Interaction of colloidal soil particles, humic substances and cationic detergents studied by X-ray microscopy

Abstract The interaction of soil colloids with humic substances and cationic detergents has been studied by X-ray microscopy. The major advantages of X-ray microscopy for these studies are the much higher resolution than achievable with light microscopy and the ability to image colloidal structures directly in aqueous media. Of particular interest was, how the coagulation force of cationic detergents will change the structure formed by the soil colloids when humic substances are present. The humic substances form a network-like structure around the soil colloids, thus increasing tremendously the surface available for chemical and physical reactions. Therefore, much more cationic detergent was necessary to introduce a coagulation of the structures formed by the soil colloids. In addition, humic substances and cationic detergents coagulate forming sphere shaped structures, where size, density and state of aggregation is a function of the concentration of the detergents. X-ray microscopic images give evidence for these results.

Key words X-ray microscopy – colloidal soil particles – humic substances – detergents

Introduction

X-ray microscopy is able to image particles and structures with colloidal dimensions directly in their aqueous environment with approximately a tenfold better resolution than with light microscopy. This can be done without preparational steps as drying or staining [1]. The capabilities of X-ray microscopy have been demonstrated with a great variety of colloidal dispersions [2–4]. Therefore, it is a unique technique for the investigation of the structure formed by soil colloids in aqueous media and the investigation of the interaction of these colloids with humic substances and detergents. As humic substances are colloidial particles themselves, the interaction of these colloids with surfactants can also be observed.

Methods

X-rays within the wavelength range between the K-absorption edges of oxygen at $\lambda = 2.34$ nm and carbon at $\lambda = 4.38$ nm are very well suited for X-ray microscopy studies of aqueous colloidal systems [5]. The photoelectric absorption and phase shift are the two dominating processes of interaction of X-rays with matter. The radiation is weakly absorbed by water but strongly absorbed by iron oxides, silicates, organic matter, etc. resulting in a good amplitude contrast of objects in aqueous environments. These differences are even larger when looking at the phase shift of X-rays penetrating water or other materials [6]. The graph in Fig. 1 shows the linear absorption coefficient of water, the phyllosilicate smectite, and the...
Fig. 1 Linear absorption coefficient of water, smectite and phenol as function of wavelength in the soft X-ray wavelength region

organic molecule phenol. The difference in absorption between the particles consisting of mineral or organic material and the water gives rise to amplitude contrast in the X-ray microscopic images shown in this paper. Thus, it is possible with an X-ray microscope to image these objects directly in aqueous media. Details of the X-ray microscope used for the experiments described here are found elsewhere [7].

The soil samples used in the work presented here are colloidal particles from the A_n-horizon of a calcareous aquic vermodoll (CAV) in Rosdorf near Göttingen (FAO: Calcaric Phaeozem) [8]. In all the experiments a 1% dispersion (weight by weight) in deionized water has been used.

Humic substances are anionic polyelectrolytes. They were extracted from this A_n-horizon following the procedure given by Stevenson [9]. Prior to the extraction of the humic substances, proteins and carbohydrates were removed by hydrolysis of the soil sample (50 g) with 500 ml 2 M hydrochloric acid for 6 h. After five times washing with distilled water and centrifugation, this sample was extracted with 500 ml 0.01 M sodiumpyrophosphate solution, adjusted to pH 7, in an overhead shaker for 24 h. After centrifugation and removal of the soil sample, 6 M hydrochloric acid was added to the supernatant until the formation of precipitate occurred. The humic substances were obtained by another centrifugation step followed by six washing and centrifugation cycles. Thereafter the humic substances were freeze-dried and stored in an ex-cicator. The humic substances have been used in a 1% dispersion in bidistilled water.

The detergents used for the described experiments are Dodecyltrimethylammoniumbromide (DTB) and Hexadecyltrimethylammoniumbromide (CTB). Both detergents have been used in a 1% solution in bidistilled water.