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Short Communication

Are silver nanoparticles always toxic in the presence of environmental anions?

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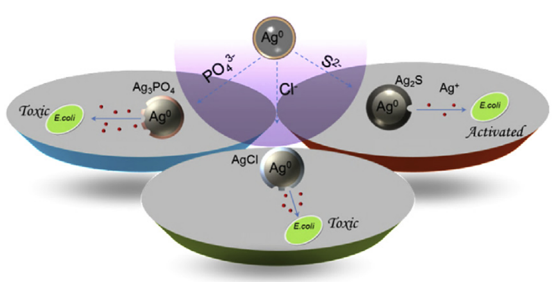
HIGHLIGHTS

- Sulfide can induce AgNPs stimulate microbial growth at certain concentrations but not toxic.
- Other environmental anions such as chloride and phosphate anions, cannot induce AgNPs stimulation to microbial growth.
- AgNPs toxicity is dependent on sulfuration rate, which is not related to either AgNP or sulfide concentration.

GRAPHICAL ABSTRACT



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ABSTRACT

Increasing amounts of silver nanoparticles (AgNPs) are expected to enter the ecosystems where their toxicity in the environment is proposed. In this study, we exploited the effect of environmental anions on AgNP toxicity. AgNP were mixed with various environmental anions, and then exposed to *Escherichia coli* to determine the effect on bacteria growth inhibition. The results demonstrated that AgNP are not always toxic in the presence of sulfide, but can stimulate microbial growth at certain concentrations. Environmental chloride and phosphate anions cannot induce the stimulation because of their weak capacity to control the release of Ag^+ from AgNP. Ag^+ that released from AgNP is proven to be responsible for AgNP toxicity. Moreover, we found that AgNP toxicity is dependent on sulfuration rate. At the same sulfuration rate, AgNP shows an identical pattern of toxicity. This study indicates that only sulfide of the tested environmental anions can induce AgNP stimulation to microbial growth in a sulfuration rate dependent pattern and the toxicity originate from Ag^+ that released from AgNP.

1. Introduction

Silver nanoparticles (AgNPs) are increasingly used in a variety of products, primarily for their unique optical, electronic, and antibacterial properties (Khan et al., 2014; Xie et al., 2014; Guo et al., 2016a, b). As a result of their capacity for oxidation and dissolution, AgNPs may transform into various forms in the environment.

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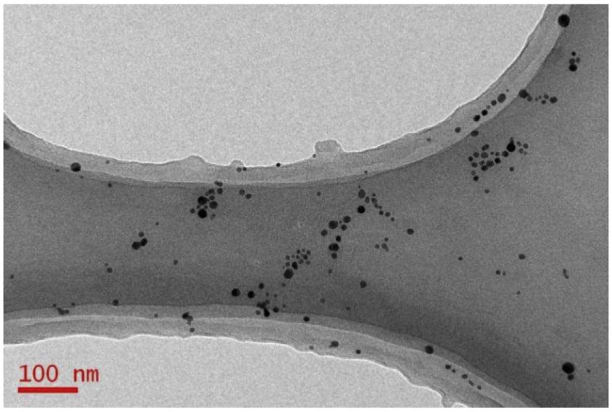

Fig. 1. TEM of AgNP.

Even a simple colloid of AgNP consists of three silver forms: Ag^0 nanoparticle, soluble Ag^+, and surface-adsorbed Ag^+ (Liu and Hurt, 2010). Both colloidal and ionic Ag can be released from AgNPs under normal washing conditions (Benn and Westerhoff, 2008). With the rapid rise in the production and use of AgNP-containing products, AgNPs might pose a hazard to humans and other organisms as a result of their potential to release of Ag^+ (Kaegi et al., 2010; Baalousha et al., 2015). To date, numerous studies have been carried out to investigate the environmental fate and transport of AgNPs, as well as their ecological impact (Reidy et al., 2013; Levard et al., 2012).

AgNP toxicity has been primarily evaluated under controlled laboratory conditions that mimic only one or two environmental factors. These results may not predict the specific behavior of AgNPs in natural environments, where numerous physicochemical and biological factors interact and vary temporally. In environmental conditions, AgNPs are oxidized to Ag^+, which then reacts with inorganic sulfide (S^{2-}) to form Ag_2S NPs or chloride to form AgCl NPs (Levard et al., 2011, 2013a, b). *Escherichia coli* (*E. coli*) can secrete extracellular polymeric substances (EPS), which embed AgNPs, thus serving as a permeability barrier to hinder their penetration into cells (Kang et al., 2014). In aquatic ecosystems, natural organic matter plays an important role in the environmental fate and transport of NPs by influencing their physicochemical properties (Nason et al., 2012; Deonarine et al., 2011), and therefore altering their toxicity (Zhang et al., 2009; Guo et al., 2016a, b). Hence, the interaction of AgNPs with constituents in their environment can have dramatic effects on their toxicity (Marambio-Jones and Hoek, 2010). A wide range of environmental parameters should therefore be considered in assessing the toxicity of AgNPs.

