for describing available FH Cr(VI) adsorption data in the presence of carbonate. However, given that the error is most apparent at low pH, where the errors in fitting the CO<sub>2</sub> adsorption data are largest (Fig. 3), it is likely that improving the CO<sub>2</sub> adsorption model will improve the overall model as well. For example, if less strongly bound outer-sphere or monodentate adsorbed CO<sub>2</sub> species are actually present, which would allow for additional inner-sphere adsorption of chromate, improving the model fit. Additional carbonate adsorption data and spectroscopic information would also be necessary to this end.
4. CONCLUSIONS

A new surface complexation model for chromate sorption on ferrihydrite was formulated using the CD MUSIC formalism. The model included unprotonated inner-sphere monodentate and bidentate species as identified in recent spectroscopic and computational investigations. The model yielded improved fits for sorption data acquired in nitrogen atmosphere compared to a TLM model with only outer-sphere complexes that was previously fitted to the same dataset. In addition, the model was able to predict chromate sorption under a wide range of pH values (5-10), chromate concentrations (5 μM and 1 mM) and ferrihydrite concentrations (0.077 g/L to 2 g/L).

Modeling carbonate sorption and chromate sorption in the presence of carbonate on ferrihydrite proved to be more challenging and yielded less satisfactory fits, however the model followed the general tendency of the experimental curves. Additional experimental and modeling efforts will be required to clarify that discrepancy.

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REFERENCES


