J. Mater. Environ. Sci. 4 (5) (2013) 617-620
ISSN : 2028-2508
CODEN: JMESCN

Particle size distribution of silver nanoparticles in different water conditions

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Received 25 Nov 2012; Revised 27 Apr 2013, Accepted 27 Apr 2013
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Abstract

The study measured the effect of different water conditions on the size distribution of silver nanoparticles. The particle size distribution of silver nanoparticles shifted towards the large size of silver nanoparticle aggregates with increasing concentration of electrolytes. Divalent cations could increase the size of silver nanoparticles more effectively compared with monovalent electrolyte. As a result, particle size of silver nanoparticles are much higher in seawater than in surface fresh water.

Keywords: silver nanoparticles; water conditions; particle size distribution

Introduction

Silver nanoparticles (AgNPs) are important disinfectant due to their antimicrobial property [1-8]. The quantity of AgNP-based nanomaterials is increasing. Currently, consumer products containing AgNPs accounted for more than 23% of all the consumer nanomaterials available on the market in 2010 [2, 5]. With the increasing application of AgNPs, their release into natural water bodies is likely to occur and the potential release raised concerns on their impact on the health of human and ecosystem due to their toxicity [5].

The proposed mechanisms of the toxicity of AgNPs include changes in membrane permeability by pitting on the cell membrane, lysis of the cell by the sorption of silver ions released from AgNPs into the cell wall and the oxidative stress induced by the reactive oxygen species formed in AgNPs suspension [2]. Recent studies reported that toxicity of AgNPs was negatively correlated to their particle size in both synthetic electrolyte solutions and natural water conditions [2]. Consequently, the environmental toxicological impact of AgNPs is greatly dependent on the mobility and particle sizes of AgNPs since large AgNP aggregates could precipitate and thus reduce their availability in environmental waters [5]. However, data for the particle sizes and their distribution of AgNPs is scarce. Therefore, it is important to study the particle size distributions of AgNPs.

In this study, AgNPs were synthesized using the Tollens' method. The obtained AgNPs were characterized using transmission electron microscope and UV-vis spectrophotometer. Particle size distribution of AgNPs in electrolyte solutions including NaCl, $CaCl_2$ and $MgCl_2$ and humic acid solutions were analyzed by dynamic light scattering (DLS) technique.

2. Materials and methods

Electrolyte solutions including NaCl and $CaCl_2$ (Sigma Aldrich) were used to study the effect of the valence of cations in the electrolyte on the particle size distribution of AgNPs. The concentration of the cations of electrolyte solutions ranges from 10-1000 mM to mimic the natural water conditions. Natural surface water and seawater were collected and filtrated using 200 nm filter membrane and autoclaved to remove pathogens.

AgNPs stabilized by sodium citrate was prepared via a Tollens method according to previously published procedures. The obtained AgNPs solutions were cleaned with deionized (DI) water using a 10 kDa nominal molecular weight cut-off (NMWCO) ultrafiltration membrane (Millipore, Model 8200; NMWCO: 3000). AgNPs were characterized by UV-vis spectroscopy (Thermoscientific). Concentration of AgNPs was measured by ICP-MS (X series, Thermo Elemental). Cryo-transmission electron microscope (Cryo-TEM) was used to observe the morphology of AgNPs. Particle size distributions of AgNPs in different electrolyte solutions and natural waters were determined by dynamic light scattering (DLS) using a Zetasizer (Nano ZS, ZEN 3600, Malvern) at 25 ^{0}C.

3. Results and discussion

3.1. Characterization of nanoparticles

Fig. 1 and 2 show the characterization of AgNPs in DI water by TEM, UV-Vis spectrometry. TEM image showed that the AgNPs are spherical. This is commonly observed in previous studies using the same manufacturing procedure [6].