In the present study, we investigated how environmental anions such as S^{2-}, Cl^-, and PO_4^{3-} can affect AgNP toxicity to varying extents. Thus, we propose that AgNPs are not always toxic to environmental microorganisms; sulfuration rate can significantly influence their toxicity profile and may even cause activation of microorganisms.

2. Methods

2.1. Preparation and characterization of AgNP suspensions

Polyvinylpyrrolidone (PVP) coated AgNPs (PVP-AgNPs) were synthesized according to the literature (Solomon et al., 2007) with slight modifications. Briefly, 5 mL of 20 mM silver nitrate (99.998% purity, Sigma Aldrich) was reduced with 12 mL of 15 mM sodium borohydride (>99% purity, Sigma Aldrich) for 3 min in the presence of 0.3% PVP10 (MW 10,000, Sigma Aldrich) in an ice bath. The

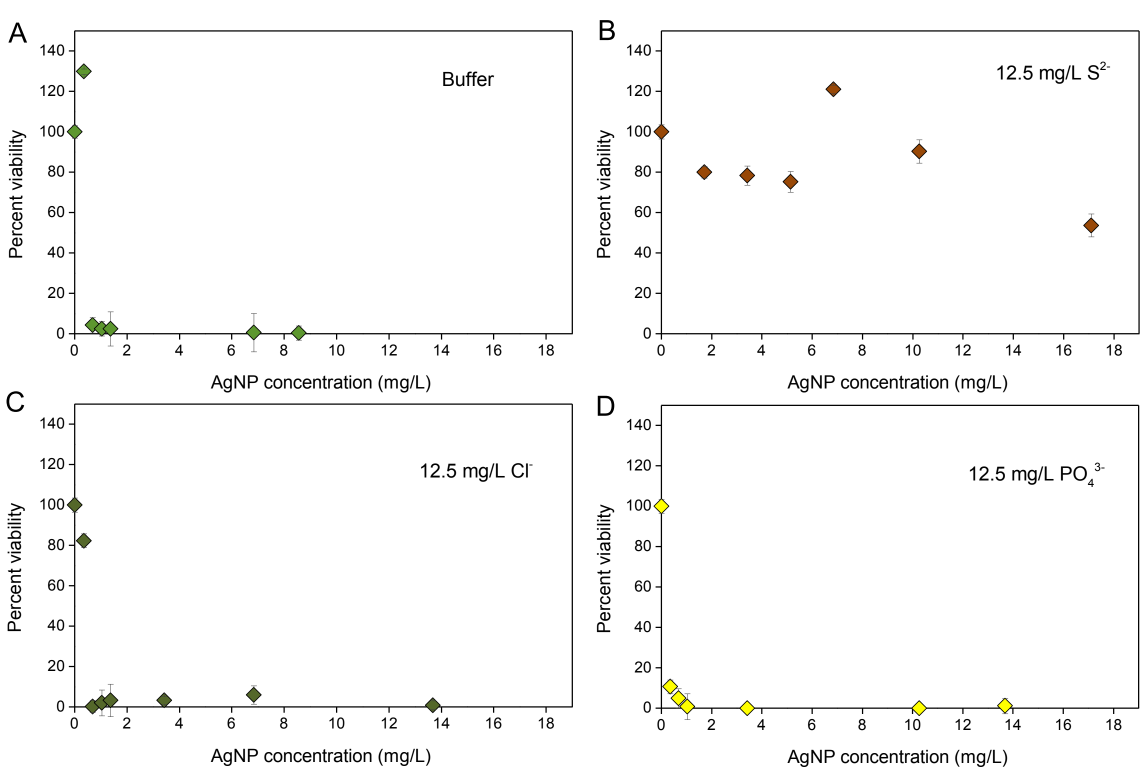

Fig. 2. AgNP toxicity to *E. coli* (A) without environmental anions, and with 12.5 mg/L of (B) S^{2-}, (C) Cl^-, and (D) PO_4^{3-}. All data plots represent the average from at least three independent experiments. Error bars represent 95% confidence intervals.