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Review

Silver nanoparticles in aquatic environments: Physiochemical behavior and antimicrobial mechanisms

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ABSTRACT

Nanosilver (silver nanoparticles or AgNPs) has unique physiochemical properties and strong antimicrobial activities. This paper provides a comprehensive review of the physicochemical behavior (e.g., dissolution and aggregation) and antimicrobial mechanisms of nanosilver in aquatic environments. The inconsistency in calculating the Gibbs free energy of formation of nanosilver [$\Delta G_{f(AgNPs)}$] in aquatic environments highlights the research needed to carefully determine the thermodynamic stability of nanosilver. The dissolutive release of silver ion (Ag^+) in the literature is often described using a pseudo-first-order kinetics, but the fit is generally poor. This paper proposes a two-stage model that could better predict silver ion release kinetics. The theoretical analysis suggests that nanosilver dissolution could occur under anoxic conditions and that nanosilver may be sulfidized to form silver sulfide (Ag_2S) under strict anaerobic conditions, but more investigation with carefully-designed experiments is required to confirm the analysis. Although silver ion release is likely the main antimicrobial mechanism of nanosilver, the contributions of (ion-free) AgNPs and reactive oxygen species (ROS) generation to the overall toxicity of nanosilver must not be neglected. Several research directions are proposed to better understand the dissolution kinetics of nanosilver and its antimicrobial mechanisms under various aquatic environmental conditions.

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1. Introduction

As a naturally occurring type-B soft metal (Bell et al., 2002; Duffus, 2002), silver has an average concentration in the Earth's crust of 0.1 mg kg^{-1} (Purcell and Peters, 1998; Wood, 2011). It has long been known that silver has excellent antimicrobial activities (Cho et al., 2005; Feng et al., 2000; Maneerung et al., 2008) mainly due to silver ion (Ag^+) release (Choi and Hu, 2008; Fan and Bard, 2002; Lok et al., 2006; Russell and Hugo, 1994; Yang et al., 2012). In fact, Ag^+ is viewed as one of the most toxic metal ions in fresh water environments (Griffitt et al., 2012; Tappin et al., 2010). Thus, silver compounds, such as silver nitrate ($AgNO_3$) and silver sulphadiazine (SSD) (Atiyeh et al., 2007; Fox, 1968), are widely used in medicinal products for preventing or treating infections/diseases (Cohen et al., 2007; Fung and Bowen, 1996; Wyatt et al., 1990; Zhang et al., 2015) caused by viruses, fungi, and bacteria (Marx and Barillo, 2014; Melaiye and Youngs, 2005; Silver et al., 2006).

Because of its strong antimicrobial activities, silver is regulated by various environmental regulations as a toxic heavy metal (Das et al., 2014; Pal et al., 2015; Thurman et al., 1989). For instance, the National Secondary Drinking Water Regulations (NSDWR) in the U.S. set the non-enforceable maximum silver level for drinking water to be 0.1 mg L^{-1} (U.S. EPA, 2013). To protect aquatic life and human health, the U.S. Environmental Protection Agency (U.S. EPA) set the acute water quality criteria for silver in freshwater and saltwater to be 3.2 μg L^{-1} and 1.9 μg L^{-1}, respectively (Baker et al., 2014; U.S. EPA, 2009). The Toxicity Characteristic Leaching Procedure (TCLP) analysis considers a leachate as a hazardous waste with a silver concentration higher than 5.0 mg L^{-1} (Watts, 1998). Many nations have set the occupational silver exposure limits as well. For instance, the Permissible Exposure Limit (PEL) of silver in air is 0.01 mg m^{-3} in the U.S., Austria, and Japan, while others, such as the United Kingdom, Australia, and Sweden, use a higher value (i.e., 0.1 mg m^{-3}) (Drake and Hazelwood, 2005; NIOSH, 1992).

Nanosilver (silver nanoparticles, AgNPs, or $Ag^0_{(nano)}$) is a zero-valent silver (Ag^0) with a size less than 100 nm (Ivask et al., 2014; Nowack et al., 2011; Sotiriou and Pratsinis, 2010) in at least one of its dimensions (Benn et al., 2010; Lee et al., 2012; Schluesener and Schluesener, 2013). It has different morphologies, such as spheres, rods, and cubes (Chen and Schluesener, 2008; Tolaymat et al., 2010; Wen et al., 2014; Xie et al., 2003). It is commonly synthesized through chemical reduction methods where a silver salt, such as $AgNO_3$ (Choi et al., 2008; Saravanan et al., 2011; Song et al., 2006; Wageh et al., 2014), silver perchlorate ($AgClO_4$) (Lee and Oh, 2014; Wuithschick et al., 2013; Yin et al., 2012), or silver tetrafluoroborate ($AgBF_4$) (Lee and Oh, 2014; Prabhu and Poulose, 2012), is reduced to AgNPs by a reducing agent, such as ethylene glycol (Sun and Xia, 2002), ethanol (Zhu et al., 2013), glucose (Wageh et al., 2014), or sodium borohydride ($NaBH_4$) (Chaloupka et al., 2010; Freire et al., 2015; Maneerung et al., 2008). Coating agents or stabilizers, such as poly(vinyl pyrrolidone) (PVP) (Huynh and Chen, 2011; Khan et al., 2011; Sun and Xia, 2002), polysaccharide (Huang and Yang, 2004; Raveendran et al., 2003; Skebo et al., 2007), poly(vinyl alcohol) (PVA) (Khanna et al., 2007; Kong and Jang, 2008; Yang et al., 2012), poly(ethylene glycol) (PEG) (Rizzello and Pompa, 2014; Simakova et al., 2014, Yang et al., 2014a), or citrate (Croteau et al., 2014; Liu and Hurt, 2010; Zhang et al., 2011b), are generally used in nanosilver synthesis to prevent aggregation. Nanosilver can also be generated through many other means, such as electrochemical reduction (Rodríguez-Sánchez et al., 2000; Yin et al., 2003; Zhang et al., 2002), irradiation (Bogle et al., 2006; Dang et al., 2014; Li et al., 2006; Shin et al., 2004), or biological reduction (Ahmad et al., 2014; Amooaghaie et al., 2015; Hennebel et al., 2009; Nadagouda et al., 2014; Patel et al., 2015; Sharma et al., 2009).

Nanosilver, compared with its bulk counterpart (bulk silver), possesses stronger, longer-term, and broader spectrum antimicrobial activities (Cho et al., 2005; Kooti et al., 2015; Rai et al., 2009; Sotiriou and Pratsinis, 2010), mainly because of its high specific surface area and the continued silver ion release from nanosilver dissolution (Choi and Hu, 2008; Fabrega et al., 2009; Kittler et al., 2010; Liu and Hurt, 2010; Navarro et al., 2008; Xiu et al., 2012). As a result, nanosilver has become one of the most commonly applied engineered nanoparticles, mainly for antimicrobial purposes (Behra et al., 2013; Cascio et al., 2015; Dziendzikowska et al., 2012; Mukunthan and Balaji, 2012; Savage et al., 2013; Slane et al., 2015). It plays an important role in drinking water disinfection (Ahmed et al., 2014; Lalley et al., 2014; Li et al., 2008; Liga et al., 2011; Loo et al., 2015), wastewater treatment (An et al., 2011; Pu et al., 2014), membrane filtration (fouling control) (Diagne et al., 2012; Kim and Van der Bruggen, 2010; Koseoglu-Imer et al., 2013; Liu et al., 2013a; Yin et al., 2013; Zodrow et al., 2009), food preservation (Buzea et al., 2007; Chaudhry et al., 2008; De Moura et al., 2012; Llorens et al., 2012; Mohammed et al., 2009; Silvestre et al., 2011), medical/clinical uses (An et al., 2011; Dos Santos et al., 2014; Ge et al., 2014; Habiboallah et al., 2014; Jeeva et al., 2014; Smock et al., 2014; Wong and Liu, 2010), and anti-odor/anti-microbial textile fabrication (Abdelgawad et al., 2014; Bajpai et al., 2014; Patra and Gouda, 2013; Perera et al., 2013; Shastri et al., 2012; Xue et al., 2012) to inactivate/control undesirable microorganisms.