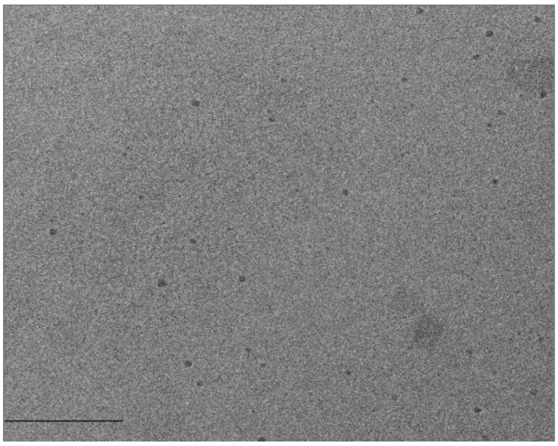

Fig. 1 TEM image of AgNPs in DI water (black line=200 nm)

Similarly, UV-Vis spectrum showed that the peak of AgNPs is at 400 nm. This observation also agrees with previous studies [4, 5]. Additionally, Fig. 2 also presents the UV-Vis spectra of AgNPs in monovalent and divalent electrolyte solutions as well as natural water conditions. Fig. 2 (a) and (b) shows that the characteristic peak of AgNPs decreases with increasing electrolyte concentration. Similarly, characteristic peak of AgNPs in seawater is lower than in surface fresh water.

