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A Method for Preparing Silver Nanoparticle Suspensions in Bulk for Ecotoxicity Testing and Ecological Risk Assessment

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Abstract Methods are needed to prepare stable suspensions of engineered nanoparticles in aqueous matrixes for ecotoxicity testing and ecological risk assessments. We developed a novel method of preparing large volumes of silver nanoparticles (AgNP) in suspension using a commercially available rotor–stator dispersion mill. AgNP in powder form (PVP capped, 30–50 nm) was suspended in deionized water and natural lake water at 1 g/L and the addition of 0.025% (w/v) gum arabic (GA) increased stability over 2 weeks after preparation. The concentrations of total and dissolved Ag in the suspensions did not change significantly over this period. Analysis of hydrodynamic diameters of the major peaks in suspension using dynamic light scattering showed that suspensions prepared with GA were stable, and this was confirmed by single-particle ICP-MS analysis. This method for dispersing AgNPs provides an inexpensive, yet reliable method for preparing suspensions for toxicity testing and ecosystem level studies of the fate and biological effects of AgNPs in aquatic ecosystems.

Keywords Nanoparticles · Silver · Stability · Toxicity

New engineered nanoparticles (ENPs) are continually being developed with unique physical and chemical properties (Vance et al. 2015). Many of these materials have the potential to be released into aquatic and terrestrial environments (Nowack et al. 2012; Batley et al. 2013). The literature on the toxicity of nanoparticles to aquatic organisms is rapidly developing (Garner et al. 2015), but it is a challenge to keep pace with demands for ecological risk assessments of new products. For instance, over 440 products containing silver nanoparticles (AgNPs) were in commerce in 2015 (http://www.nanotechproject.org 2015). These ENPs vary in size, shape, surface coatings and the matrix in which they are suspended, and all of these parameters can affect the fate and toxicity of these materials (Schultz et al. 2014; Peijnenburg et al. 2015). One of the challenges of toxicity testing of ENPs is standardization of the mode and methods of exposure. There is currently no consensus on the best approaches for preparing nanomaterials in aqueous media for ecotoxicity studies (OECD 2012). Dispersion of nanomaterials in test media has been done by stirring, sonication, grinding, and by using solvents or stabilizing agents, and all of these methods have their advantages and disadvantages (Handy et al. 2011). One of the most widely used methods, which is ultrasonication, may remove surface coatings or result in hydroxylation of the particle surface.

Acute toxicity is typically assessed using standardized test methods involving static exposures of test organisms for 48 or 96 h, with no renewal of test suspensions. Since ENPs are subject to transformations over time, such as agglomeration and dissolution in aquatic matrixes (Schultz et al. 2014), the characteristics of the ENPs in suspension may change dramatically over the duration of a static, non-renewal assay. For chronic toxicity tests conducted over periods of several days or weeks, static assays with suspensions renewed on a daily basis (Martin et al. 2017) or flow-through test systems (Pham et al. 2012; Murray et al. 2017) have been used, but these approaches require large amounts of stock material in suspension. Mesocosm testing has been recommended in order to evaluate the fate and effects of ENPs on an ecosystem scale (Schaumann et al. 2015),

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but these studies are expensive due to the large amounts of ENP suspensions required (Cleveland et al. 2012; Lowry et al. 2012; Furtado et al. 2015).

The toxicity of ENP suspensions can vary over time of storage (Kittler et al. 2010), or with aging of the particles (Mallevre et al. 2016). Ideally, toxicity testing should be done with suspensions of ENPs that are freshly prepared on a frequent basis. However, this is often not practical when suspensions of ENPs are obtained from commercial suppliers. ENPs can be obtained in powder form at a much lower cost than commercially available ENP suspensions, but these particles must be suspended in aquatic matrixes before toxicity testing. Toxicity can vary with the method used to suspend the particles in water (Handy et al. 2012), as well as the aquatic matrix (Gao et al. 2009). An ideal method for dispersing ENPs in aqueous matrixes should: (i) be rapid and inexpensive, (ii) produce consistent results, (iii) not change the characteristics of the ENPs, and (iv) produce a suspension that is stable over extended periods of time.