On account of its strong antimicrobial activities and other unique physiochemical properties, such as excellent catalytic activity (Bamoharram et al., 2009; Jiang et al., 2011), high nonlinear optical performance (Krishna et al., 2010; Rativa et al., 2008; Tilaki and Mahdavi, 2006; Zhang et al., 2007), and specific electronic properties (Cho et al., 2005; Dubey et al., 2009), silver nanoparticles have been widely used for more than 100 years (Lea, 1889, 1891; Nowack et al., 2011) with many potential applications. The Nanoparticle Database has concluded that currently 68 nanosilver products exist among the 645 commercialized single-element nanoparticles worldwide (Nanowerk LLC, 2015). Another database

claims that 435 of the 1814 nanomaterial-based consumer products in 32 countries contain silver nanoparticles (Vance et al., 2015), in agreement with the estimation that nanosilver occurs in roughly 30% of the available nanotechnology-based products (Sharma, 2014; Wijnhoven et al., 2009). The production of nanosilver in the U.S. was estimated to be in the range of 2.8 tons per year to 20.0 tons per year in 2011 (Hendren et al., 2011) and in Europe 5.5 tons per year in 2012 (Piccinno et al., 2012). Worldwide, the current supply or consumption of silver nanoparticles was predicted to be 55 tons per year (media value) (Piccinno et al., 2012) or even higher (i.e., 360 tons per year to 450 tons per year) (Future Markets, 2011; Lazareva and Keller, 2014). Considering the worldwide total annual silver supply/demand of 31,036 tons in 2013 and 32,937 tons in 2014 (The Silver Institute, 2014), around 0.2% of the silver supplied is in its nano-form.

Nanosilver in various consumer products is eventually released to sewage (Benn and Westerhoff, 2008; Farkas et al., 2011; Geranio et al., 2009; Künniger et al., 2014; Lombi et al., 2014; Lorenz et al., 2012), solid waste treatment facilities (e.g., landfills), and natural aquatic environments (Brar et al., 2010; Colman et al., 2014; Hedberg et al., 2014; Nam et al., 2014; Panyala et al., 2008; Yang et al., 2013b). It has been shown that the transport of nanosilver in the sewer system would at least partly sulfidize nanosilver (Brunetti et al., 2015; Kaegi et al., 2013), which could dramatically reduce its toxicity (Devi et al., 2015; Reinsch et al., 2012; Starnes et al., 2015) and prevent AgNPs from reaching the wastewater treatment facilities in their pristine form. However, it is still a great concern that nanosilver might adversely affect an aquatic ecosystem due to its wide usage and strong antimicrobial effects (Colman et al., 2014; Foldbjerg et al., 2015; Liu et al., 2014b; Matzke et al., 2014; Siripattanakul-Ratpukdi and Fürhacker, 2014).

The physiochemical properties of nanosilver, such as its silver ion release while dissolving, govern the antimicrobial activities of nanosilver as well as its bioavailability, dominant transformation/dissolution products, and equilibrium concentration in aquatic environments. However, the understanding of its physiochemical properties and antimicrobial mechanisms is incomplete. This review aims to summarize the current state-of-the-art research on the physiochemical behavior of nanosilver (e.g., its thermodynamics and dissolution kinetics) and its antimicrobial mechanisms in aquatic environments.

2. Gibbs free energy of formation of nanosilver [$\Delta G_{f(AgNPs)}$] in aquatic environments

2.1. Components of $\Delta G_{f(AgNPs)}$ in aquatic environments

$\Delta G_{f(AgNPs)}$ in aquatic environments is a fundamental parameter needed to understand the physiochemical behavior of nanosilver, but it is not well addressed in the literature. Commonly, the real $\Delta G_{f(AgNPs)}$ in aquatic environments is significantly underestimated (Ivanova and Zamborini, 2010) in that only the surface free energy of AgNPs is considered (Levard et al., 2012) or that it is even assumed to be zero (Liu and Hurt, 2010).

$\Delta G_{f(AgNPs)}$ in aquatic environments has at least two indispensable parts: 1) Gibbs free energy of formation of nanosilver as a pure material in a vacuum (surface free energy) and 2) the extra free energy involved when dispersing AgNPs in water. The Standard Gibbs free energy of formation of nanosilver $\left[\Delta G^0_{f(AgNPs)}\right]$ can be calculated using the Gibbs–Thomson equation (Equation (1)) (Cai et al., 1998; Plieth, 1982; Verhoeven, 1975), if only the surface free energy, or the work required to create the nanoparticle surface (Leite and Ribeiro, 2012), is considered:

$$\Delta G^0_{f(AgNPs)} = \frac{2\sigma_{Ag}\ M_{Ag}}{\rho_{Ag}\ r_{AgNPs}} = \frac{28.79\ \ kJ\ nm\ mol^{-1}}{r_{AgNPs}} \quad (1)$$

where r_{AgNPs} is the spherical radius of nanosilver (nm), σ_{Ag} is the surface free energy of silver (1.4×10^{-3} kJ m^{-2}) (Cai et al., 1998; Plieth, 1982), M_{Ag} is the atomic weight of silver (107.87 g mol^{-1}) (Aston, 1935), and ρ_{Ag} is silver density (10.49×10^6 g m^{-3}) (Khanna et al., 2007). According to Equation (1), the smallest nanosilver or one silver atom (radius ~ 0.16 nm) (Jia et al., 2012; Wang and Mak, 2003; Zhao and Mak, 2004) would have a $\Delta G^0_{f(AgNPs)}$ value of approximately 180 kJ mol^{-1}.

$\Delta G^0_{f(AgNPs)}$ might also be defined as the change in Gibbs free energy that occurs when nanosilver is formed from its element (i.e., bulk silver) in its most thermodynamically stable state under standard-state conditions (Sawyer et al., 2003; Stumm and Morgan, 1995). As an example, Gibbs free energy of bulk silver with a face-centered cubic (FCC) crystal structure (House, 2012) and icosahedral silver nanoparticles containing a certain amount of silver atoms has been reported (Sirenko and Belashchenko, 2012). Thus, $\Delta G^0_{f(AgNPs)}$ as a function of the average number of silver atoms in each nanosilver can be calculated by subtracting the Gibbs free energy of silver bulk (stable FCC phase) from the Gibbs free energy of nanosilver (Table 1) (Sirenko and Belashchenko, 2012). Here the calculated $\Delta G^0_{f(AgNPs)}$ has positive values. Since both silver nanoparticles and bulk silver normally have an FCC crystal structure with a lattice parameter of 4.07 Å (Galashev and Polukhin, 2011; House, 2012; Roy et al., 2002; Taleb et al., 1998; Theivasanthi and Alagar, 2012), each unit cell of nanosilver has four silver atoms on average. As a result, the nominal r_{AgNPs} can be roughly calculated using Equation (2):

$$r_{AgNPs} = \left[\frac{\left(4.07\text{Å}\right)^3 \times 3}{16 \times \pi} A\right]^{1/3} \quad (2)$$

where A is the average number of silver atoms in each silver nanoparticle.

