Structural organization and formation of iron-organic matter nanoaggregates: A kinetic approach coupling Quick-EXAFS and MCR-ALS chemometry

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Among natural nanoaggregates, those composed of iron (Fe) and organic matter (OM) are of peculiar importance. They are produced from organic soils and organic soil horizons in contrasted areas such as wetlands, peatlands and permafrosts. They are considered as vector for transport of many contaminants such as metals and metalloids. Iron oxyhydroxides and natural OM are indeed known to be strong sorbents of metals and metalloids regarding their high density of binding sites. Under environmental condition, Fe-OM nanometric associations are formed by the oxidation/hydrolysis of Fe(II)-OM complexes. No information is currently available on the species that are formed at the early stage of the reaction and about their evolution with the running time reaction. However, the early-formed Fe species and the impact of OM on their evolution are critical regarding the structural diversity of the Fe-OM associations observed in the environment and produced in the laboratory. The present study therefore aims at singling out and following the nucleation-growth process of Fe-species in such Fe-OM nanometric associations in order to identify if their structural arrangement is acquired at the early stage of the reaction or is a consequence of the aging. It demonstrates that Fe(II) oxidation/hydrolysis leads to the synthesis of Fe-oligomers (Fe-oligo) and ferrihydrite-like nanoparticles (Fh-NP), bound to OM, which proportion varies according to the Fe/OM ratio and the OH^- availability. Fh-NP and Fe-oligo grow concomitantly during Fe(II) oxidation. After complete Fe(II) oxidation, Fh-NP polymerizes at the expense of Fe-oligo. The organization of these structures constraints their binding sites density and availability, which induces dramatic environmental implications regarding their capacity to trap metallic pollutants.