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Reduction of silver nanoparticle toxicity by sulfide

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ABSTRACT

Silver nanoparticles have been widely used in consumer products due to their excellent antimicrobial properties. Release of nanosilver into natural waters may induce negative environmental impacts on local microorganism communities. This work evaluated the influence of anions such as sulfate, phosphate, chloride and sulfide on the toxicity of silver nanoparticles. Results revealed that sulfide anion could significantly reduce their toxicity in comparison with other anions, which provides an in-depth investigation on the toxicity control of released silver nanoparticles. Copyright © 2013 VBRI Press.

Keywords: Silver nanoparticles; toxicity; sulfide; particle size; nanosilver; anion.

Introduction

Silver nanoparticles (SNPs) have been broadly applied in different industrial fields due to their antimicrobial and catalytic properties **[1-11]**. It is estimated that silver nanoparticle-contained consumer products accounted for more than 23% of all the nanotechnology-based products in market **[2]**. Due to their wide applications, release of silver nanoparticles into sewage and natural waters is inevitable and could induce negative environmental impacts on the local microbial communities **[1]**.

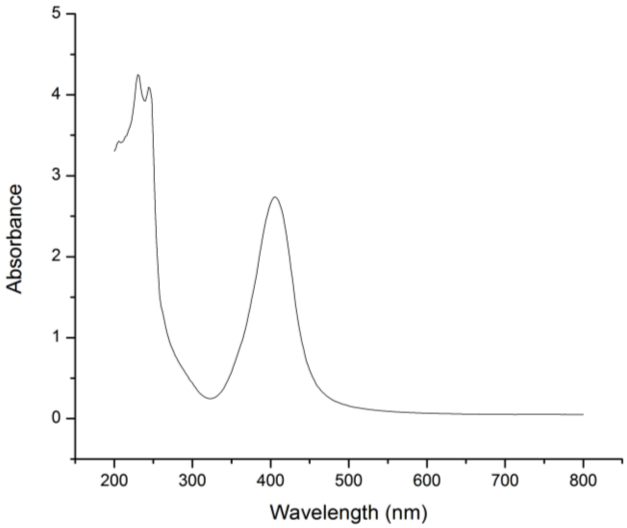
Previous literatures have indicated that the release of silver nanoparticles can cause high toxicity on microbial communities such as bacteria and protozoa. Up to 90% of antimicrobial ability was reported by Zhang et al, (2012) on *Escherichia coli* **[2, 6].** Although it has been indicated that the toxicity of silver nanoparticles can be reduced by the anions such as chloride, phosphate or sulfate, further studies on the reduction of the toxicity is needed **[2]**. Previous works have focused on the bacteria reduction using anionic ligands that commonly found in natural water systems. In our work, we have discovered a new approach using anionic ligand sulfide to further reduce the toxicity of silver nanoparticles.

This work evaluated the reduced toxicity of silver nanoparticles in presence of sulfide. Silver nanoparticles were prepared using a Tollen's method **[1, 2, 4]**. The toxicity of silver nanoparticles was measured by regular plate count method. Physicochemical properties (silver ion release, particle size and zeta potentials) of silver nanoparticles in different water chemistry conditions were measured using zetasizer.

Experimental

Tollen's method was used to synthesize silver nanoparticles according to previous literature **[1, 2, 4]**. In brief, the initial concentrations of the reactants were 1×10^{-3} M and 1×10^{-2} M for $AgNO_3$ and maltose, respectively. The concentration of ammonia was 5×10^{-3} M. SNPs obtained were cleaned by ultrafiltration and the pH was adjusted using DI water. The concentration of SNPs was measured using an ICP-MS (Thermo elemental) by dissolving SNPs in 2% HNO_3 solution. UV-Vis spectroscopic characterization (Thermo Scientific) was used for silver nanoparticle characterization. Atomic force microscopic (5600LS, Agilent) image was used to characterize the size and morphology of SNPs.

Ten mg/L of the anionic ligands (chloride, sulfate, phosphate, and sulfide) was used to mimic natural water conditions. All the cations presents in these solutions were sodium. 1 mg/L of SNPs was used for the toxicity evaluation. A commonly used plate count method was used for toxicity evaluation **[2, 6, 8]**. Zetasizer (ZEN 3600, Malvern) was used for the physicochemical properties such as particle size and zeta potential. A control group was used to test SNPs in DI water conditions for the toxicity and physicochemical properties evaluations. All the abovementioned reagents used were in ACS grade and used as received.



Fig, 1. UV-Vis spectrum of synthesized silver nanoparticles.

Results and discussion

The synthetic approach of the SNPs is according to the Tollens' method, which used saccharides as reducing agents to reduce silver ion into elemental silver. The UV-Vis spectroscopy characterization of the SNPs showed that the characteristic peak was located at around 400 nm (**Fig. 1**), which is consistent with other published data **[4, 5]**. AFM image of the nanoparticles showed that the nanoparticles are spherical and well-dispersed (**Fig. 2**).

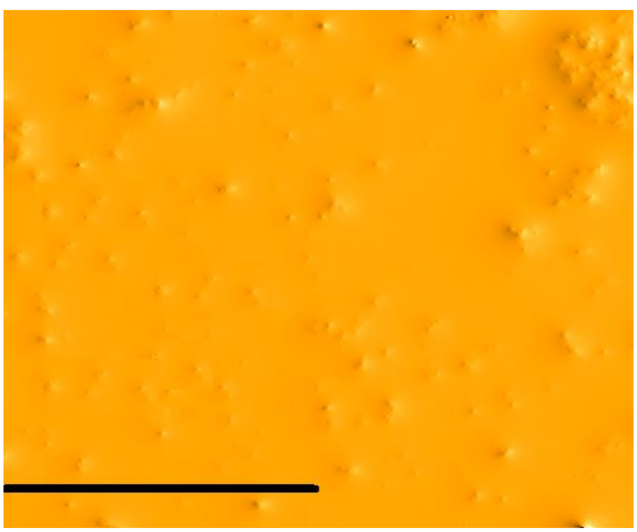


Fig. 2. AFM image of silver nanoparticles (black line=25 µm).

