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Characterization of silver nanoparticle aggregates using single particle-inductively coupled plasma-mass spectrometry (spICP-MS)

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HIGHLIGHTS

- spICP-MS was recommended for characterization of silver nanoparticle aggregates.
- The gradually increase of mass in an aggregate was observed in spICP-MS analysis.
- The number of single particles in an aggregate was calculated based on the mass.
- The aggregates structures are characterized by mass fractal dimension.

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ABSTRACT

The single particle-inductively coupled plasma-mass spectrometry was applied to characterize the aggregates of AgNPs. was applied to characterize the aggregates of AgNPs. Two sizes of citrate-AgNPs and PVP-AgNPs were used at relatively high and predicted environmental concentrations under various ionic strengths. Citrate-AgNP aggregated with increases in the ionic strength, whereas PVP-AgNPs were sterically stable. The critical coagulation concentrations were 85 mM and 100 mM $NaNO_3$ for 60 nm and 100 nm citrate-AgNPs at 2 mg L^{-1} as total Ag obtained by dynamic light scattering (DLS). At 2 mg L^{-1} as total Ag, the mass of an aggregate gradually increased with increasing ionic strength for both citrate-AgNP during spICP-MS analyses. The average number of single particles derived from the mass in an aggregate was calculated to be 8.68 and 5.95 for 60 nm and 100 nm citrate-AgNPs at 85 mM and 100 mM $NaNO_3$, respectively after 2 h. The mass fractal dimensions were determined to be 2.97 and 2.83, further implying that the aggregate structures were very rigid and compact. Only marginal increases in the average mass and number of single particles in the aggregate units were found during 24 h under environmentally relevant AgNP concentrations. The average number of single particles constituting an aggregate unit for 60 nm and 100 nm citrate-AgNPs was 1.24 and 1.37 after 24 h at a high ionic strength. These results indicate that under environmentally relevant conditions, the collision frequency is predominant in the aggregation and that NPs are likely to encounter natural colloids such as clay and organic matter to form hetero-aggregates.

1. Introduction

Engineered nanoparticles (ENPs) are used in a wide range of industries and consumer products. With this rapid rise in use of goods containing ENPs, there has also been a significant concern raised about their environmental safety, especially with regards to their potential toxicity to humans and ecosystems. ENPs are able to persist in or penetrate into the environment or organisms, thereby causing a hazard. In addition, products containing ENPs release them into the environment throughout the product lifecycle (Nowack et al., 2011, 2012; Sun et al., 2014). Notably, silver nanoparticles (AgNPs) are the fastest growing category of ENPs in products due to their antibacterial effects, though concerns about

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their stability and hazards have been increasing exponentially (Shoults-Wilson et al., 2011; Maurer-Jones et al., 2013), with some studies demonstrating that AgNPs are released from sock fabrics and clothing during washing (Benn and Westerhoff, 2008; Geranio et al., 2009; Kulthong et al., 2010). It should also be noted that problems related to the released AgNPs are concurrently dependent on the given environmental conditions (e.g., pH, ionic strength, and presence of organic or inorganic matter due their surface structure, shape, solubility, etc.) (French et al., 2009; Chinnapongse et al., 2011). Therefore, it is necessary to not only understand the properties of AgNPs in their initial state but also to determine AgNP property changes when exposed to relevant environmental conditions in order to predict the fate and toxicity of AgNPs (Darlington et al., 2009).

The fate of AgNPs, including aggregation, sedimentation, and dissolution, has been investigated in aqueous environments, with aggregation being a particularly important consideration affecting their stability (Elzey and Grassian, 2010; Stebounova et al., 2011). The aggregation state of AgNPs has typically been monitored using dynamic light scattering (DLS), which measures fluctuations in the scattered light intensity due to particle diffusion caused by Brownian motion. The Z-average size used in DLS can be expressed as the intensity based harmonic mean, and is calculated from the intensity weighted distribution. According to the Rayleigh theory, the intensity of light in DLS is proportional to the particle diameter. The intensity distribution can then be converted to a number and volume distribution using the Mie theory (Steinke and Shepherd, 1988). In brief, a small portion of large particles has greater influence on the Z-average size than a large portion of small particles; the spectra of the number and volume distributions significantly differ from those of the intensity distribution, which increases the polydispersity index (PDI) value (Filella et al., 1997; Hassellöv et al., 2008). As such, DLS does not provide information pertaining to the accurate size distribution in case samples that have broad size distributions. Also, DLS has low sensitivity, with typical detection limits being in the mg L^{-1} range, with few below the μg L^{-1} level (Sapsford et al., 2011). For these reasons, previous studies have conducted stability experiments for AgNPs in the mg L^{-1} range (Stebounova et al., 2011; Römer et al., 2011), even though predicted environmental concentration of exposed AgNPs ranged from 1 to 10^{-5} μg L^{-1} in surface water (Mueller and Nowack, 2008; Gottschalk et al., 2009) and from 10^{-1}–10^{-3} μg L^{-1} in waste water treatment plant effluent (Mitrano et al., 2012a,b; Hendren et al., 2013).

