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Silver nanoparticle behaviour in lake water depends on their surface coating

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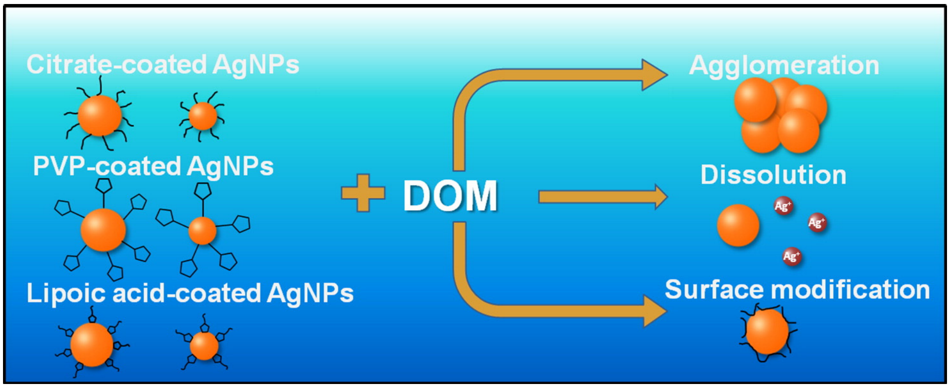
HIGHLIGHTS

- Surface coating rather size determines the stability of AgNPs in lake water (LW).
- Stability of AgNPs decreases in the order PVP AgNPs > CIT AgNPs > LIP AgNPs.
- Addition of DOM increased the stability of AgNPs in the order LW + EPS > LW + SRHA > LW.
- Influence of DOM on AgNP behaviour depends on the surface coating characteristics.
- SP-ICP-MS and AsFlFFF allow to study AgNPs at low environmental concentrations.

GRAPHICAL ABSTRACT



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ABSTRACT

The present study examines the stability of silver nanoparticles (AgNPs) of three different coatings – citrate (CIT), polyvinyl pyrrolidone (PVP) and lipoic acid (LIP) and two sizes - 20 and 50 nm in lake water (LW) over time. Using a combination of asymmetric flow field-flow fractionation (AsFlFFF), surface plasmon resonance (SPR), and single particle inductively coupled plasma mass spectrometry (SP-ICP-MS), the influence of size, surface coating, exposure time, as well as the presence and nature of dissolved organic matter (DOM) on the transformation of AgNPs at low environmental concentrations was thoroughly investigated. The results revealed that the AgNP stability in lake water are complex interplay between the surface coating characteristics, exposure time and presence and nature of DOM. Among the studied variables surface coating was found to play the major role of determining AgNPs behaviour in lake water. PVP-coated AgNPs agglomerated to a lesser extent as compared with the CIT- and LIP-AgNPs. For a given surface coating, DOM of pedogenic and aquagenic origin increased the stability of the AgNPs (LW + EPS > LW + SRHA > LW). Moreover, extracellular polymeric substances (EPS; aquagenic origin) stabilized lipoic acid-coated AgNPs more effectively than Suwannee River Humic Acids (SRHA; pedogenic origin), showing that DOM nature has to be also considered for improved understanding the AgNP stability in aquatic environment.

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1. Introduction

Nowadays, the production and use of engineered nanomaterials in a wide range of applications and consumer products is constantly increasing (The Project on Emerging Nanotechnologies, 2016). Due to their antimicrobial properties, silver nanoparticles (AgNPs) are one of the most commonly used engineered nanomaterials (Schluesener and Schluesener, 2013). The widespread use of these AgNPs implies their unavoidable release into the environment which raised the concerns about the potential risks to human health and the environment (Klaine et al., 2012; Schaumann et al., 2015). AgNPs may be released from textiles by washing (Benn and Westerhoff, 2008) or from outdoor facades (Kaegi et al., 2010) into surface waters, where they may induce harm on aquatic ecosystems (Furtado et al., 2014).

Once in the aquatic environment, AgNPs are subject of various transformation such as agglomeration, dissolution or various surface modifications which will determine their persistence and effects (Bae et al., 2010; Newton et al., 2013; Wang et al., 2016; Yang et al., 2012). The transformations depend on the nanomaterial properties (e.g. surface coating and size of NPs) and ambient environment variables (e.g. dissolved organic matter (DOM)) (Aiken et al., 2011; El Badawy et al., 2010; von Moos et al., 2014). Importance of surface coating for AgNPs transformations, like dissolution and/or agglomeration, in aquatic environments has been demonstrated. For instance, low release of Ag ions from citric acid coated (CIT) AgNPs was observed as compared with polyvinyl pyrrolidone (PVP) and tannic acid coated AgNPs of 5, 10 and 50 nm in lake and river waters (Dobias and Bernier-Latmani, 2013). Similarly, 8 nm PVP-coated AgNPs released about 10 times higher Ag ions than 7 nm citrate-coated AgNPs in EPA water (Yang et al., 2012). The dissolution rate of AgNPs followed the order: bare-AgNPs > PVP-coated AgNPS > citrated-coated AgNPs; whereas for aggregation rate: bare-AgNPs > citrate-coated AgNPs > PVP-coated AgNPs under environmental light irradiation conditions (Li et al., 2013). Moreover, uncoated, citrate-coated and sodium borohydride-coated AgNPs were found to aggregate at high ionic strength and/or acidic pH, whereas both factors had no impact on aggregation of PVP-coated AgNPs (El Badawy et al., 2010).

