MODELING CHROMATE PARTITION IN SOIL MINERALS/WATER PHASES

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Introduction

The fate of Chromate in the environment is always highly concerned because of its low adsorption behavior and high toxicity to organisms. Previous studies showed that Cr(VI) in soils tend to be retained by minerals with high point of zero charges (PZC), such as goethite, ferrihydrite and aluminum oxides, while will be reduced and detoxified to Cr(III) by soil organic matters (SOM) or other inorganic reductants. Prediction the partition of Cr(VI) in soil solid/water phase will assist to better describe its mobility in the upper soil and the vadose zone. The purpose of this study was to develop a mechanistic based multi-surface model to predict the Cr(VI) partition in soils. The adsorption of Cr(VI) onto soil minerals was predicted via consideration of various reactive surfaces (including goethite, HFO and gibbsite) and competitive ions (such as phosphate). Each of them was described by a surface complexation model. 12 soils with various properties from China were used to screen out the best model.

Methods

12 soils were sampled from the middle to southern area of China and SOM were gently removed by $NaClO_3$(Kaiser and Guggenberger, 2003) to eliminate its reduction effect to Cr(VI). The soil types are mainly ferrosols and Alfisol with a relatively wide range of iron oxide content. The adsorption of Cr(VI) onto the soil minerals was investigated using batch experiments with a function of pH and Cr(VI) loading concentrations. The total amounts of iron and alumina oxides were estimated by the dithionite method(DCB-Fe, DCB-Al) and the amounts of amorphous iron (oxy)hydroxides were estimated by oxalate extraction (Ox-Fe). The effective PO_4^{3-} in soils was extracted by $NaHCO_3$ for 15 days at 25°C.

Three reactive surfaces in soils were considered to bind Cr(VI) in this study: crystalline iron hydroxides, crystalline alumina hydroxides, and amorphous iron oxides which were represented by goethite, gibbsite and HFO, respectively. The adsorption of Cr(VI) onto goethite was described by a charge distribution multi-site surface complexation model (CD-MUSIC) with model parameters showed in Table 1(Xie et al., 2015); while Cr(VI) adsorption onto HFO and gibbsite were modeled using the two-site Diffuse Double Layer model from Dzombak and Morel(1990) and Karamalidis and Dzombak(2010) respectively and model parameters were used without adjustment. Various modeling scenarios were considered to predict Cr (VI) partition in soils, e.g. including various reactive surfaces, with or without considering the competitive effect of PO_4^{3-}, different way to determine the effective surface areas for goethite in soils.

Table 1. The CD-MUSIC model parameters of Cr(VI) adsorption onto geothite surfaces

Surface reaction	Δz_0	Δz_1	Δz_2	log K
Adsorption reaction				
$2\equiv FeOH^{-1/2} + 3H^+ + CrO_4^{2-} = \equiv Fe_2O_2CrOOH + H_2O$	1	0	0	26.10
$\equiv FeOH^{-1/2} + H^+ + CrO_4^{2-} = \equiv FeOCrO_3^{-3/2} + H_2O$	0.54	-1.54	0	11.65

Results

The adsorption of Cr(VI) onto soils shows a positive relationship with soil iron oxide content and a negative relationship with pH. Modeling the Cr(VI) adsorption on soil minerals with only considering the DCB-Fe as goethite with default parameters can overall well predict the data ($R^2 = 0.825$), suggesting that crystalline iron oxides are the primary adsorption surfaces for Cr(VI). After consideration the P competition, the prediction increases to $R^2 = 0.841$ and most significant improvement was observed in soils with lower Fe/P ratio. The effective surface areas of goethites in soils are critical parameters for the modeling. Although a default value $63.5 m^2/g$ from Xie et al's (2015) study gave relatively good prediction ($R^2 = 0.825$), but underestimation of Cr(VI) adsorption at acidic condition for soils with high iron contents was observed, suggesting that the goethites in ferrisol had higher active surface areas for Cr(VI) adsorption. Using the surface areas derived from maximum adsorption capacity of each soil, the model estimation was improved to $R^2 = 0.876$ without considering P and $R^2 = 0.911$ with considering P. While including HFO in the models leaded to significant overestimation of Cr(VI) adsorption for all soil samples, indicating that the model parameters of HFO might overestimate the HFO contribution. Because the DCB-Al contents in the soils were relatively low, their contribution to Cr(VI) retention is neglectable.

Conclusion

Partition of chromate in soil minerals/water phases can be successfully predicted by a CD-MUSIC model for goethite with default parameters suggested by Xie et al. (2015). Including the competition effect of PO_4^{3-} and more careful consideration of goethite effective surface areas will improve the prediction.

References

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