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Disaggregation of silver nanoparticle homoaggregates in a river water matrix

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HIGHLIGHTS

- Citrate coated silver nanoparticles aggregate rapidly in Rhine River water matrix.
- Aggregate morphology is determined by the Ca^{2+} concentration and NOM.
- Silver nanoparticle aggregates can be fragmented only partially.
- Mechanical forces plus NOM or low ionic strength are required for aggregate breakup.
- Silver nanoparticle aggregate morphology changes with concentration of ions and NOM.

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ABSTRACT

Silver nanoparticles (Ag NPs) could be found in aquatic systems in the near future. Although the interplay between aggregate formation and disaggregation is an important factor for mobility, bioavailability and toxicity of Ag NPs in surface waters, the factors controlling disaggregation of Ag NP homoaggregates are still unknown. In this study, we investigated the reversibility of homoaggregation of citrate coated Ag NPs in a Rhine River water matrix. We characterized the disaggregation of Ag NP homoaggregates by ionic strength reduction and addition of Suwannee River humic acid (SRHA) in the presence of strong and weak shear forces. In order to understand the disaggregation processes, we also studied the nature of homoaggregates and their formation dynamics under the influence of SRHA, Ca^{2+} concentration and nanoparticle concentration.

Even in the presence of SRHA and at low particle concentrations ($10\ \mu g\ L^{-1}$), aggregates formed rapidly in filtered Rhine water. The critical coagulation concentration (CCC) of Ca^{2+} in reconstituted Rhine water was $1.5\ mmol\ L^{-1}$ and was shifted towards higher values in the presence of SRHA. Analysis of the attachment efficiency as a function of Ca^{2+} concentration showed that SRHA induces electrosteric stabilization at low Ca^{2+} concentrations and cation-bridging flocculation at high Ca^{2+} concentrations. Shear forces in the form of mechanical shaking or ultrasound were necessary for breaking the aggregates. Without ultrasound, SRHA also induced disaggregation, but it required several days to reach a stable size of dense aggregates still larger than the primary particles.

Citrate stabilized Ag NPs may be in the form of reaction limited aggregates in aquatic systems similar to the Rhine River. The size and the structure of these aggregates will be dynamic and be determined by the solution conditions. Seasonal variations in the chemical composition of natural waters can result in a sedimentation-release cycle of engineered nanoparticles.

1. Introduction

Silver nanoparticles (Ag NPs) are widely used as antibacterial agents in different commercial products like clothes, socks, cosmetic products, food storage containers, household appliances, and children's toys (The project on emerging nanotechnologies, 2014). Ag NPs released into the environment from, for instance, socks or children's products by washing have been observed (Benn and Westerhoff, 2008; Geranio et al., 2009; Quadros et al., 2013). A large part of the Ag NPs released into the waste water may be sulfidized and accumulated as Ag_2S in the sludge of the waste water treatment plant (WWTP) (Kaegi et al., 2011; Kim et al., 2010). Ag NPs will most likely enter surface waters via application of sewage sludge in agriculture or after direct discharge of WWTP effluents. The presence of dissolved oxygen can induce oxidation and dissolution of Ag NPs (Liu and Hurt, 2010; Lowry et al., 2012). However, dissolution of Ag NPs is decreased with increasing pH value (Liu and Hurt, 2010) and increasing concentration of natural organic matter (NOM) (Liu and Hurt, 2010). Hence, in surface waters containing

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NOM and having neutral or slightly alkaline pH values the dissolution of Ag NPs will be reduced. Furthermore, the aggregation of citrate coated Ag NPs in surface water leads to their decreasing dissolution (Li and Lenhart, 2012). Release of Ag NPs into the surface waters can result in increasing risk potential and threat for microorganisms (El Badawy et al., 2011; Fabrega et al., 2009), aquatic invertebrates (*Daphnia magna*) (Das et al., 2013; Pokhrel et al., 2013), fish (Lee et al., 2012), or algae (Navarro et al., 2008).

Fate, bioavailability and toxicity of Ag NPs are often controlled by aggregation (Lowry et al., 2012; Schaumann et al., 2014). As shown by Li and Lenhart (2012), uncoated and citrate coated Ag NPs undergo rapid aggregation in river water. Aggregation of Ag NPs is controlled rather by multivalent than by monovalent cations (Baalousha et al., 2013; El Badawy et al., 2010, 2012; Huynh and Chen, 2011; Li et al., 2012). Furthermore, Ca^{2+} ions are more efficient in inducing aggregation of citrate coated Ag NPs than Mg^{2+} ions (Baalousha et al., 2013; Huynh and Chen, 2011) due to higher stability constants of calcium citrate complexes compared with magnesium citrate complexes (Field et al., 1975). At high concentration (100 mmol L^{-1}), chloride can also influence the aggregation of Ag NPs and lead to their bridging by AgCl as observed by Li et al. (2012). Furthermore, uncharged organic compounds can also induce the aggregation of Ag NPs (Moskovits and Vlckova, 2005). NOM generally stabilizes Ag NPs through electrosteric forces at low ionic strengths (Furman et al., 2013; Klitzke et al., 2014), but leads to enhanced aggregation due to cation-bridging flocculation at high Ca^{2+} concentrations (Baalousha et al., 2013; Huynh and Chen, 2011; Philippe and Schaumann, 2014b).