The purpose of the present study was to develop a reliable and consistent method to prepare stable suspensions of AgNP in a laboratory setting. This was done using a commercially available rotor–stator dispersion mill capable of producing large volumes of stable suspension. Commercially available AgNP in powder form was used for suspension preparation, and the optimal parameters were determined for dispersing the AgNPs in both deionized and natural lake water. The suspensions were characterized in terms of particle size and shape, total Ag content, as well as the proportion of dissolved and colloidal fractions. A method was developed for consistently preparing AgNP suspensions for use in toxicity tests and ecosystem level studies.

Materials and Methods

AgNP was purchased in powder form from Nanostructured and Amorphous Materials, Inc. (NanoAmor, Houston, TX, USA). The AgNPs were capped with 0.2% (w/w) polyvinylpyrrolidone (PVP) and according to a certificate of analysis provided by the manufacturer, contained 99.9% silver, an average particle size of 30–50 nm, a specific surface area of 5–10 m^2/g, and the ENPs were spherical in shape. The cost, according to the manufacturer as of February, 2016, was $220 USD for 25 g. Suspensions of this material prepared by sonication in deionized (MilliQ) water have been used in other ecotoxicity studies (Bilberg et al. 2010). The organic stabilizers, gum arabic (GA), cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) were purchased from Sigma Aldrich (Oakville, ON).

AgNP suspensions were prepared using a Model L rotor–stator dispersion mill purchased from Kady® International (Scarborough, ME, USA). Suspensions were prepared by adding 2.5 g AgNP and 0.025% stabilizing agent to 2.5 L MilliQ water or lake water in the jacketed reservoir of the mill (Fig. 1). MilliQ water (18.2 MΩ) was prepared using a MilliQ Element System (Millipore Corp., Billerica, MA, USA). Natural lake water was obtained from the epilimnion of Lake 222, a small oligotrophic lake at the Experimental Lakes Area, ON. Lake 222 water has an average pH of 6.6, conductivity of 43 µS/cm, and dissolved organic carbon (DOC) content of 12.1 mg/L. The rotor–stator dispersion head consists of a "2" slotted rotor operating inside a stator. The maximum rotor speed is 16,000 rpm and it operates at 3 hp. The most efficient milling occurs at high viscosities, which provides the most energy for mixing, such that the sheering forces ensure thorough mixing of the NPs and prevent agglomeration (Kritzer, Kady® International, pers comm). This benchtop model of the mill allows for the preparation of 2–3 L of suspension. All wetted parts are stainless steel. The suspension is mixed within a jacketed reservoir with cooling from tap water to keep the suspension cool during mixing. In the present study, 2.5 L of suspension were prepared by milling at the maximum speed (i.e., 16,000 rpm).

Treatments using various mixing times from 15 to 60 min, stabilizing agents (i.e., GA, CTAB, SDS) and MilliQ and lake water were used to optimize the preparation of AgNP suspensions ($n = 3$ per treatment). The stability over a 2-week period was monitored in all suspensions by assessing the total silver concentrations, contributions of dissolved and colloidal Ag, and particle size distributions. Hydrodynamic diameters of AgNPs were determined using dynamic light scattering (DLS) and core particle sizes of AgNPs were determined using single particle inductively coupled plasma mass spectrometry (spICP-MS).

Fig. 1 Kady® International rotor–stator dispersion mill used for preparing AgNP suspensions

For the determination of total silver (TAg) in the suspensions, AgNP stock suspensions (1 g/L) were vortexed immediately after preparation and diluted to 10 mg/L in MilliQ water. Samples were acidified to 20% (v/v) with nitric acid (HNO$_3$) of BDH Aristar® Plus grade purchased from VWR (Radnor, PA, USA), and indium (5 µg/L) was added as a recovery standard. The samples were digested at 80 °C for 2 h. Digested samples were further diluted to 100 µg/L in 4% HNO$_3$ prepared in MilliQ water, and rhodium (5 µg/L) was added as an internal standard. Acidified samples were stored at 4 °C until analysis by inductively coupled plasma mass spectroscopy (ICP-MS). Analysis was conducted with an X-Series 2 instrument purchased from Thermo Scientific (Nepean, ON, Canada). The quadrupole instrument was operated in peak hopping scan mode with a dwell time of 25 ms for monitoring of ^{107}Ag, ^{115}In, and ^{103}Rh, with data processed using the Thermo PlasmaLab (Thermo Scientific) software. The instrument operating conditions were manually optimized daily. External calibration was with standard solutions from 0.1 to 200 µg/L of Ag, with In and Rh as internal standards.