Moreover, based on Equation (2), $\Delta G^0_{f(AgNPs)}$ as a function of nanosilver size can be obtained (Table 1). Therefore, it can be seen that $\Delta G^0_{f(AgNPs)}$ has a strong linear relationship with the reciprocal of r_{AgNPs} (Fig. 1) (Sirenko and Belashchenko, 2012).

In addition to the surface free energy of ideally spherical nanosilver (Equation (1)), other important types of energy of AgNPs, such as the energy associated with cavity formation in the fluid, the energy associated with the edge and corner of nanoparticles, and the energy due to perturbation (Barnard, 2006; Barnard and Zapol, 2004a; Kuna et al., 2009; Takeda et al., 2011;

Table 1
Calculated Standard Gibbs free energy of formation of nanosilver [$\Delta G^0_{f(AgNPs)}$] as a function of its radius and silver atom number.

r_{AgNPs}[a], nm	A[b], #	$\Delta G^0_{f(AgNPs)}$[c], J mol^{-1}
0.37	13	83,000
0.60	55	48,600
0.84	147	34,400
1.08	309	26,700
1.31	561	21,700
1.55	923	18,600

Note.
[a] Spherical radius of silver nanoparticles calculated using Equation (2).
[b] Number of silver atoms in each silver nanoparticle.
[c] Calculated by subtracting the Gibbs free energy of bulk silver (crystalline silver, FCC phase, 298 K) from the Gibbs free energy of icosahedral silver nanoparticles (298 K) (Sirenko and Belashchenko, 2012).

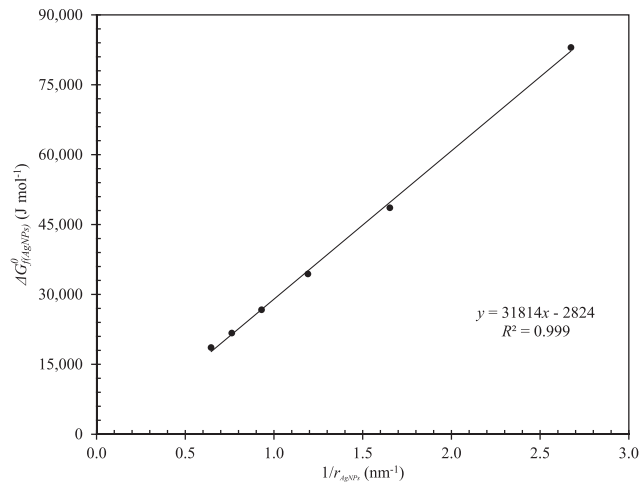

Fig. 1. Standard Gibbs free energy of formation of silver nanoparticles [$\Delta G^0_{f(AgNPs)}$] as a function of particle radius (r_{AgNPs}) (Sirenko and Belashchenko, 2012).

Table 2
Calculated Gibbs free energy of formation of silver nanoparticles [$\Delta G_{f(AgNPs)}$] in aquatic environments with different particle radii.

r_{AgNPs}[a], nm	ΔE[b], V	E[c], V	$\Delta G_{f(AgNPs)}$[d], J mol^{-1}
6.2	−0.1075	0.275	50,635
8.4	−0.0900	0.292	48,946
10.3	−0.0650	0.317	46,534
13.3	−0.0500	0.332	45,087
14.0	−0.0410	0.341	44,219
19.0	−0.0120	0.370	41,420
22.8	−0.0003	0.382	40,292

Note.
[a] Spherical radius of nanosilver.
[b] Shift in the electrode potential of silver nanoparticles versus bulk silver, read from "Figure 3" reported by Ivanova and Zamborini (2010). ΔE is calculated by subtracting the electron potential of bulk silver from the electron potential of nanosilver.
[c] The calculated electrode potential of silver nanoparticles, based on the electrode potential of bulk silver (0.382 V). The electron potential of bulk silver is assumed to be the same as the electron potential of nanosilver with an average diameter of 45.5 nm (Ivanova and Zamborini, 2010).
[d] $\Delta G_{f(AgNPs)}$ in aquatic phase, calculated by $\Delta G_{f(AgNPs)} = -Z{\cdot}F{\cdot}E + 77{,}120$ J mol^{-1} (the Nernst equation), where Z is the amount of electrons (e^-) transferred (1 mol), F is the Faraday constant (96,485 C mol^{-1}), and 77,120 J mol^{-1} is the Standard Gibbs free energy of formation of $Ag^+_{(aq)}$.

Yang et al., 2010), should be considered and further clarified, especially when the nanoparticles are small (Barnard and Zapol, 2004b). Particularly, shape or morphology (as well as the crystal structure) of nanosilver has a significant impact on its thermodynamic properties. AgNPs are usually treated as ideal spheres (Cai et al., 1998; Levard et al., 2012) while real nanosilver is generally irregularly shaped (Pal et al., 2007; Theivasanthi and Alagar, 2012). AgNPs with different shapes have a potential to reform to their equilibrium shape for energy minimization (Cao and Wang, 2011; Henry, 2007) and the energy associated with this potential, the Gibbs–Wulff energy (Gräf et al., 2000), should be taken into account (Meier et al., 2005).

Furthermore, when nanosilver forms a suspension in water, it will associate with even more types of important energy. Nanosilver is usually coated by capping agents (for particle stabilization) or covered by natural organic matter (NOM) in aquatic environments. In addition, the surface of AgNPs in aquatic environments might not be Ag^0 but most likely a very thin layer of silver compounds (e.g., silver monoxide or Ag_2O). Besides, the nanosilver surface is usually charged in water and thus a new energy term associated with electrostatic interactions (e.g., the repulsion energy) needs to be considered (Amovilli, 1994; Floris and Tomasi, 1989; Wang and Li, 2009). All those factors would have a significant impact on the actual $\Delta G_{f(AgNPs)}$ in aquatic environments and should not be neglected.

2.2. Calculation of $\Delta G_{f(AgNPs)}$ in aquatic environments

Considerable disagreement in the literature exists as to how to calculate the $\Delta G_{f(AgNPs)}$ in aquatic environments. An experiment was conducted to measure the shift in the electrode potential (ΔE) of nanosilver versus bulk silver (Ivanova and Zamborini, 2010), from which the $\Delta G_{f(AgNPs)}$ in aquatic environments can be calculated via the Nernst equation (Table 2) (Ivanova and Zamborini, 2010; Stumm and Morgan, 1995). Furthermore, the Standard electrode potential (E^0) of the half-reaction of $Ag^+_{(aq)} + e^- \rightarrow Ag^0_{(nano)}$ was reported to be between −1.8 V and 0.8 V (Förster, 2003), suggesting that the $\Delta G^0_{f(AgNPs)}$ in aquatic environments would be between 0 kJ mol^{-1} and 251 kJ mol^{-1}. In both cases, the calculated $\Delta G_{f(AgNPs)}$ [or $\Delta G^0_{f(AgNPs)}$] in aquatic environments is generally positive.

