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Experimental studies on organic-inorganic interactions between fulvic acid and goethite in the aquatic environment

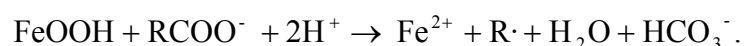
ABSTRACT

Humic substances (HS) have abundant hydrophilic functional groups such as –COOH and –OH that give their aqueous solubility, binding sites for metals, buffer capacities and other reactive characteristics. Because of their high abundance and reactivities, HS contribute primarily to the material cycling at the earth's surface. Therefore, long-term behaviors of HS in aquatic environments should be evaluated.

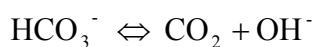
In this thesis, for studying reaction kinetics of organics by accelerating them at higher temperatures, new spectroscopic methods under hydrothermal conditions have been first developed. The reaction gas cell FT-IR system was constructed by combining a gas cell FT-IR with a reaction vessel to observe the formation of CO₂ by the interactions of a fulvic acid and an iron oxide. Two in-situ hydrothermal spectroscopic methods were developed here for monitoring hydrothermal organic reactions: UV-VIS spectroscopy for the determination of organic contents and aromatic natures; and ATR-IR spectroscopy for the characterization of functional groups.

By using these spectroscopic methods, hydrothermal transformations of humic substances (Nordic fulvic and humic acids) were studied. Two reactions, aromaticity decrease and decarboxylation, were dominant for the fulvic acid under hydrothermal conditions. Firstly, the long-term decrease of absorbance at 254 nm (Abs₂₅₄) of dissolved humic substances in the batch hydrothermal experiments (80% decrease of Abs₂₅₄ during several hundreds of hours at 80-180 °C) correspond mainly to the aromaticity decrease of humic structures with a relatively high activation energy of 85 kJ mol⁻¹. Secondly, the rapid initial Abs₂₅₄ decrease of about 10% during 1-10 hours at 80-180 °C, observed by the in-situ UV spectroscopy with a low activation energy of 29 kJ mol⁻¹, corresponds to the decarboxylation reaction leading to the CO₂ formation (22 kJ/mol) detected by the reaction gas cell FT-IR.

The interactions of these organics with an iron oxide (goethite) have been studied. These experiments suggest that the fulvic acid is supposed to be decomposed and finally oxidized to CO₂ on the goethite surface following the fast adsorption in aqueous environments. The first process is the very rapid adsorption of the fulvic acid on goethite within 10 minutes at 25-80 °C (activation energy: 26 kJ mol⁻¹) and the second one is its slower adsorption (activation energy: 30 kJ mol⁻¹). The second adsorption process has similar rates and activation energy to the enhanced CO₂ formation from the fulvic acid in the presence of goethite (activation energy: 32 kJ mol⁻¹). The reaction scheme can be estimated as follows with the obtained stoichiometric relations:



HCO₃⁻ formed in micro pore environments (pH 7) on the goethite surface might diffuse from the micropore to the bulk medium (pH 4), where it was changed to CO₂ by the following reaction:



The obtained half-lives at 25°C of transformation of the fulvic acid (enhanced CO₂ formation by goethite: 10 hours, decarboxylation leading to CO₂ formation: 1 month and major decomposition mainly by aromaticity decrease: 100 years) are much faster than the age estimates from the ¹⁴C dating (several hundred years to 50,000 years). The results of this thesis suggest that some parts of humic substances are easily decomposable, especially for their reactive functional groups such as carboxyls, with very short half-lives. Since these reactive groups are important binding sites for environmental pollutants such as heavy metals, their instability, especially in the presence of goethite, should be considered for re-evaluating fate and long-term behavior of environmental pollutants and CO₂ formation.