Colloidal and dissolved Ag (dAg) fractions for all suspensions were estimated by ultrafiltration with Centrifugal Filtration Units (CFUs) using Amicon Ultra-4 CFUs (Millipore, Etobicoke, ON, Canada), as described by Hadioui et al. (2013). The filter units have a pore size of 3 kDa which corresponds to a size of <1 nm. The filtrate was acidified to 4% nitric acid, and indium (5 µg/L) was added as an internal standard. The retentate in the filter unit was then acidified with 20% nitric acid and digested at 80 °C for 2 h until the solution was clear. The retentate fraction was centrifuged and diluted to 4% nitric acid for analysis of total Ag by ICP-MS. The fractions of dissolved and colloidal were determined using a mass balance approach and were compared to the TAg concentrations determined as described above for the stock suspensions.

The hydrodynamic diameters of AgNPs were determined by DLS using a Nicomp 380 instrument (Particle Sizing Systems, Port Richey, FL, USA). Stock suspensions (1 g/L) were sonicated in a sonicator bath for 20 min, and then vortexed immediately before pipetting. Suspensions were diluted to 40 mg/L in MilliQ water and compared against a standard curve of polystyrene spheres (certified mean diameter 96 ± 3.1 nm) supplied by Agar Scientific (Stansted, Essex, UK). Analysis by spICP-MS was performed to quantify the size and particle concentrations of AgNPs in the stock suspensions. Stock suspensions were placed in a sonicator bath for 20 min, vortexed, and then serially diluted to 50 ng/L. The analysis was conducted essentially as described by Telgmann et al. (2014) using an X-Series 2 quadrupole instrument (Thermo Scientific, Nepean, ON, Canada), operating with a dwell time of 5 ms. The size limit for detection of AgNPs using this spICP-MS system was 40 nm.

Electromicrograph images were obtained using transmission electron microscopy (TEM) to obtain information on morphology, size and shape of the nanoparticles. TEM images were obtained with a Philips CM20 TEM (200 kV) coupled with an energy dispersive X-ray spectrometer (EDAX), as previously described by Sabri et al. (2012).

Differences in Ag concentrations and particle sizes between treatments were evaluated using non-parametric Kruskal–Wallas test and the Dunn's Method *post-hoc* test. All statistical analysis was conducted with the SigmaStat add-on to SigmaPlot©, v.12 (Systat Software, San Jose, CA, USA).

Table 1 Mean ± SD (*n* = 3) of total Ag (TAg), colloidal Ag and dissolved Ag (dAg) in AgNP suspensions (mg/L) sampled when freshly prepared and at 14 days post-preparation

Treatment	TAg	Colloidal Ag	dAg	% dAg
Fresh				
Mixing time				
15 min[a]	658 ± 31.4	656 ± 40.9	1.69 ± 0.05	0.26
30 min	790 ± 58.8	788 ± 48.1	1.92 ± 0.17	0.24
60 min	781 ± 71.2	779 ± 60.0	2.09 ± 0.41	0.27
Stabilizer				
None[a]	658 ± 31.4	656 ± 40.9	1.69 ± 0.05	0.26
CTAB	960 ± 70.8	960 ± 70.8	ND	0.0
SDS	929 ± 61.5	928 ± 42.3	0.97 ± 0.21	0.10
GA[b]	869 ± 81.0	868 ± 71.4	1.05 ± 0.17	0.12
Media + GA				
MilliQ[b]	869 ± 81.0	868 ± 71.4	1.05 ± 0.17	0.12
Lake water	808 ± 69.7	807 ± 58.7	0.28 ± 0.08	0.04
14 Days post-prep				
Mixing time				
15 min[1]	872 ± 70.2	871 ± 61.2	1.63 ± 0.27	0.19
30 min	902 ± 91.6	900 ± 71.4	2.37 ± 0.17	0.26
60 min	866 ± 51.8	864 ± 64.5	2.36 ± 0.35	0.15
Stabilizer				
None[a]	872 ± 70.2	871 ± 61.2	1.63 ± 0.27	0.19
CTAB	746 ± 81.0	746 ± 81.0	ND	0.0
SDS	1103 ± 104	1102 ± 81.7	1.59 ± 0.18	0.14
GA[b]	906 ± 87.1	906 ± 41.8	0.13 ± 0.05	0.01
Media + GA				
MilliQ[b]	906 ± 87.1	906 ± 41.8	0.13 ± 0.05	0.01
Lake water	812 ± 47.5	812 ± 47.5	ND	0.0