Disaggregation after adsorption of humic acid (HA) onto surface of aggregates of nanoparticles (NPs) was observed for iron oxide NPs (Baalousha, 2009), citrate coated Ag NPs (Fabrega et al., 2009), TiO_2 NPs (Loosli et al., 2013) and ZnO NPs (Omar et al., 2014). Shear forces can play a relevant role for the aggregation reversibility. Sonication induced disaggregation of TiO_2, ZnO, and CeO_2 aggregates in the absence of NOM (Zhou et al., 2012) and TiO_2 aggregates in the presence of HA (Horst et al., 2012). Furthermore, nanoparticle aggregates can be disaggregated by impact of light (Bennett et al., 2012; Zhou et al., 2012) and heat (Zhou et al., 2012). Ionic strength is another important key factor controlling the aggregation reversibility and is relevant for river systems changing their ionic level over the year; for instance, by flooding events. The Ca^{2+} and DOC concentration are subjected to seasonal variations as demonstrated for several rivers (Etchanchu and Probst, 1988; Leite et al., 2011). Depending on the wet/dry periods the concentration of Ca^{2+} and DOC in the river water can be changed by a factor of 22 (Leite et al., 2011) and 6 (Etchanchu and Probst, 1988; Leite et al., 2011) within one year respectively. Disaggregation was investigated only in synthetic aqueous phases (Baalousha, 2009; Bennett et al., 2012; Fabrega et al., 2009; Horst et al., 2012; Loosli et al., 2013; Omar et al., 2014; Zhou et al., 2012) and investigation of aggregation reversibility of engineered nanoparticles in surface waters still lacks.

In this work, we investigated the reversibility of homoaggregation of citrate coated Ag NPs in a river water matrix. In particular, we characterized the effect of NOM, ionic strength reduction and shear forces on the disaggregation of homoaggregates of Ag NPs. In order to understand the character of the homoaggregates, we also studied the aggregation kinetics under the influence of NOM, Ca^{2+} concentration and nanoparticle concentration in the filtered river water matrix. In order to avoid heteroaggregation, the generation of homoaggregates of Ag NPs was performed in a river matrix free of natural colloids.

2. Material and methods

Deionized water (resistivity: 18.2 MΩ·cm, Direct-Q UV, Millipore, Molsheim, France) was used for sample preparation in all experiments.

2.1. Synthesis of Ag NPs

For synthesis of Ag NPs, the citrate reduction method adapted and modified from Turkevich et al. (1951) was used. Trisodium citrate (5 mmol, Sigma-Aldrich, St. Louis, USA) was dissolved in 950 mL deionized water. In this solution a pH value of 11 was adjusted using 1 mol L^{-1} NaOH solution (1 N standard solution, Carl Roth, Karlsruhe, Germany). $AgNO_3$ (1 mmol, ≥99.9%, p.a., Carl Roth, Karlsruhe, Germany) was dissolved in 50 mL deionized water. The citrate solution was boiled under magnetic stirring (hotplate magnetic stirrer, RCT basic, IKA Labortechnik, Staufen, Germany). After boiling was started, the solution of $AgNO_3$ was added to the citrate solution dropwise within 5 min and further boiled and stirred for 20 min. After boiling was stopped, the dispersion was cooled to room temperature. The water losses induced through evaporation were compensated by filling up of the dispersion to 1 L with deionized water. The final pH value of the dispersion of Ag NPs was 9.44. The synthesized dispersion of Ag NPs was stored in dark at 4 °C.

2.2. Preparation of SRHA stock solution

As a model NOM, Suwannee River humic acid (SRHA) standard II was used. SRHA was purchased from the International Humic Substances Society (IHSS, St. Paul, USA). 10 mg SRHA was dissolved in 50 mL demineralized water. In the solution a pH value of 10 was adjusted using 1 mol L^{-1} NaOH. The concentration of SRHA stock solution was 200 mg L^{-1}. After pH adjustment, the solution was filtered using 0.1 μm cellulose nitrate membrane filter (Whatman, Dassel, Germany) to remove undissolved fraction and stirred with a magnetic stirrer for 24 h. The prepared SRHA stock solution was stored in dark at 4 °C.

2.3. River water

The river water was sampled from old arm of River Rhine near to Leimersheim, south-west Germany. The sample was collected at 2 m distance from the river bank on December 06, 2013. The sampling area is continuously supplied with fresh water from River Rhine. The pH value and temperature were measured directly after sampling (SG2-FK SevenGo, Mettler Toledo, Schwerzenbach, Switzerland). After sampling, the collected Rhine water was transported immediately to the laboratory and was stored in dark at 4 °C. In Rhine water the electrical conductivity was measured using a conductivity meter (multi-parameter analyser C863, Consort, Turnhout, Belgium). Rhine water was filtered using 0.45 μm (Supor 450, Life Sciences, polyethersulfone, PALL, Dreieich, Germany), 0.1 μm (cellulose nitrate, Whatman, Dassel, Germany) and 50 kDa (polyethersulfone, Sartorius, Göttingen, Germany) membranes. Total organic carbon (TOC) concentration was determined by a TOC analyzer (multi N/C 2100, Analytik Jena AG, Jena, Germany) and the element concentration was measured after stabilization in 1% HNO_3 (sub-boiled) using inductively coupled plasma optical emission spectroscopy (ICP-OES, 720, Agilent Technologies, Santa Clara, USA) in unfiltered Rhine water (RW) as well as in Rhine water filtered with 0.45 μm ($RW_{0.45μm}$) and 50 kDa (RW_{50kDa}) membranes.

2.4. Dynamic light scattering and zeta potential measurements

Hydrodynamic diameter and zeta potential were measured using a particle analyzer (laser wavelength: 658 nm, Delsa Nano C, Beckman Coulter, Fullerton, USA). Dynamic light scattering (DLS) at a scattering angle of 165° was applied for particle size measurement. For the calculation of particle size distribution from the autocorrelation function the CONTIN algorithm was chosen. Zeta potential was determined via electrophoretic light scattering technique and was calculated from electrophoretic mobility using the Smoluchowski equation (Schultz et al., 2008).

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