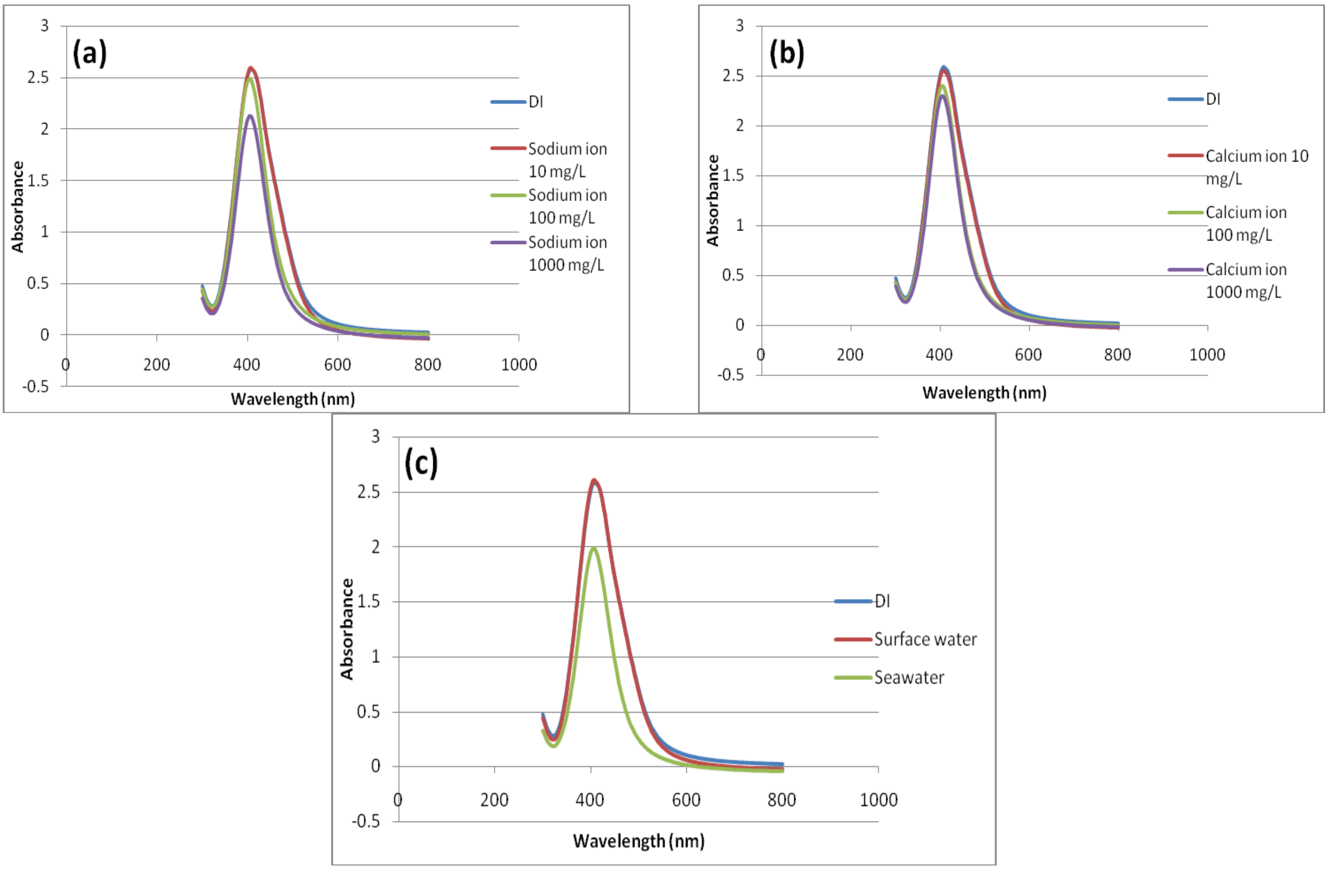

Fig. 2 UV-Vis spectra of AgNPs in monovalent electrolyte solution (a); divalent electrolyte solution (b); and natural water conditions (c)

3.1. Particle size distribution of silver nanoparticles under different water conditions

Fig. 3 presents the particle size distributions of AgNPs in electrolyte solutions. Results showed that the particle size distribution shifted towards large size of particle aggregates with increasing electrolyte concentrations and the number of AgNPs in small sizes was decreasing. In addition, comparison between particle size distributions of AgNPs in monovalent electrolyte (NaCl) and divalent electrolyte ($CaCl_2$) solutions revealed that larger AgNP aggregates were produced in $CaCl_2$ solution than in NaCl at the same concentration.

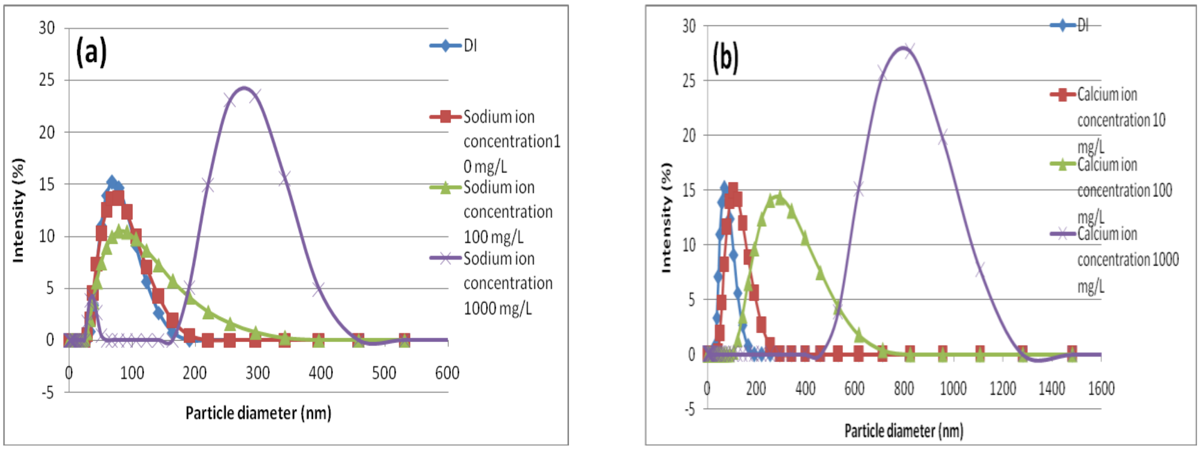

Fig. 3 Particle size distribution of AgNPs in monovalent and divalent cationic electrolyte solutions

