2.3.P05

Adsorption of acetate and benzoate to the goethite surface

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Migration and bioavailibility of metal ions and organic compounds in aquatic environments are influenced by the presence of carboxylic acids. The abundance of carboxylic acids and the diversity in their structural composition account for the occurrence of carboxylates in geochemical processes. Correlation between molecular structure of carboxylates and their reactivity in natural waters needs to be estimated, for better understanding of their influences on geochemical processes as well as increasing predictability of their behaviour. In this study we focus on adsorption of acetate and benzoate to the surface of goethite. To elucidate structural information and speciation of these two carboxylic acids at the goethite/water interface a series of experiments have been performed, where carboxylate concentration, ionic strength and pH have been varied. The results obtained from in situ ATR-FTIR spectroscopy and quantitative measurements show ionic strength, pH and IR spectral characteristics, which indicate outher sphere adsorption of both acetate and benzoate. Benzoate exhibits a higher affinity for the goethite surface as compared to acetate. This effect will be discussed in terms of the aromatic electronic structure of benzoate.

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Metal-glyphosate complexation in solution and at the goethite-solution interface

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Glyphosate (N-(phosphonomethyl) glycine, PMG) is a widely used herbicide due to its high activity, very low toxicity to animals and short residence time in soil. The herbicide is adsorbed mainly through the leaves and inhibits an enzyme in the shikimic acid pathway of aromatic amino acid biosynthesis. Since the shikimic acid pathway is only found in plants and microorganisms the glyphosate is essentially non-toxic to mammals and birds.

In a few days glyphosate is immobilized and degraded in the soil to the non-toxic products CO_2, PO_4^{3-} and NH_3 or adsorbed to colloidal fractions as organic matter and clay minerals. Glyphosate has a relatively low solubility in water and is insoluble in other solvents. It is strongly polar and has a zwitterion structure depending on pH. In this ligand four protons per molecule can dissociate from carboxylic, amino and phosphonate groups. However, only three protonation constants can be accurately determined, corresponding to the carboxylate, amino and one of the phosphonate hydroxyl groups.

Metal ions are believed to play a role in the adsorption process of glyphosate to colloidal fractions, which makes the coordination chemistry of glyphosate very interesting. Clay minerals and organic matter play an important role in controlling the mobility of heavy metals in soil and sediment. To understand the processes that occur in the environment it is important to examine the role of the solid-water interface and its interactions with the aqueous phase.

Glyphosate (PMG) has been studied with respect to its acid-base properties and complexation with cadmium(II) and copper(II), respectively. Adsorption experiments of PMG and PMG-Cu(II) complexes onto the surface of goethite (α-FeOOH) have been done and interpreted in terms of a surface complexation model. The model is based on data obtained from measurements with FT-IR, XPS, EXAFS [1] and potentiometric titrations.

Reference

[1] Sheals J. Molecular characterisation of glyphosate complexes in aqueous solution and at the solution-mineral interface. *PhD thesis*, 2002. Umeå University, Sweden.