$\Delta G_{f(AgNPs)}$ in aquatic environments can also be calculated using the equilibrium constant (Equations (3) and (4)) of the redox reaction between dissolved molecular oxygen (O_2) and nanosilver (Sawyer et al., 2003):

$$\Delta G_r = -R\ T\ \ln K \tag{3}$$

$$K = \frac{\left[Ag^+_{(aq)}\right]}{\left[H^+_{(aq)}\right]\left[O_{2(aq)}\right]^{1/4} C^{\theta}_{AgNPs(E)}} \tag{4}$$

where ΔG_r is the Gibbs free energy change of the redox reaction (J mol^{-1}), R is the universal gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature (K), K is the equilibrium constant, $C_{AgNPs(E)}$ is the equilibrium concentration of nanosilver (mol L^{-1}), $[H^+_{(aq)}]$ is the equilibrium concentration of protons (H^+) (mol L^{-1}), $[O_{2(aq)}]$ is the equilibrium concentration of O_2 (mol L^{-1}), $[Ag^+_{(aq)}]$ is the equilibrium concentration of Ag^+ (mol L^{-1}), and θ is a coefficient related to the properties of nanosilver. The value of θ falls into the range of [0, 1]. When nanosilver is treated as a normal solid or bulk silver, $\theta = 0$, while when it is viewed as a true solute, $\theta = 1$. Actually, nanosilver with a size less than 1.5 nm will show strong molecular characteristics (or, θ is close to 1). On the other hand, crystalline characteristics dominate for nanosilver with a size larger than 2.0 nm (or, θ is close to 0). However, for nanosilver with a size in the range of 1.5 nm–2.0 nm, its molecular and crystal characteristics are comparable (or, θ is between 0 and 1) (Kiss et al., 2011). Equations (3) and (4) have been also successfully applied for calculating the Gibbs free energy of formation of zinc dioxide nanoparticles ($nanoZnO_2$) in aquatic environments (Lah and Johan, 2011; Wolanov et al., 2013). Although nanosilver is generally larger than 2.0 nm, the $[Ag^+_{(aq)}]$ is strongly related to the size of nanosilver, suggesting that nanosilver might be roughly treated as a true solute (i.e., $\theta \approx 1$) in aquatic environments (Zhang et al., 2011b). The calculated $\Delta G_{f(AgNPs)}$ in aquatic environments via this means is either positive (Table 3a) (Zhang et al., 2011b) or negative (Table 3b) (Liu and Hurt, 2010; Liu et al., 2010).

Finally, one study revealed that the $\Delta G_{f(AgNPs)}$ of Daxad 19 coated nanosilver in distilled water decreased with its size. AgNPs with diameters of 4.5 nm, 7.5 nm, and 15.0 nm had $\Delta G_{f(AgNPs)}$ values of -10.18×10^3 J mol^{-1} (water temperature 353 K), -10.88×10^3 J mol^{-1} (water temperature 373 K), and -13.07×10^3 J mol^{-1} (water temperature 393 K), respectively

Table 3a
Gibbs free energy of formation of nanosilver [$\Delta G_{f(AgNPs)}$] in aquatic environments calculated using equilibrium constants.

r_{AgNPs}[a], nm	$C_{AgNPs(0)}$[b], mg L^{-1}	$C_{AgNPs(E)}$[c], mg L^{-1}	K[d]	$\Delta G_{f(AgNPs)}$[e], J mol^{-1}	$\overline{\Delta G_{f(AgNPs)}}$[f], J mol^{-1}
10	0.300	0.180	2,124,088	−9,436	−(10,044 ± 859)
10	0.600	0.426	1,301,378	−10,651	
20	0.300	0.231	951,701	−11,427	−(11,571 ± 204)
20	0.600	0.474	846,947	−11,716	
40	0.300	0.270	354,015	−13,878	−(14,181 ± 430)
40	0.600	0.552	277,055	−14,486	

Note.
[a] Spherical radius of nanosilver.
[b] Initial nanosilver concentration.
[c] Equilibrium nanosilver concentration, read from "Table S3" reported by Zhang et al. (2011b).
[d] Equilibrium constant of the redox reaction between dissolved molecular oxygen (O_2) and nanosilver (Equation (4), $\theta = 1$), assuming O_2 concentration (7.8 mg L^{-1}) and proton concentration ($10^{-5.6}$ mol L^{-1}) were constant.
[e] $\Delta G_{f(AgNPs)}$ in aquatic phase, calculated by Equation (3).
[f] Calculated average Gibbs free energy of formation of nanosilver [$\overline{\Delta G_{f(AgNPs)}}$] in aquatic phase, reported as average value ± half range. The experiment was conducted at 298 K.

Table 3b
Gibbs free energy of formation of nanosilver [$\Delta G_{f(AgNPs)}$] in aquatic environments calculated using equilibrium constants.

r_{AgNPs}[a], nm	$C_{AgNPs(0)}$[b], mg L^{-1}	$\%C_{AgNPs(E)}$[c], %	K[d]	$\Delta G_{f(AgNPs)}$[e], J mol^{-1}	$\overline{\Delta G_{f(AgNPs)}}$[f], J mol^{-1}
2.4	0.20	0.01	3.69×10^{11}	71,614	68,580 ± 4,291
2.4	0.05	0.01	3.19×10^{10}	65,546	
30.0	0.05	30.00	1.37×10^{6}	−10,532	N/A

Note.
[a] Spherical radius of nanosilver.
[b] Initial nanosilver concentration.
[c] Percentage of nanosilver concentration against total silver concentration at equilibrium, read from "Figure 5A" ($r_{AgNPs} = 2.4$ nm) reported by Liu and Hurt (2010) and "Figure 3D" ($r_{AgNPs} = 30.0$ nm) reported by Liu et al. (2010).
[d] Equilibrium constant of the redox reaction between dissolved molecular oxygen (O_2) and nanosilver (Equation (4), $\theta = 1$), assuming O_2 concentration (9.1 mg L^{-1}) and proton concentration ($10^{-5.56}$ mol L^{-1}) were constant.
[e] $\Delta G_{f(AgNPs)}$ in aquatic phase, calculated by Equation (3).
[f] Calculated average Gibbs free energy of formation of silver nanoparticles [$\overline{\Delta G_{f(AgNPs)}}$] in aquatic phase, reported as average value ± half range. The experiment was conducted at 298 K.

(calculated using Equation (3)) (Lah and Johan, 2011).

All these studies showed a universal trend: the overall $\Delta G_{f(AgNPs)}$ in aquatic environments increases as particle size decreases, since smaller particles have higher specific surface areas and hence more surface free energy (Cai et al., 1998; Plieth, 1982; Verhoeven, 1975). However, as discussed above, data in the current literature are somewhat controversial because nanosilver with comparable sizes in aquatic environments can have either negative or positive $\Delta G_{f(AgNPs)}$ values. Consequently, some factors (e.g., surface coating and charge) other than the surface free energy contribute significantly to the $\Delta G_{f(AgNPs)}$ in aquatic environments and must be carefully considered.

Therefore, more well-designed experimental work is needed to quantify how the actual $\Delta G_{f(AgNPs)}$ in real aquatic environments is impacted by aquatic biochemical conditions as well as the particle size, morphology, and/or other surface properties of nanosilver. The new findings will provide a more comprehensive understanding of the thermodynamic characteristics of nanosilver in aquatic environments.

3. Dissolution of silver nanoparticles in aquatic environments

3.1. General discussion

Thermodynamic considerations can help to assess whether silver ion release is possible or not, but thermodynamics do not allow us to evaluate whether these processes occur spontaneously in the real environment, or on what timescale the dissolution occurs (Sawyer et al., 2003; Stumm and Morgan, 1995). The question of

Table 4
Important terminal electron acceptors and main wastewater treatment processes under aerobic, anoxic, and anaerobic conditions.

Condition	Potential terminal electron acceptors	Significance in wastewater treatment
Aerobic/oxic	Dissolved molecular oxygen (O_2)	Complete organic matter oxidization (e.g., COD removal) and biological nutrient removal (e.g., nitrification, microbial phosphorus uptake, and microbial polyphosphate regeneration)
Anoxic	Inorganic nitrogen [mainly nitrate (NO_3^-) and nitrite (NO_2^-) but other species such as nitric oxide (NO), nitrous oxide (N_2O), and molecular nitrogen (N_2) may be considered]	Denitrification
Anaerobic	Proton (H^+), ferric ion (Fe^{3+}), inorganic sulfur [mainly sulfate (SO_4^{2-}) and sulfite (SO_3^{2-}) but other species such as thiosulfate ($S_2O_3^{2-}$), dithionite ($S_2O_4^{2-}$), and elemental sulfur (S^0) may be considered], and inorganic carbon [e.g., carbon dioxide (CO_2), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-})]	Soluble organic matter removal, insoluble organic matter stabilization, methane generation, and biological nutrient removal (e.g., phosphorus release from phosphorus accumulating organisms or PAOs)

Table 5
Thermodynamic properties of selected half-reactions.