The nominal Ag concentrations were 1 g/L for all suspensions. Experimental treatments included mixing time and addition of different organic stabilizers

CTAB cetyltrimethylammonium bromide, *SDS* sodium dodecyl sulfate, *GA* gum arabic

[a] Same treatment (no added stabilizer in MilliQ)

[b] Same treatment (0.025% GA in MilliQ)

Results and Discussion

Suspensions of 30–50 nm PVP-capped AgNPs were prepared at nominal concentrations of 1 g/L to increase viscosities for the rotor–stator dispersion mill to work as designed. The stability of suspensions was monitored at various time points over a 2-week period but the results for suspensions freshly prepared and at 2 weeks after preparation are summarized in Table 1. Overall, measured TAg concentrations were significantly higher in suspensions prepared with the addition of organic stabilizers ($p < 0.05$), and dAg accounted for <1% TAg immediately after preparation and 14 days after preparation. One interesting observation was that dAg was not detected in AgNP suspensions prepared in natural lake water, which probably occurs because of complexation of silver ions with DOC (Furtado et al. 2014). The mixing time did not appear to have a significant effect on suspension stability (Table 1). Based solely on the concentrations of TAg, colloidal Ag and dAg, there were no significant differences between suspensions prepared with CTAB, SDS, and GA organic stabilizers. GA prepared from the acacia tree is a complex mixture of glycoproteins and polysaccharides that has been previously used as a stabilizing agent for AgNP (Cheng et al. 2011; Juby et al. 2012). CTAB surfactant has been used in the synthesis and stabilization of AgNP (Olenin et al. 2008; Wang et al. 2008) and SDS anionic surfactant has also been used to stabilize AgNP (Wang et al. 2008; López-Miranda et al. 2012).

Fresh preparations of AgNP suspensions prepared with different organic stabilizers were analyzed by TEM for imaging of the size and shape of the individual particles. The photomicrographs show evidence of agglomeration as an artifact of the preparation of the samples for TEM (Fig. 2). However, the AgNP in suspensions prepared without stabilizers were less spherical in shape and more agglomerated than AgNP suspensions with additional stabilizers (Fig. 2a). The shapes of AgNPs in the suspensions prepared with CTAB, SDS, and GA were more spherical. The particle sizes determined by TEM analysis were generally within the range of sizes described by the manufacturer (i.e. 30–50 nm). Analysis by EDAX confirmed that the particles were composed of Ag.

Analysis by spICP-MS indicated that the majority of AgNPs in suspension were <50 nm in size, and particle sizes were all <175 nm, aside from a few events indicating

