

Surface Complexation Modeling of Herbicide Adsorption by Goethite: 4-chloro-2-methylphenoxyacetic acid (MCPA)

M. KERSTEN¹, D. TUNEGA² AND I. GEORGIEVA³

¹Gutenberg-University, Mainz 55099, Germany
kersten@uni-mainz.de

²University of Natural Resources and Life Sciences, Vienna
1190, Austria (daniel.tunega@boku.ac.at)

³Bulgarian Academy of Sciences (IGIC), Sofia, Bulgaria
(igeorgieva@svr.igic.bas.bg)

Interactions between goethite surfaces and MCPA were studied using density functional theory (DFT) calculations. Different surface OH groups and MCPA proton states were used to mimic effect of pH on the theoretically possible outer- and inner-sphere surface complexes, their binding energies and bond lengths. Modeling not only a solvated but also the protonated surface provided a major breakthrough showing that there were energetically optimized hydrogen bonded MCPA structures on the predominant (110) goethite surface. Both an outer-sphere complex with the MCPA anion and a monodentate inner-sphere complex with the neutral MCPA molecule were found as the most energetically stable. The DFT modeling results predicted the latter forming by sharing one of the oxygens between the MCPA carboxylate group and a singly coordinated surface hydroxyl group, releasing a H₂O molecule (Fig. 1). All the other complexes including the bidentate inner-sphere option had higher relative energies and were therefore less likely. The two most probable structures were used to constrain a surface complexation model using charge distribution CD-MUSIC parameters according to the Brown bond valence concept with the DFT-predicted surface complex structures. Their adsorption constants were fitted to experimental batch equilibrium data.

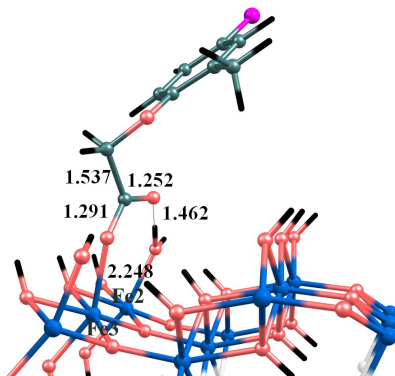


Figure 1: DFT optimized model of inner sphere complex