Half-reaction	Redox couple (1 e^-)	ΔG_r^{0}[a], kJ mol^{-1}	$\Delta G_r'$[b], kJ mol^{-1}	E'[c], V
$\frac{1}{2}O_{3(g)} + H^+_{(aq)} + e^- = \frac{1}{2}H_2O_{(l)} + \frac{1}{2}O_{2(g)}$	$\frac{1}{6}O_{3(g)}/\frac{1}{2}H_2O_{(l)}$[d]	−200.190	−160.236	1.661
$\frac{1}{2}O_{3(g)} + H^+_{(aq)} + e^- = \frac{1}{2}H_2O_{(l)} + \frac{1}{2}O_{2(aq)}$	$\frac{1}{6}O_{3(g)}/\frac{1}{2}H_2O_{(l)}$[e]	−192.030	−152.076	1.576
$\frac{1}{2}HOCl_{(aq)} + \frac{1}{2}H^+_{(aq)} + e^- = \frac{1}{2}H_2O_{(l)} + \frac{1}{2}Cl^-_{(aq)}$	$\frac{1}{2}HOCl_{(aq)}/\frac{1}{2}Cl^-_{(aq)}$	−144.197	−124.220	1.287
$\frac{1}{3}NO^-_{2(aq)} + \frac{4}{3}H^+_{(aq)} + e^- = \frac{1}{6}N_{2(g)} + \frac{2}{3}H_2O_{(l)}$	$\frac{1}{3}NO^-_{2(aq)}/\frac{1}{6}N_{2(g)}$	−145.720	−92.448	0.958
$\frac{1}{4}O_{2(aq)} + H^+_{(aq)} + e^- = \frac{1}{2}H_2O_{(l)}$	$\frac{1}{4}O_{2(aq)}/\frac{1}{2}H_2O_{(l)}$	−122.670	−82.716	0.857
$\frac{1}{4}O_{2(g)} + H^+_{(aq)} + e^- = \frac{1}{2}H_2O_{(l)}$	$\frac{1}{4}O_{2(aq)}/\frac{1}{2}H_2O_{(l)}$	−118.590	−78.636	0.815
$Ag^+_{(aq)} + e^- = Ag^0_{(bulk)}$	$Ag^+_{(aq)}/Ag^0_{(bulk)}$	−77.120	−77.120	0.799
$Fe^{3+}_{(aq)} + e^- = Fe^{2+}_{(aq)}$	$Fe^{3+}_{(aq)}/Fe^{2+}_{(aq)}$	−74.270	−74.270	0.770
$\frac{1}{5}NO^-_{3(aq)} + \frac{6}{5}H^+_{(aq)} + e^- = \frac{1}{10}N_{2(g)} + \frac{3}{5}H_2O_{(l)}$	$\frac{1}{5}NO^-_{3(aq)}/\frac{1}{10}N_{2(g)}$	−120.040	−72.095	0.747
$\frac{1}{8}NO^-_{3(aq)} + \frac{5}{4}H^+_{(aq)} + e^- = \frac{1}{8}NH^+_{4(aq)} + \frac{3}{8}H_2O_{(l)}$	$\frac{1}{8}NO^-_{3(aq)}/\frac{1}{8}NH^+_{4(aq)}$	−84.946	−35.004	0.363
$\frac{1}{6}NO^-_{2(aq)} + \frac{4}{3}H^+_{(aq)} + e^- = \frac{1}{6}NH^+_{4(aq)} + \frac{1}{3}H_2O_{(l)}$	$\frac{1}{6}NO^-_{2(aq)}/\frac{1}{6}NH^+_{4(aq)}$	−86.088	−32.817	0.340
$\frac{1}{4}CO_{2(g)} + H^+_{(aq)} + e^- = \frac{1}{24}C_6H_{12}O_{6(aq)} + \frac{1}{4}H_2O_{(l)}$	$\frac{1}{4}CO_{2(g)}/\frac{1}{24}C_6H_{12}O_{6(aq)}$	1.083	41.036	−0.425
$H^+_{(aq)} + e^- = \frac{1}{2}H_{2(g)}$	$H^+_{(aq)}/\frac{1}{2}H_{2(g)}$	0.000	39.954	−0.414
$\frac{1}{2}Fe^{2+}_{(aq)} + e^- = \frac{1}{2}Fe^0_{(s)}$	$\frac{1}{2}Fe^{2+}_{(aq)}/\frac{1}{2}Fe^0_{(s)}$	39.435	39.435	−0.409
$\frac{1}{8}CO_{2(g)} + \frac{1}{8}HCO^-_{3(aq)} + H^+_{(aq)} + e^- = \frac{1}{8}CH_3COO^-_{(aq)} + \frac{3}{8}H_2O_{(l)}$	$\frac{1}{4}CO_{2(g)}/\frac{1}{8}CH_3COO^-_{(aq)}$	−12.465	27.489	−0.285
$\frac{1}{8}CO_{2(g)} + H^+_{(aq)} + e^- = \frac{1}{8}CH_{4(g)} + \frac{1}{4}H_2O_{(l)}$	$\frac{1}{8}CO_{2(g)}/\frac{1}{8}CH_{4(g)}$	−16.346	23.608	−0.245
$\frac{1}{8}SO^{2-}_{4(aq)} + \frac{19}{16}H^+_{(aq)} + e^- = \frac{1}{16}H_2S_{(g)} + \frac{1}{16}HS^-_{(aq)} + \frac{1}{2}H_2O_{(l)}$	$\frac{1}{8}SO^{2-}_{4(aq)}/\frac{1}{8}HS^-_{(aq)}$	−26.846	20.600	−0.214
$\frac{1}{6}SO^{2-}_{3(aq)} + \frac{5}{4}H^+_{(aq)} + e^- = \frac{1}{12}H_2S_{(g)} + \frac{1}{12}HS^-_{(aq)} + \frac{1}{2}H_2O_{(l)}$	$\frac{1}{6}SO^{2-}_{3(aq)}/\frac{1}{6}HS^-_{(aq)}$	−39.269	10.673	−0.111

Note.
[a] ΔG_r^0 is the Standard Gibbs free energy change of each half-reaction.
[b] $\Delta G_r'$ is the Gibbs free energy change of each half-reaction under biochemical standard state conditions.
[c] E' is the electrode potential of the redox couple under biochemical standard state conditions, calculated by $\Delta G_r' = -Z \cdot F \cdot E'$ (the Nernst equation), where Z is the amount of electrons (e^-) transferred (1 mol), and F is the Faraday constant (96,485 C mol^{-1}).
[d] Oxygen generated by this half-reaction is in a gas state.
[e] Oxygen generated by this half-reaction is in an aqueous state.

timescale is very important as this eventually determines the exposure of the environment to a certain form of silver (e.g., nanosilver or silver ions) and the corresponding concentrations. For instance, once formed, Ag_2S may not be the most thermodynamically stable form of silver compounds, but it still will persist in aquatic environments due to its intensely slow reaction kinetics. It is easy to misunderstand this concept and inappropriately predict how long it will take nanosilver to completely dissolve in oxygenated water using thermodynamic analysis alone (Zhang et al., 2011b).

