

The hydrothermal transformation of fulvic acids in the presence of goethite as studied by ultraviolet and infrared spectroscopies

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Fulvic acid, a representative dissolved organic matter, plays important roles in material cycling in aquatic environments. Some previous studies suggested relatively fast transformation of the dissolved organic matter based on their hydrothermal heating experiments. In addition, the natural organic matter usually co-exists with inorganic materials. Therefore, thermal transformation of fulvic acids in the presence of minerals should be evaluated.

In order to observe hydrothermal transformation of a fulvic acid in the presence of a representative mineral, goethite, a heatable liquid cell was set in an ultraviolet-visible (UV-Vis) spectrometer. Changes in absorption intensity (absorbance) at 254 nm, which is usually used as a measure of dissolved organic matter contents, of the fulvic acid solution with goethite powders were monitored in-situ in the UV-Vis spectrometer at 80 to 180 C. The 254 nm absorbance decreased exponentially with time during the heating. The first order reaction rate constants were determined for the fulvic acid with and without goethite. The decrease rate constants of the fulvic acid with goethite were about 4 orders of magnitudes larger than those without goethite, while activation energy values remain similar around 35 kJ/mol.

Another series of hydrothermal batch experiments were conducted with the same fulvic acid and goethite. The hydrothermal vessel was connected to a long path gas cell infrared (IR) spectrometer to sample volatile compounds formed during the heating experiments. The product solutions were also analyzed by ion-chromatography. CO₂ was found to be emitted during the fulvic acid transformation by this gas-cell IR spectroscopy. Several mono- and di-carboxylic acids were formed based on ion-chromatography.

These results suggest that the hydrothermal transformation of the fulvic acid is greatly accelerated by the presence of goethite and the carboxyls are the main reacted functional groups. The oxidation and decarboxylation mechanisms will be discussed.