Association Of Particles And Structures In The Presence Of Organic Matter


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Abstract. The influence of organic matter, the humic substances, on the precipitation behavior of the iron in groundwater aquifers were studied. Size and structure of these associations are determined with the fractal geometry. The humic substances are characterized spectroscopically. For differentiation of organic and inorganic substances the contrast at the carbon K-absorption edge used. Spectra taken at different spots of the samples to investigate, if there are differences in the spectra with and without iron.

INTRODUCTION

The size of most of the particles which can be found in aquifers are in the colloidal range that means between 1nm and 1µm. With soft X-ray microscopy at a resolution down to 30 nm we are able to investigate those particles in their natural aquatic state and under atmospheric pressure. In the energy range of the water window we can use the natural contrast between the surrounding water and these particles for imaging.

A big part of organic matter in aquifers are the so-called humic substances. Most of the organic Carbon on earth is bonded in those substances. They are anionic polyelectrolytes and can act as complexing agent for metals. In this way they serve as carriers of substances in natural water and play an important role in the environment [1]. In this paper we focus on the interaction of iron with humic substances first on precipitation processes in groundwater and then on the usage of iron as flocculation agent for humics.

ANAROBIC GROUNDWATER WITH ORGANIC MATTER

In colloidal systems chemical and physical reactions are enhanced due to the large surface of the colloidal particle. When studying properties of natural colloidal systems, one major issue is the question, whether the shape of the associations formed can be described morphometrically. Fractal geometry can be used for describing the size and
shape of the associations.[2][3] The higher the fractal dimension, the smaller is the relation of surface to mass of the association.

In groundwater, iron is an abundant cation. In anaerobic groundwater aquifers it is present in a reduced form as a bivalent cation. When this ground water get in contact with oxygen the bivalent iron cation is oxidized to a trivalent state; insoluble iron compounds are formed in consequence. The images in figure 1, taken with the Göttingen transmission X-ray microscope at BESSY, show aggregates of such particles in originally anaerobic groundwater after oxidization. First, small single aggregates of iron containing particles occur. For studying the formation of these structures in the presence of organic matter different amounts of a humic acid were added to the dispersion. Larger aggregates and also networks appear due to the amount of the organic matter. The iron particles may act as nuclei for additional aggregation processes. The determination of the fractal dimension with box-counting shows that the with increasing organic content the fractal dimension increase significant from $D_f = 1.60$ without organic matter to $D_f = 1.75$ for 10 % organic matter that means that the associations not just grow bigger but also become denser. That means that available surface become smaller, which in an important parameter for the transportation of substances.

**FIGURE 1.** When anaerobic ground-water gets in contact with oxygen small single aggregates of iron containing particles occur. Adding different amounts of a humic substance (1 to 10 % HS) to the dispersion the formation of larger aggregates consisting of these particles begins influenced by the organic matter. The associations grow bigger and denser with increasing organic content. With a high content (10% HS) of humic substances also networks appear.
Spectroscopical Characterization Of Humic Substances

A humic substance extracted from a soil near Göttingen, has been analyzed spectroscopically in a dry state as well as in an aqueous dispersion in comparison to a dry sample of a synthetic fulvic acid. The NEXFAS spectra, taken at the NSLS with the Stony Brook STXM at the carbon-K-absorption edge, are shown in figure 2 [4][5]. Differences between the samples can be clearly seen. Both, the colloidal humic substance and the fulvic acid are substances of heterogeneous chemical composition. Therefore, uncertainties may arise in this assignment of the resonances (tab. 1). But some resonances can be certainly assigned. The resonance at 288 eV is the $\pi^*$ resonance of the CO-double bond of the carboxyl group [6]. The fact that the fulvic acid has more acidic groups than the humic acids, can be seen in the NEXAFS spectra, the resonance of the CO-double bond of the carboxyl group is more prominent in the spectra of the fulvic acid than in the spectra of the humic acid. So, there is a possibility to distinguish between these two substances spectroscopically. The broad peak above 290 eV can be assigned to resonances of the aromatic groups of the molecules. These resonances are higher for the humic acid, which have a more aromatic character than the fulvic acid.

FIGURE 2. NEXAFS-spectra of a synthetic fulvic acid, dry, and a colloidal humic substance extracted from a soil, a calcareous aquic vermundoll, dry and in aqueous dispersion.
<table>
<thead>
<tr>
<th>Energy/ eV</th>
<th>Resonances and absorption edges</th>
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<tbody>
<tr>
<td>285.9</td>
<td>$\pi^*$ C=H</td>
</tr>
<tr>
<td>287.0</td>
<td>3s CH$_3$, CH$_2$</td>
</tr>
<tr>
<td>287.9</td>
<td>3s CH$_2$, CH$_2$</td>
</tr>
<tr>
<td>288.4</td>
<td>$\pi^<em>$ C=O $\pi^</em>$ C=H$_6$</td>
</tr>
<tr>
<td>292.0</td>
<td>$\sigma^*$ C-C</td>
</tr>
<tr>
<td>293.9</td>
<td>$\sigma^*$ C=H$_6$</td>
</tr>
<tr>
<td>298.1</td>
<td>K $L_{III}$ (294.6 eV)</td>
</tr>
<tr>
<td>300.8</td>
<td>K $L_{II}$ (297.3 eV)</td>
</tr>
</tbody>
</table>

Also differences between the spectra of the aqueous and dry sample of the humic acid can be observed. The absorption peaks 298.1 and 300.8 eV can be assigned to the LIII – and LII- edges of potassium. The ionic bonding of the potassium to the humic substance leads to a shift in the positions of these peaks compared to edge energies tabulated in the Henke-data[7]. These peaks do not occur in the spectra of the hydrated humic acid which may be caused by dilution. The potassium-cations were solved in the aqueous suspension and diluted, so they can not be detected anymore.

**FLOCCULATION OF HUMIC SUBSTANCES WITH IRON**

After the spectroscopic characterization of the humic substances the flocculation of those substances with iron cations were studied. Iron chloride FeCl$_3$ were added as flocculation agent in a dispersion of humic acid. This agent are used for removing organic matter in sewage. Through the addition of metal cations the charge of humic substance is reduced and the solubility decrease. The formation of flocs begin. Figure 3 shows those flocs dried on a silicon nitride window.

![Figure 3. STXM images of a dry sample of a humic acid which is flocculate with iron taken near K absorption edge of carbon. The carbon map (right) is calculated by dividing the left image, taken at an energy with strong absorption for carbon, by the center image, taken at weak absorption. The highlighted areas indicates areas with a high carbon amount](image-url)
Taking images above and below the carbon K-absorption edge with the Stony Brook STXM at the NSLS allows to show the distribution of carbon in the sample (right image figure 3). The dark dots in the center image, taken at an energy for weak absorption for carbon are iron particles, which have still a strong absorption at this energy.

For the spectroscopic characterization of the flocculation process NEXAFS-spectra of these humic acid with and without iron were taken (figure 4). There is a significant change between both spectra in the relations of the peak height of this resonance for the CO double bond and the aromatic peak. The height of the resonance peak of the CO double bond decrease compared to the broad aromatic peak above 292 eV. It is known that the carboxyl ions plays a prominent role in the complexation of cations by humic acids, but there are also some evidence in IR spectra that the oxygen of the CO double bond of carboxyl-group can be involved in the metal-ion binding [8]. This could be the reason for the decrease of the resonance of the CO double bond at 289 eV in the spectra.

FIGURE 4. NEXAFS-spectra of a humic acid without (left) and with iron (right). taken at the C-absorption edge

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