Silver ion release is one of the most important steps of nanosilver transformation in aquatic environments. Without Ag^+ release, the majority of the important nanosilver transformation products, such as silver chloride (AgCl), Ag_2S, Ag_2O, and silver(I) complexes, would not form. In addition, the main antimicrobial mechanism of nanosilver is generally ascribed to silver ion release (De Matteis et al., 2015; Le Ouay and Stellacci, 2015; Xiu et al., 2012). As a result, to better understand the fate and behavior of nanosilver in aquatic systems, research on silver ion release, its kinetics, and how it is affected by environmental factors should be well summarized.

Many factors in an aquatic environment affect nanosilver dissolution, but among them, the biochemical environment might be determinative (Grady et al., 2011). Based on the terminal electron acceptor species, aquatic environments can be divided into aerobic (oxic), anoxic, and anaerobic conditions (Table 4) (Grady et al., 2011; Metcalf and Eddy, 2014; Sawyer et al., 2003; Stumm and Morgan, 1995). The dissolution patterns and kinetics of silver nanoparticles could be quite different under such varying redox conditions.

The ΔG_r of a hypothetical reaction between nanosilver and a specific electron acceptor can be used to predict whether the oxidative dissolution of silver nanoparticles would occur meaning whether nanosilver can be oxidized by this electron acceptor. A negative value of ΔG_r indicates the dissolution of silver nanoparticles is thermodynamically feasible (Haynie, 2008; Sawyer et al., 2003; Stumm and Morgan, 1995). Table 5 presents the ΔG_r and the electrode potentials of the redox couples of some important half-reactions related to AgNP dissolution in aquatic environments (Grady et al., 2011; Metcalf and Eddy, 2014; Rittmann and McCarty, 2001; Stumm and Morgan, 1995).

3.2. Nanosilver dissolution under aerobic conditions: modeling

The overall redox reaction between dissolved molecular oxygen and nanosilver in water is described in the following equation (Hoskins et al., 2002; Liu and Hurt, 2010; López-Heras et al., 2015):

$$Ag^0_{(nano)} + \frac{1}{4}O_{2(aq)} + H^+_{(aq)} = Ag^+_{(aq)} + \frac{1}{2}H_2O_{(l)} \tag{5}$$

This reaction is thermodynamically favorable, indicated by the negative value of ΔG_r under biochemical standard-state conditions ($\Delta G_r'$) (LaRowe and Helgeson, 2007; Sawyer et al., 2003; Wood, 1988). Water is produced through the formation of reactive oxygen intermediates, such as hydrogen peroxide (H_2O_2), and the downstream reactions between the intermediates and nanosilver. The whole process can be represented by a two-step reaction (Liu and Hurt, 2010; Liu et al., 2010):

$$H^+_{(aq)} + \frac{1}{4}O_{2(aq)} \xrightarrow{\text{AgNPs(slow)}} Ag^+_{(aq)} + \text{Intermediates} \xrightarrow{\text{AgNPs (fast)}} Ag^+_{(aq)} + \frac{1}{2}H_2O_{(l)} \tag{6}$$

Since the intermediates (e.g., H_2O_2) are more reactive and stronger than O_2 as oxidants, the second step is much faster than

the first one. Consequently, the first step is the rate-limiting step. The redox reaction also indicates that nanosilver dissolution requires the presence of protons and is more favorable under acidic conditions, which was experimentally confirmed (Hedberg et al., 2014).

Quantitatively, nanosilver dissolution has been usually described by a pseudo-first-order reaction kinetics (Liu and Hurt, 2010; Liu et al., 2010; Sharma et al., 2014; Zhang et al., 2011b):

$$-\frac{dC_{AgNPs(t)}}{dt} = k\ C_{AgNPs(t)} \quad \text{or} \quad C_{AgNPs(t)} = C_{AgNPs(0)}\ e^{-k\,t} \tag{7}$$

where t is the reaction time (h), k is the pseudo-first-order reaction rate constant (h^{-1}), $C_{AgNPs(t)}$ is the AgNP concentration at time t (mg L^{-1}), and $C_{AgNPs(0)}$ is the initial AgNP concentration (mg L^{-1}). The half-life of AgNPs ($t_{1/2}$) is independent of $C_{AgNPs(0)}$ and can be expressed as (Connors, 1990; Stumm and Morgan, 1995):

$$t_{1/2} = \frac{\ln 2}{k} \tag{8}$$

Furthermore, the concentration of released Ag^+ over time can be predicted using Equation (9) (Sawyer et al., 2003; Stumm and Morgan, 1995; Zhang et al., 2011b):

$$C_{Ag^+(t)} = C_{AgNPs(0)(1-e^{-k\cdot t})} \tag{9}$$

where $C_{Ag^+(t)}$ is the concentration of released Ag^+ at time t (mg L^{-1}).

However, the pseudo-first-order kinetic assumption might not be valid for the whole nanosilver dissolution process in water [Fig. 2A (Zhang et al., 2011b) and 2B (Liu and Hurt, 2010)], as the reaction rate "constant" k is actually not constant over time. The pseudo-first-order kinetic model also cannot well explain the oxidation of nanosilver by other oxidants such as sodium hydrochloride (NaOCl) (Fig. 2C) (Yuan et al., 2013a). In addition, one example showed that the Tween 80 coated nanosilver in a natural river matrix released silver ions relatively quickly for the first 6 h to reach a silver ion concentration of 40 μg L^{-1} (roughly equal to 3% of the total silver amount). This value was maintained for the following 2 – 3 days (Figure 5 in the reference) (Li and Lenhart, 2012), indicating that the whole silver ion release process cannot be well-modeled using the pseudo-first-order