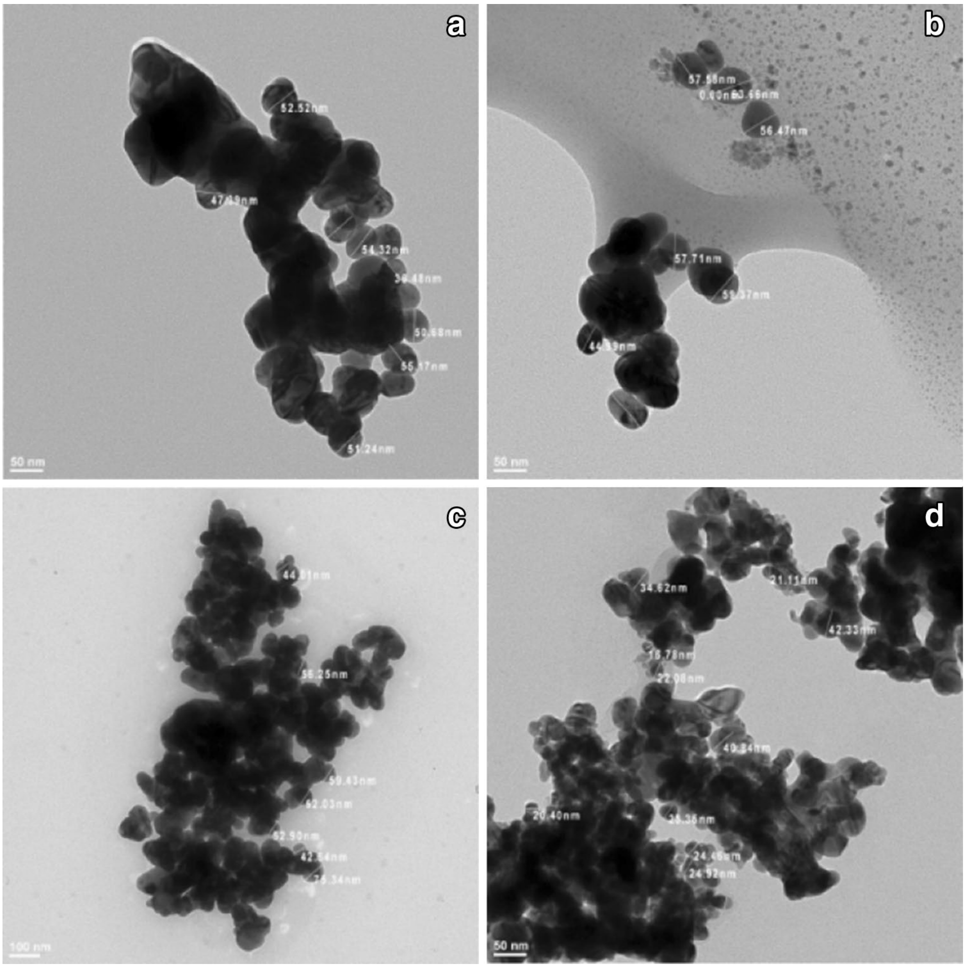

Fig. 2 Transmission electron microscopy photomicrographs of **a** 1 g/L silver nanoparticles (AgNP) in MilliQ water with no chemical stabilizers added, **b** 1 g/L AgNP and 0.025% CTAB, **c** 1 g/L AgNP and 0.025% SDS, and **d** 1 g/L AgNP and 0.025% GA

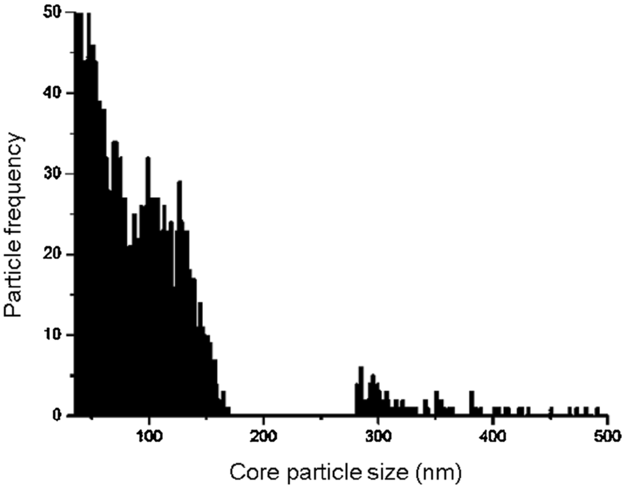

Fig. 3 Particle frequencies of Ag nanoparticles in 1 g/L AgNP stock suspension prepared in lake water with 0.025% gum arabic, diluted to 50 ng/L and analyzed by single particle ICP-MS

the presence of larger agglomerates that were <500 nm in size (Fig. 3). The highest frequency of AgNPs consistently occurred at 40 nm, which was at the size detection limit for the spICP-MS method. This analytical technique is typically used for analysis of more dilute suspensions of ENPs, and the lower size limit of this method limited the scope of the spICP-MS analysis. Recent developments in spICP-MS methods are reducing the lower size limit of this analytical method (Furtado et al. 2016).

