



Surface-enhanced Raman spectroscopy (SERS) to detect natural organic coatings on silver nanoparticles

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Applications for engineered inorganic nanoparticles (EINP) are rising and causing a higher risk for EINP to be released into the environment. Their stability and transport behaviour under environmental conditions is strongly depending on their surface properties which on the other hand depend on the presence or absence of a surface coating. We assume that EINP get coated soon after their release into the environment e.g. by humic substances like humic or fulvic acids and NOM. Often EINP are stabilized by a coating agent like citrate or polyvinylpyrrolidone. Therefore, the replacement of the initial coating material or a multilayer coating has to be considered. Characterization of natural coatings on EINP is crucial to predict their environmental behaviour, but analytical methods to investigate organic coatings are scarce. To investigate humic- and fulvic acid coatings on silver nanoparticles (Ag NP) Raman micro-spectroscopy (RM) was used. RM is limited in its sensitivity, but silver nanoparticles cause an enhancement of the Raman signal of adsorbed substances by a factor of 10^3 - 10^6 , so called surface-enhanced Raman spectroscopy (SERS).

The Raman spectrum of humic acids is dominated by the carbonaceous parts of the humic acids which are known from carbon analysis and referred to as defect (D) and graphite (G) peak of carbon. Humic acids of different origin (humic acid from a lignite, suwannee river humic acid) showed differences in the D and G ratios indicating a difference in the structure of the contained carbon. With SERS humic and fulvic acid coatings on Ag NP were analysed: 1-100 mg/L humic acid stock solution were mixed with citrate and hydroxylammoniumchloride stabilized Ag NP, centrifuged and resuspended in deionized water (washing) to remove all coating material not associated with Ag NP. This washing step was repeated up to four times. SERS proved that the coating was still present after the fourth washing step. As SERS is only sensitive for substances in the immediate vicinity of the surface (i. e., with a distance of less than 10nm) of the Ag NP, together with AF⁴ measurements which showed an increase of the diameter of a few nm between uncoated and humic acid coated Ag NP, this indicates a thin but rather stable coating.