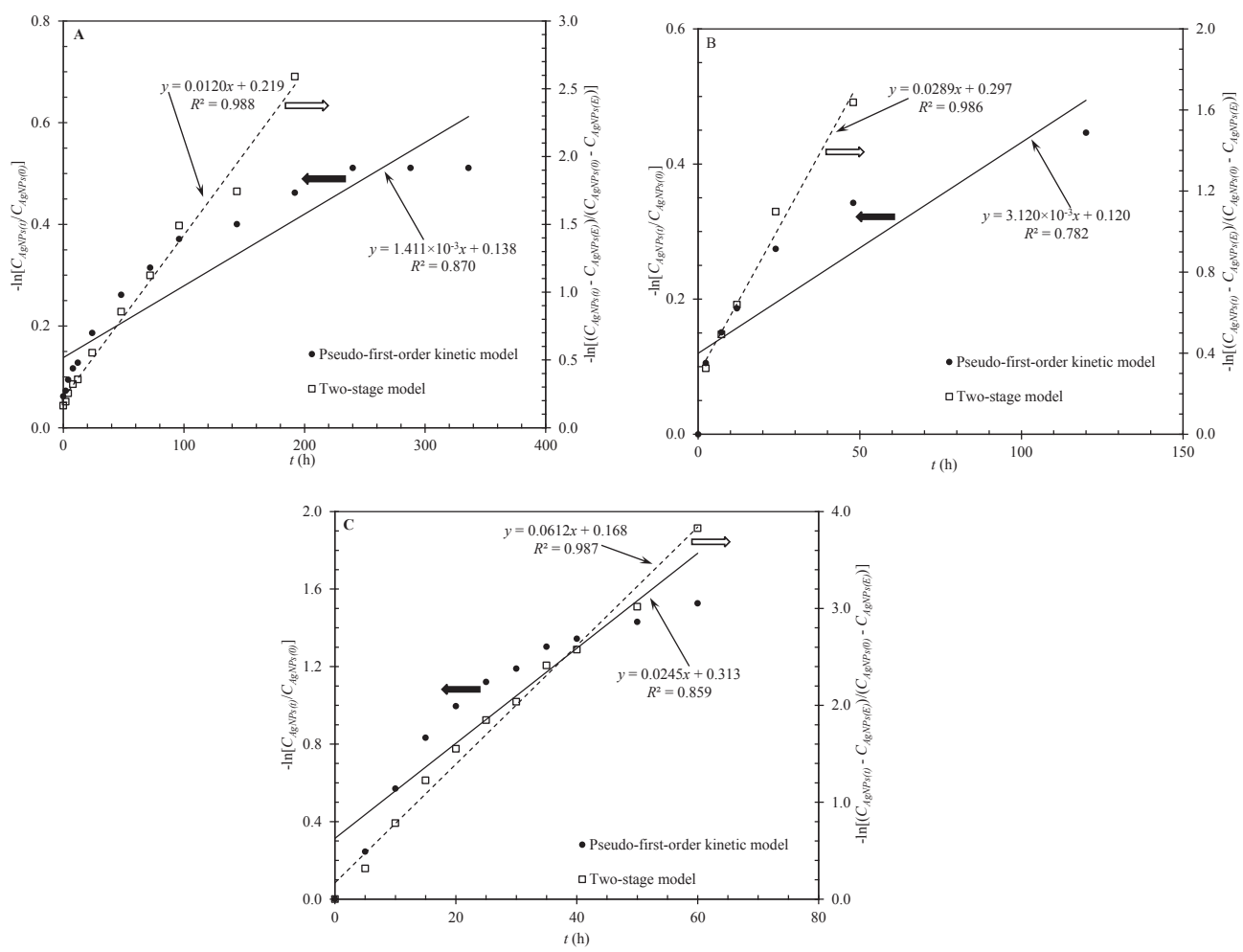

Fig. 2. The experimental data (●) and simulation results (solid line) of nanosilver dissolution based on the pseudo-first-order kinetic model. The experimental data (□) and simulation results (dashed line) of nanosilver dissolution based on the two-stage model. $C_{AgNPs(t)}$ indicates the nanosilver concentration at time t. (A): Initial nanosilver concentration $C_{AgNPs(0)} = 0.3$ mg L^{-1}, initial nanosilver spherical radius $r_{AgNPs} = 10$ nm, temperature $T = 298$ K, dissolved molecular oxygen concentration $[O_{2(aq)}] = 7.8$ mg L^{-1}, and pH = 5.6 (Zhang et al., 2011b). (B): Initial nanosilver concentration $C_{AgNPs(0)} = 0.05$ mg L^{-1}, initial nanosilver spherical radius $r_{AgNPs} = 2.4$ nm, temperature $T = 277$ K, dissolved molecular oxygen concentration $[O_{2(aq)}] = 9.1$ mg L^{-1}, and pH = 5.68 (Liu and Hurt, 2010). (C): Initial nanosilver concentration $C_{AgNPs(0)} = 5$ mg L^{-1}, equilibrium nanosilver concentration $C_{AgNPs(E)} = 1$ mg L^{-1} (assumed), sodium hypochlorite (NaOCl) concentration $C_{NaOCl} = 20$ mM (in a borate buffer solution), initial nanosilver spherical radius $r_{AgNPs} = 10$ nm, pH = 7.5, and temperature = 298 K (thermostatic) (Yuan et al., 2013a).

kinetics.

On the other hand, it can be clearly seen from Fig. 2 that if the initial nanosilver concentration reaches or exceeds its solubility (saturation), the dissolution of nanosilver falls into two stages. In the first stage, not all the nanosilver participates in its dissolution and only the "active" part of nanosilver (i.e., the available active surface of AgNPs) should be considered when developing the kinetic model. In other words, the nanosilver dissolution (first stage) follows a "modified" first-order kinetics when only the "active" part of nanosilver participates (Equation (10)). In the second stage, the dissolution ceases due to the solubility limit of nanosilver and/or significant aggregation, yielding a zero reaction rate (no apparent silver ion release). As a result, the whole nanosilver dissolution process can be simulated using Equation (10) (Grady et al., 2011; Kittler et al., 2010; Sawyer et al., 2003):

$$\begin{aligned} & C_{AgNPs(t)} - C_{AgNPs(E)} \\ & = \left[C_{AgNPs(0)} - C_{AgNPs(E)}\right] e^{-k\,t} \quad \text{if} \quad C_{AgNPs(0)} \geq C_{AgNPs(t)} > C_{AgNPs(E)} \\ & \frac{d}{dt} C_{AgNPs(t)} = 0 \qquad\qquad\qquad\qquad \text{if} \quad C_{AgNPs(t)} = C_{AgNPs(E)} \end{aligned} \tag{10}$$

where $C_{AgNPs(E)}$ is the equilibrium nanosilver concentration for its dissolution process (mg L^{-1}).

This two-stage model fits well with the data in the literature [Fig. 2A (Zhang et al., 2011b) and 2B (Liu and Hurt, 2010)]. It can also reasonably describe the oxidization of nanosilver by NaOCl (Fig. 2C) (Yuan et al., 2013a). In addition, during the oxidative dissolution process, nanosilver might reform from the released silver ions continuously and substantially (Glover et al., 2011; He et al., 2011; Li and Lenhart, 2012), suggesting that apparently not all the nanosilver is responsible for silver release, but only the "active" part of nanosilver should be considered when developing the dissolution model. Furthermore, as mentioned above, nanosilver dissolution depends on its initial concentration. If this concentration is lower than the solubility of nanosilver (which is size dependent in the nano-range and can also be affected by the presence of silver(I) complexing ligands as well as the physicochemical properties of the solution), all nanosilver will eventually dissolve. In this case, Equation (9) would be valid for modeling the nanosilver dissolution process.

Evidently, the dissolution of nanosilver in aquatic environments is very complex because it is impacted by many factors such as environmental conditions, particle morphology, particle size distribution, aggregation status, and the surface area to mass ratio (He et al., 2013). For instance, in oxygenated water, nanosilver is quickly oxidized and a layer of Ag_2O can form on its surface, generating a so-called "core–shell" structure (Chen et al., 2006; Li et al., 2010; Sukhov et al., 1997; Yin et al., 2002). The Ag_2O layer (the "shell") will significantly affect the dissolution of nanosilver (the "core") as it will act as a barrier to impede the reaction between nanosilver and dissolved molecular oxygen/protons by reducing the available surface of nanosilver for dissolution. Thus, after the formation of the Ag_2O layer, nanosilver will dissolve following a different pattern compared with the pristine AgNPs. To precisely predict the silver ion release process, all these factors should be well considered. Therefore, such a complex reaction is more than the two-stage model can fully explain. However, in general, the two-stage model as represented by Equation (10), even though simple and straight forward, can be used to predict the silver ion release process with good accuracy under relatively simple aquatic environmental conditions.

3.3. Nanosilver dissolution under aerobic conditions: influencing factors

An important factor that determines Ag^+ release from nanosilver dissolution is particle size. At the same total silver concentration, AgNPs with a smaller size have higher specific surface areas and hence more surface active sites for Ag^+ production (Liu and Hurt, 2010; Zhang et al., 2011b). Not surprisingly, smaller AgNPs result in faster Ag^+ release (Dobias and Bernier-Latmani, 2013; Taghavy et al., 2013; Wang et al., 2014). In addition, because both the $\Delta G_{f(AgNPs)}$ and the equilibrium constant of nanosilver dissolution decrease with particle size, small silver nanoparticles tend to have higher equilibrium Ag^+ concentrations than large ones (Liu and Hurt, 2010). For instance, one study revealed that in natural water bodies the dissolution of 5-nm nanosilver was more significant than the dissolution of 10-nm nanosilver, which, in turn, tended to release more silver ions than 50-nm nanosilver (Dobias and Bernier-Latmani, 2013). This explains at least to some extent why at the same overall silver concentrations, nanosilver with a smaller size usually shows stronger antimicrobial activities (Chaloupka et al., 2010; Choi and Hu, 2008; Hamilton et al., 2014; Park et al., 2011; Shi et al., 2013; Wang et al., 2014).

