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Microscopic Mechanisms for Humic Acid Coprecipitated with Ferrihydrite

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Iron (Fe) (hydr)oxides show the promise to bind large amounts of organic matter (OM) and control the OM repository in soils. Their interaction with OM has been demonstrated as the key process to stabilize OM against the decomposition. On account of the ubiquity of Fe and OM in surface waters, sediment, and soils, poorly ordered Fe (hydr)oxides often form in the OM-rich environments, wherein Fe (hydr)oxides and OM are likely associated into complex assemblages in terms of adsorption and coprecipitation. In this study, we aimed to develop at a molecular scale the surface and structural characteristics for OM/Fe coprecipitates with C/(C+Fe) molar ratio ≤ 0.36 and to determine such attributes to what degree affect the OM stabilization.

The OM/Fe coprecipitates were synthesized using commercial humic acid (AHA) and humic acid extracted from a peat soil collected in Taiwan (YHA). In terms of local molecular coordination, the Fe K-edge EXAFS data suggested that the Fe domains precipitated with the YHA at C/(C+Fe) molar ratio of 0.18 consists of the least coordiantion numbers for the edge- and corer-shared FeO6 octahedral linkage than the coprecipitates with YHA at C/(C+Fe) molar ratios of 0.28 and 0.36. Given that the number of linked FeO_6 polyhydra could be translated to the domain size, such results implied the increasing degree of structural development of Fe domains with coprecipitated C/(C+Fe) molar ratio > 0.18. Changes in Fe domain were not found in coprecipitates with AHA, suggesting that the OM composition might affect the OM/Fe association. The FTIR and NMR data indicated a greater amount of active functional groups such as amine, amide, and carboxy in YHA thatn in AHA. In coprecipitates with YAH at C/(C+Fe) of 0.18, the polar fucntional groups significantly associated with Fe, hindering the structural development of Fe domain. As the C/(C+Fe) increased up to 0.28, the increaseing amount of YHA might induce the reorganization of humic acid stricutres, leading to the formation of hydrophobic microenvironments referred to as intramolecualr humic pseudomicelles that showed less impact on Fe domains. For the samples with AHA, the association between OM and Fe is more like OM adsorption on ferrihydrite rahter than the copreiptation.