Studying α-Al_2O_3-Eu-fulvic acid interactions by means of ESI-FTMS

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Introduction

Modelling of the behaviour of metal pollutants such as lanthanides (Ln) requires knowledge on Ln sorption species forming at soil mineral surfaces. Of interest is the sorption of humic substances (HSs), which is known to enhance surface reactivity and sorptive capacity of minerals towards Ln, at low soil pH. HSs are expected to fractionate during sorption, as they are complex mixtures of organic compounds with specific chemical nature, structure and reactivity. To address the effect of HS sorptive fractionation on Ln sorption, we investigated the (co)sorption of Eu^{III} and a reference fulvic acid (Pahokee Peak Fulvic Acid, PPFA) onto alumina colloids, with the aim of gaining molecular-scale insights on chemical identity of sorbed PPFA compounds by using ESI-FTMS analysis of solutions before and after sorption.

Results and conclusion

Batch (co)sorption experiments of PPFA (25mg.L^{-1}) and Eu^{III} (10μM) in 2.5g.L^{-1} α-Al_2O_3 colloid suspensions at pH 5 showed that sorption of PPFA induced (i) surface charge reversal of the colloids and (ii) almost quantitative sorption of Eu, suggesting strong Eu-PPFA-alumina surface interactions. ESI(-)-MS analysis of native PPFA solution confirmed the complex nature of PPFA. Thanks to high resolving power and mass accuracy of mass spectrometer, ca. 7000 compounds were detected. An elemental formula was assigned to 5040 compounds, which belonged to the families of tannins/lignins or polycyclic aromatic compounds (PACs). Examination of MS spectra of supernatants evidenced a strong sorptive fractionation of PPFA. 37% of the compounds detected in the native PPFA solution were quantitatively sorbed, the others being partitioned between solution and alumina surface to very varying degrees. A main result is that the quantatively sorbed molecules were mostly tanins/lignins with high O/C ratios (> 0.5) and some highly unsaturated PACs, while more aliphatic compounds showed very weak affinity for the surface. Thus, the PPFA compounds showing the highest affinity for the alumina surface were tanins/lignins exhibiting multiple oxygen functionalities. It is suggested that these highly reactive compounds are those involved in the sorption of Eu at the alumina surface at acidic pH.