Fig. 3 indicated that the antimicrobial properties of SNPs in electrolyte solution containing sulfide was the lowest possibly due to the high value of stability constant of Ag_2S. As the Ag_2S complex is very stable, oxidation of the complex might be unlikely. As the toxicity of SNPs was mainly induced by the silver ion release, the stable Ag_2S complex may reduce the silver ion release and thus mitigate their toxicity. AgCl formation due to the interaction between Ag^+ and Cl^- may also reduce the toxicity of SNPs by inhibit the SNPs oxidation. SNPs in sulfate and phosphate containing solutions were not as significant as in chloride and sulfide containing solutions. This might be due to the less stability constants.

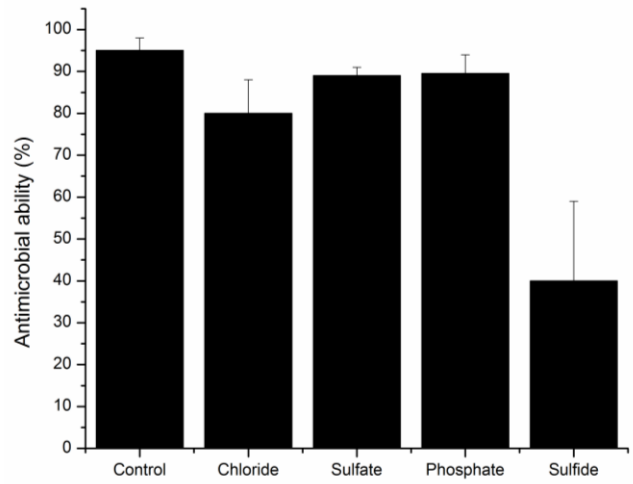


Fig. 3. Antimicrobial properties of silver nanoparticles in different anionic solutions (24 h)

Fig. 4 reported the particle size of SNPs in different anionic solutions. As indicated by the figure, the largest SNPs were found in sulfide anionic solution, which might also be due to the formation of Ag_2S complex. Particle size of SNPs in sulfate, phosphate and chloride anionic solutions were similar to that in DI water. Particle size of SNPs was reported to be sensitive to the valence of cations present in water. As only Na^+ is present in these water conditions, particle size could not be influenced significantly.

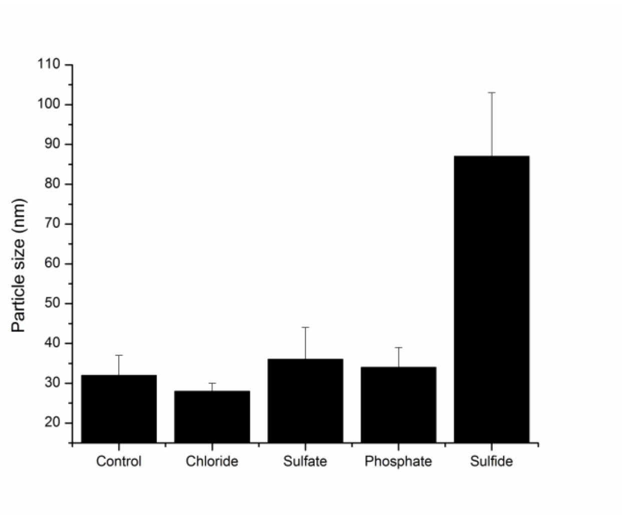


Fig. 4. Particle size of SNPs in different anionic solutions (24 h).

Fig. 5 shows that the zeta potential of SNPs in sulfide solution was the highest, which is consistent with particle size measurement. Zeta potential indicates the stability of SNPs. A lower absolute value of SNPs indicates a less stable nanosuspension. As antimicrobial properties of SNPs is reported to be associated with the stability of the nanosuspension. Our antimicrobial properties are also related to the zeta potential.

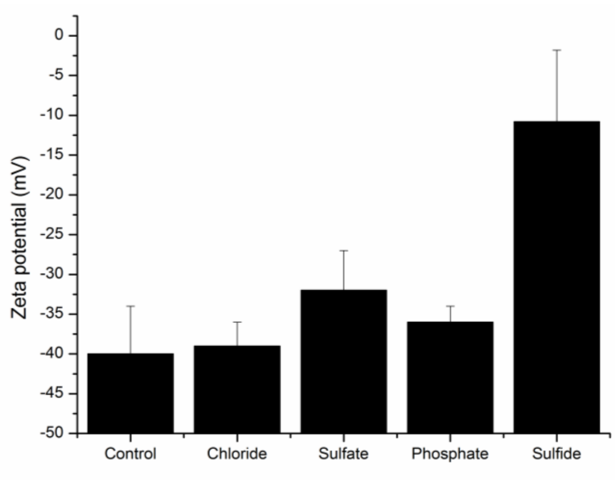


Fig. 5. Zeta potential of SNPs in different anionic solutions (24 h).

Conclusion

In summary, this study revealed that the toxicity of SNPs depends on the types of anions present in different water conditions. Results showed that the particle size and zeta potential are the highest for SNPs present in sulfide containing electrolyte solutions, while the toxicity of SNPs in sulfide containing electrolyte solution is the lowest. Our results indicate that the toxicity of SNPs present in sewage could be mitigated due to the present of high sulfide concentration.

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