Among different environmental variables, humic substances (HS), an important component of DOM in aquatic environments, were shown to increase the stability of citrate and/or PVP-coated AgNPs in artificial seawater (António et al., 2015), under sunlight (Yu et al., 2014), in a high ionic strength buffer (Gunsolus et al., 2015) or in the presence of cations (Baalousha et al., 2013; Cumberland and Lead, 2009). Extracellular polymeric substances (EPS) were also shown to have important implications for the environmental transformations of NPs (Louie et al., 2016). For instance, EPS induced size increase of carbonate-coated AgNPs (Kroll et al., 2014), agglomeration of PVP-coated AgNPs (Joshi et al., 2012), and stabilization of AgNPs with unknown coating (Khan et al., 2011). Some studies have suggested a different behaviour between citrate-coated and PVP-coated AgNPs in the presence of DOM (Gunsolus et al., 2015; Yin et al., 2015). Nevertheless, the role of the nanoparticle surface coatings in the NP stability and interactions with the DOM present in freshwater is still to explore in particularly at environmentally relevant concentrations.

Given the low concentrations of engineered nanomaterials in the natural water (e.g. predicted environmental concentration (PEC) of silver-based nanomaterials is in the ng L^{-1} level (Peijnenburg et al., 2015)), the study of their fate requires the use of the most sensitive analytical techniques. Single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) and asymmetric flow field-flow fractionation (AsFlFFF) are among the most suitable techniques for the analysis of inorganic engineered nanoparticles in environmental samples (Laborda et al., 2016, 2015; von der Kammer et al., 2011). SP-ICP-MS has been used to detect native Ag particles in influent and effluent samples from waste water treatment plants (Mitrano et al., 2012; Tuoriniemi et al., 2012), in the effluent of a AgNPs producing washing machine (Farkas et al., 2011) and in urban runoff waters (Heithmar and Pergantis, 2010). Moreover, this technique has also been applied to study the behaviour of AgNPs in simulated washing machines procedures (Mitrano et al., 2015) and the dissolution of AgNPs in different types of water (Mitrano et al., 2014; Telgmann et al., 2014; Yang et al., 2016). On the other hand, AsFlFFF has been used to detect and quantify AgNPs in influent water collected from a wastewater treatment plant (Hoque et al., 2012). The combination of the information obtained by these two techniques has been applied to study the agglomeration process of AgNPs in artificial seawater (António et al., 2015) and the persistence and transformations of AgNPs in a littoral lake mesocosmos (Furtado et al., 2014).

The present work examines the influence of the AgNP size and coating, exposure time, and the presence and the nature of DOM on the stability of the Ag NPs in lake water at environmentally relevant concentrations. By using a combination of AsFlFFF, SP-ICP-MS and surface plasmon resonance (SPR), the AgNPs stability was characterized following the changes in size distributions and number of AgNPs, two critical aspects in the evaluation of the persistence of nanomaterials in the environment.

2. Material and methods

2.1. Silver nanoparticles, standards and reagents

AgNPs with primary size of 20 and 50 nm were selected as representative of small and medium size nanoparticles, respectively. The capping agents chosen were citrate (CIT), which is displaceable and stabilizes by charge repulsion, polyvinyl pyrrolidone (PVP) which stabilizes sterically and lipoic acid (LIP) which is conjugatable and stabilizes by charge repulsion. Suspensions of silver nanoparticles (AgNPs) with nominal diameters of 20 and 50 nm and coated with CIT, PVP and LIP were purchased from NanoComposix (San Diego, USA). The characteristics of these particles in ultrapure water are given in Table 1. Polystyrene standards of 22, 58 and 97 nm (Postnova Analytics, Landsberg, Germany) were used for calibration of the AsFlFFF system. Stock solutions of these standards were diluted with the carrier before injecting into the channel. The carrier was prepared by dissolving the corresponding

Table 1

Characteristics of the studied AgNPs suspensions in ultrapure water. Nominal particle and hydrodynamic diameters, zeta potential, surface area and silver purity are as provided by the supplier. Hydrodynamic diameters and median particle diameters of AgNPs suspensions in ultrapure water were measured by AsFlFFF-UV–vis and SP-ICP-MS respectively (mean ± standard deviation, $n = 3$). AgNPs suspensions were injected directly into the channel for AsFlFFF measurements and diluted with ultrapure water before SP-ICP-MS measurements.

Suspension	Zeta potential	Surface area	Silver purity	Hydrodynamic diameter / nm		Particle diameter / nm	
				Nominal	AsFlFFF-UV–vis	Nominal	SP-ICP-MS
20 nm Cit-AgNPs	−40.5 mV	27.6 m^2/g	99.99%	27.2	27.3 ± 0.9	19.9 ± 2.9	33.8 ± 0.4
20 nm PVP-AgNPs	−24.4 mV	26.1 m^2/g	99.99%	44.2	35.8 ± 2.4	21.3 ± 2.7	25.6 ± 0.6
20 nm Lip-AgNPs	−44.2 mV	22.3 m^2/g	99.99%	43.4	37.6 ± 0.6	24.5 ± 3.9	26.6 ± 0.5
50 nm Cit-AgNPs	−45.5 mV	10.8 m^2/g	99.99%	56.8	59.6 ± 3.8	51.6 ± 5.4	51.3 ± 0.3
50 nm PVP-AgNPs	−53.5 mV	11.3 m^2/g	99.99%	63.6	70.7 ± 2.3	49.9 ± 4.6	40.7 ± 0.5
50 nm Lip-AgNPs	−43.5 mV	11.9 m^2/g	99.99%	51.9	56.2 ± 1.1	47.0 ± 5.0	46.6 ± 0.4