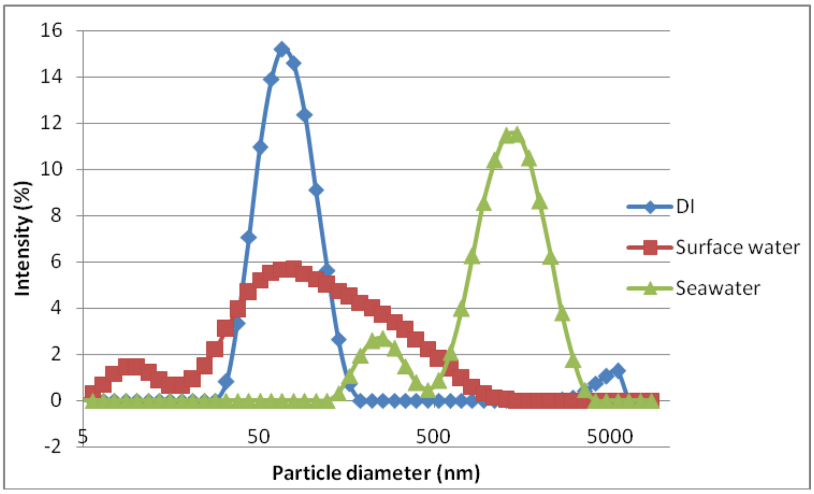

Fig. 4 Particle size distribution of AgNPs in different natural water conditions

Fig. 4 presented the particle size distribution of AgNPs in surface water and seawater conditions. Particle size distributions showed that AgNPs in seawater shifts to higher particle size in comparison with in surface water.

Table 1. Particle size of AgNPs in different electrolyte solution and natural water conditions

Water conditions	Particle size (nm)
DI	68.2
10 mg/L Na^+	66
100 mg/L Na^+	77.3
1000 mg/L Na^+	227
10 mg/L Ca^{2+}	98.7
100 mg/L Ca^{2+}	262.3
1000 mg/L Ca^{2+}	1013
Surface water	62.8
Seawater	873

Table 1 summarized the particle size of AgNPs in different water conditions. This observation has clearly demonstrated that particle size of AgNPs in different water conditions is subjected to the concentration and valence of cations. Divalent cations can induce much intense aggregation than monovalent cations.

Previous studies indicated that the cations in electrolyte solutions could influence the aggregation of AgNPs due to the screening process that can eliminate the energy barrier between nanoparticles. Zhang et al, (2012) (a) showed that AgNPs formed larger aggregates in presence of divalent cations such as Mg^{2+} or Ca^{2+} than monovalent cations, which is likely due to the high aggregation rates of AgNPs in divalent electrolyte solutions [6]. The authors also indicated that the aggregation rate of AgNPs increased with increasing cationic electrolyte concentration. Similarly, Zhang et al. (2012) has provided evidence that the aggregation rates of AgNPs with different capping agents were higher in divalent electrolyte solutions than in monovalent electrolyte solutions [7-14]. Zhang et al. (2012) also proposed that the presence of natural organic matter could induce steric repulsion and mitigate the AgNP aggregation [2]. These above-mentioned observations agree with our particle size measurements according to the DLVO theory, which states that the stability of a nanosuspension is sensitive to the valence and concentration of counter-ions presence in the solution [4-6].

AgNPs in natural waters showed that there was a significant difference in size distribution of AgNPs in surface fresh water and seawater. Larger AgNP aggregates were found in seawater as seawater contains much higher concentrations of cations such as Ca^{2+} and Mg^{2+} in comparison with surface fresh water. These observations agree with previously published data which indicated that natural organic matter could play an important role to increase the steric repulsion force between nanoparticles by adsorbed onto their surfaces [2, 6].

Conclusion

Conclusively, this study presented the effect of types and amount of electrolytes on the size distribution of AgNPs. It was observed that AgNP aggregates became larger with increasing concentration of electrolyte. Additionally, Ca^{2+} can generate large AgNP aggregates more effectively than Na^{+}. The significance of this study lies in that it pointed out the conditions that can make AgNP suspension unstable, which could guide the applications of AgNP as an antimicrobial reagent.

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