Owing to its precise and accurate analytical power for use with inorganics, inductively coupled plasma-mass spectrometry (ICP-MS) is considered a promising tool for detecting metal nanoparticles in environmental samples (Laborda et al., 2011; Gray et al., 2012). The operation of ICP-MS in single-particle mode (spICP-MS) enables researchers to determine the size and distribution of individual nanoparticles and the number concentration of particles (Mitrano et al., 2014). In contrast to traditional ICP-MS analyses, single particles enter the plasma instead of there being a constant flow of metal ions, and ionized particles then move to the detector as a cluster of ions. The fundamental assumption of spICP-MS is that each pulse represents a single particle event, which depends on the dwell time, a constant flow rate, and a sufficiently low particle number concentration. Therefore, thousands of intensity readings are acquired, each having a very short dwell time (<20 ms) in spICP-MS; each reading can be collected as a function of time, where pulses above the background indicate the measurement of an individual nanoparticle. The height and the frequency of pulses then represent the sizes and the number of particles.

Using spICP-MS to characterize synthesized colloids in a suspension has been presented by Degueldre et al. (Degueldre and Favarger, 2003; Degueldre et al., 2004, 2006a, 2006b), who proposed theoretical equations between the intensity and particle size and also demonstrated the feasibility of using spICP-MS for various metal nanoparticles. Pace et al. (2011; 2012a) then suggested an improved spICP-MS protocol by discussing the transport efficiency in quantifying and sizing ENPs. Laborda et al. (2013) and Cornelis and Hassellov (2014) investigated detailed metrological criteria for implementation of spICP-MS and distinguished dissolved ion signals from nanoparticle signals. Mitrano et al. (2012a,b) reported that silver and other metal or metal oxide particles could be detected and quantified in waste water treatment plant effluent at low ENP concentrations and in complex matrices using spICP-MS. Field-flow fractionation coupled to ICP-MS (FFF-ICP-MS) was subsequently applied to study the size and the size distribution of nanoparticle mixtures, based on two or more different sizes of particles (Gray et al., 2012; Mitrano et al., 2012a,b). FFF-ICP-MS can detect smaller-sized particles compared to spICP-MS; however, techniques may be applied before the analysis by loading the channel at a specific concentration.

This study applied spICP-MS to better understand the aggregation of AgNPs at both high concentrations used in previous studies due to the sensitivity limit of measurement techniques (2 mg L^{-1} as total Ag) and environmentally relevant concentrations (10–40 ng L^{-1} as total Ag) under various ionic strengths. The mass of an aggregate was calculated and converted to the number of AgNP in an aggregate. In addition, the effect of ionic strength on the aggregation behavior of citrate- and PVP-AgNPs was evaluated with respect to the stability ratio and fractal dimensions of aggregates, obtained using DLS, a common method for this task.

2. Materials and methods

2.1. Characterization of AgNPs

Mono-disperse suspensions of two sizes (nominal diameter: 60 nm and 100 nm) of citrate- and PVP-coated AgNPs were purchased from NanoComposix Inc. (USA). The suspensions had a mass concentration of 20 mg L^{-1} Ag. To estimate the transport efficiency, gold NPs (RM 8013, nominated to 60 nm) were obtained from NIST (USA). Silver and gold calibration standards (Agilent Technologies, USA) were serially diluted in 2% (v/v) HNO3 and HCl, respectively. All solutions were prepared using Millipore deionized water, after 0.1 μm filtration (mixed cellulose ester filter, Advantec, USA).

The morphology and sizes of AgNPs were obtained using transmission electron microscopy (TEM; Tecnai 12, FEI, USA) at 120 kV. The samples were prepared using carbon-coated copper TEM grid which was readily wet by 10 μL of fresh AgNP suspension. The grid was kept in a petri dish (MILLIPORE) to prevent contamination and was let stand at room temperature overnight. The size distribution was obtained by measuring at least 200 particles, and a Gaussian curve was fitted to the histogram using Origin 9.1 Pro software (OriginLab, USA). The hydrodynamic size and zeta potential were measured using DLS (Zetasizer Nano ZS system, Malvern Instrument, USA), in which the AgNP suspensions were probe-sonicated (Digit/Sonifi 450, BRANSON Ultrasonics Corporation, USA) for a few seconds before characterization. Silver NP suspensions of 10^3–10^4 particles mL^{-1} in DI water were also probe-sonicated and directly analyzed using spICP-MS.

2.2. Aggregation of AgNPs by DLS and TEM

The aggregation tests by DLS were conducted at 2 mg L^{-1} as total Ag, which was the optimum concentration for DLS measurements. Silver NPs were suspended in a quartz glass cuvette containing $NaNO_3$ electrolytes (0.1–300 mM) at pH 5.7 (Hellma, USA).