Interaction experiments between silica and humic acid solution

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Various interactions between inorganic and organic substances are known to occur in the surface environment of the earth. They play an important role in the geochemical cycle of materials including environmental issues such as water pollution. In order to clarify the behaviour of the substances, we have to simplify the interactions occurred in the natural systems and investigate mechanism and rate of their interactions. In this study, we conducted experiments on silica and humic acid as representative inorganic and organic phases present in the natural aquatic environment. We focused on 1) the behaviour of a humic acid in the presence of silica and 2) dissolution rate of silica in the presence of the humic acid. The products were analyzed mainly by visible and infrared spectroscopy and liquid chromatography.

Materials

Silica gel (Cica) for flush chromatography was used for the inorganic material. The mean size is between 40 and 100 μ m and the specific surface area is 650 m²/g. Humic acid (EGA) as organic material was purified by dissolving in alkaline (NaOH) solution and precipitating in HCl solution (pH 2) three times. The purified humic acid was dissolved in 0.1 N NaOH solution with ultrasonic shaking to dissolve completely and the solution was diluted to 100, 10 and 1 mg/L of humic acid.

Experimental procedures

20 mL of the humic acid solutions (100, 10 and 0 mg/L) was adjusted to 0.1 and 0.001 M of the ionic strength by using NaCl. Then 1 g of the silica gel

powder was introduced into the solutions and stirred well. After the sedimentation of the silica gel, the pH of the solution was adjusted to 4. The experiments were performed at room temperature for 1, 4 and 10 days. After the experiments, solution and solid phases were separated by filtration $(0.1 \ \mu\text{m})$ and analysed by visible, infrared spectroscopy and liquid chromatography.

Results and discussion

Concentrations of the humic acid in solution containing the silica gel decreased more for higher ionic strength. And the concentrations did not change significantly after 1 day. The results can be interpreted by the adsorption of the humic acid on the silica surface for the higher ionic strength. This adsorption process seems to reach an equilibrium state after about 1 day. The size exclusion chromatography revealed that smaller humic acid fractions remained in the solution with higher ionic strength. The larger molecular size portions of the humic acid are therefore considered to be adsorbed onto the silica.

On the other hand, the concentration of Si determined by the molybdate blue and ICP methods increased with time both in the presence and absence of the humic acid. Thus the solubility and the dissolution rate of Si did not change significantly in the presence of humic acid. However, in another series of experiments using a different silica gel having smaller surface area ($45 \text{ m}^2/\text{g}$), the dissolution rate of Si decreased in the presence of humic acid. Therefore, the surface structure of the silica gel can be an important parameter for the dissolution of Si in the presence of humic acid.