The DLS results for suspensions prepared in MilliQ water without stabilizers illustrated in Fig. 4a showed that there were large agglomerates present with mean hydrodynamic diameters of approximately 200 and 1000 nm immediately after preparation (Fig. 4a1). In these preparations without stabilizers, the average hydrodynamic diameter of particles increased by at least fourfold over 14 days (Fig. 4a2). There were no significant differences in DLS results with increasing mixing time (data not shown), indicating that 15 min is sufficient to introduce the sheering forces required to suspend the AgNP in MilliQ or lake water. Of the organic stabilizers tested, gum arabic (GA) was the most favourable, with the majority of AgNPs in suspension having hydrodynamic diameters of 30–50 nm in size over 14 days (Fig. 4c), consistent with the certified sizes from the supplier. The addition of CTAB and SDS may have caused dissolution of the NPs because the average particle size after 14 days was consistently <15 nm (Fig. 4b2); twofold lower than the certified diameter and significantly lower ($p < 0.05$) than the treatment with GA in MilliQ water (Fig. 4c) Further, our experience with CTAB is that it is toxic to aquatic biota, whereas GA has low toxicity.

GA was used in the subsequent tests comparing the effects of aqueous media on AgNP stability. The preparation of AgNP suspensions in natural lake water resulted in stable particle size distributions over 14 days (Fig. 4d). Previous studies on the fate of AgNPs in mesocosms in a dimictic lake at the Experimental Lakes Area, ON indicated that AgNPs were stable in the lake water because of the low ionic strength and relatively high DOC concentrations (Furtado et al. 2015).

This novel method of preparing stable suspensions of AgNPs with a commercially available rotor–stator dispersion mill is much less expensive than using large amounts of prepared suspensions that are commercially available. The AgNP in powder form can be readily suspended in aqueous media with the addition of a small amount (i.e. 0.025%) of GA to provide additional stabilization. This method would be particularly useful for laboratories that conduct large-scale toxicity tests with aquatic biota, especially for chronic toxicity testing. In addition, the method

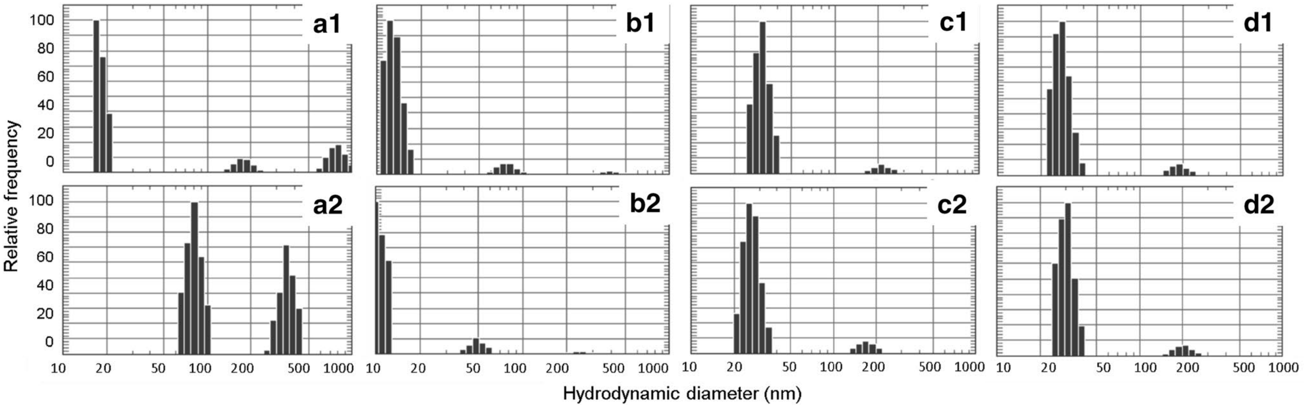

Fig. 4 Fractograms of hydrodynamic diameter (nm) determined by Dynamic Light Scattering for 1 g/L silver nanoparticle (AgNP) suspensions prepared with differing stabilizers or media: **a** MilliQ water; **b** 0.025% CTAB in MilliQ water; **c** 0.025% GA in MilliQ water; **d** 0.025% GA in lake water. Suspensions were monitored at 0 (**a–d1**) and 14 days (**a–d2**)

would be useful for preparing large volumes of AgNP suspensions for ecosystem level studies.

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