Furthermore, the size-dependent toxicity of AgNPs (Gliga et al., 2014; Kennedy et al., 2012; Kim et al., 2012; Lok et al., 2007; Morones et al., 2005) indicates that the total available surface of nanosilver most likely determines the kinetics of its dissolution. However, it is still not very clear whether smaller AgNPs also dissolve faster than larger ones when surface normalized, which then would be a nano-effect (possibly caused by lattice strain which may become important at particle sizes <10 nm). Therefore, it seems that the kinetics of the nanosilver dissolution process might be determined by its available active surface, but the nano-effect might also significantly affect this process, especially when the particles are small enough.

In aquatic environments, particle size of nanosilver is affected by its aggregation, a process where over time its size increases due to the formation of larger particles. Generally speaking, since nanosilver in oxygenated water undergoes relatively fast dissolution during the very early dissolution process (Liu and Hurt, 2010; Zhang et al., 2011b), aggregation does not significantly affect the initial dissolution, which might be well-modeled using a first-order kinetics. However, the dissolution process is significantly complicated by aggregation later on (Kent and Vikesland, 2012), which could substantially slow down nanosilver dissolution (Liu and Hurt, 2010; Zhang et al., 2011b). Finally, when the particle size is large enough, dissolution ceases (Equation (10)). On the other hand, if the aggregation is limited or negligible for the whole dissolution process, a first-order reaction kinetics can be used for datum fitting. For instance, a first-order kinetics could explain the dissolution process of nanosilver in an air-saturated phosphate buffer very well as the aggregation was inhibited because the AgNPs were immobilized on glass substrates (Kent and Vikesland, 2012).

Aggregation also explains why the initial nanosilver concentration affects silver ion release kinetics. For instance, when other parameters are fixed, the higher the initial nanosilver concentration, the slower the initial silver ion release (Zhang et al., 2011b). This is because AgNPs with higher initial concentrations tend to aggregate faster, leading to less surface area available for dissolution. According to the Stocks–Einstein equation, a high nanosilver concentration might further decrease the speed of silver ion release by inhibiting the collision probability between individual AgNPs and protons/oxygen (Mackay et al., 2003).

In addition to particle size, nanosilver dissolution is affected by many other factors, such as pH, water temperature, ionic strength,

electrolyte composition, the presence of surfactants, and the concentration of silver(I)-complexing/precipitating ligands (e.g., Cl^-, S^{2-}, and HS^-) (Behra et al., 2013; Jin et al., 2010; Leo et al., 2013; Levard et al., 2013b; Liu et al., 2011; Pokhrel et al., 2013). For instance, anions could efficiently accelerate the dissolution speed of nanosilver by forming silver(I) complexes or precipitates when reacting with silver ions (Chambers et al., 2014; Levard et al., 2013b; Sawyer et al., 2003; Yin et al., 2014). Surface coating is another factor that plays an important role in nanosilver dissolution. In oxic natural water bodies, dissolution of PVP coated and tannic acid coated nanosilver is more significant than that of citrate coated AgNPs (Dobias and Bernier-Latmani, 2013). Regarding the effects of water temperature on Ag^+ release, the Arrhenius equation makes an accurate prediction (Laidler, 1984; López-Heras et al., 2015; Peleg et al., 2012). As an example, in air-saturated water (pH 5.68) with an incubation time of 2 d, the amount of released Ag^+ at 310 K was about four times the amount found at 277 K (Liu and Hurt, 2010). Finally, under aerobic conditions, many other oxidants, such as NaOCl, ozone, dichlorine monoxide (Cl_2O), and H_2O_2, can serve in addition to dissolved molecular oxygen as terminal electron acceptors and oxidize nanosilver quickly (He et al., 2012; Ho et al., 2010; Kang et al., 2008; Wang et al., 2013a; Yuan et al., 2013a). Those chemicals can also affect the nanosilver dissolution process in oxygenated water.

3.4. Nanosilver dissolution under anoxic and anaerobic conditions

The oxygen-mediated dissolution of AgNPs, including the influence of environmental factors, is well documented (Levard et al., 2012; Liu and Hurt, 2010; Reinsch et al., 2012; Yang et al., 2013b; Yu et al., 2013; Zhang et al., 2011b). However, it is less clear whether nanosilver dissolution can occur under anoxic conditions using nitrate/nitrite as terminal electron acceptors.

Bulk silver can readily dissolve in dilute nitric acid [nitrogen dioxide (NO_2) or nitric oxide (NO) being the final products] and in sulfuric acid [sulfur dioxide (SO_2) being the final product] (Burns et al., 1981; Chambers and Holliday, 1975; Martinez et al., 1993) at a low pH in the absence of dissolved oxygen. In addition, the anoxic oxidization of bulk silver by nitrite [molecular nitrogen (N_2) being the reduction product] is also thermodynamically favorable at a neutral pH based on the thermodynamic data in Table 5 (Equation (11)) (Henglein, 1993; Liu and Hurt, 2010; Sawyer et al., 2003):

$$\begin{aligned} &Ag^0_{(bulk)} + \frac{1}{3}NO^-_{2(aq)} + \frac{4}{3}H^+_{(aq)} \\ &\quad = Ag^+_{(aq)} + \frac{1}{6}N_{2(g)} + \frac{2}{3}H_2O_{(l)} \Delta G'_r = -15.32 \ \text{kJ mol}^{-1} \end{aligned} \tag{11}$$

Furthermore, the $\Delta G'_r$ of bulk silver oxidization by nitrate is positive but close to 0 kJ mol^{-1} at a neutral pH (Equation (12)) (Sawyer et al., 2003):

$$\begin{aligned} &Ag^0_{(bulk)} + \frac{1}{5}NO^-_{3(aq)} + \frac{6}{5}H^+_{(aq)} \\ &\quad = Ag^+_{(aq)} + \frac{1}{10}N_{2(g)} + \frac{3}{5}H_2O_{(l)} \Delta G'_r = 5.025 \ \text{kJ mol}^{-1} \end{aligned} \tag{12}$$

Assuming $\Delta G^0_{f(AgNPs)}$ is positive, the $\Delta G'_r$ of nanosilver oxidization by nitrite/nitrate might be negative at a near-neutral pH, especially when the particle size is small (size effect) (Cai et al., 1998). Thus, dissolution of nanosilver might be thermodynamically favorable under anoxic conditions at a neutral pH.

On the other hand, under strictly anaerobic conditions, the reactions between nanosilver and most of the electron acceptors are thermodynamically unfavorable, as evident by the positive $\Delta G'_r$ values (Table 5). However, the reactions between nanosilver and hydrogen sulfide (H_2S) have negative $\Delta G'_r$ values (Equation (13)) (Chen et al., 2013; Liu et al., 2013b):

$$\begin{aligned} &Ag^0_{(nano)} + \frac{1}{2}H_2S_{(g)} = \frac{1}{2}Ag_2S_{(s)} + \frac{1}{2}H_{2(g)} \quad \Delta G'_r = -7.30 \ \text{kJ mol}^{-1} \ - \ \Delta G^0_{f(AgNPs)} < 0 \ \text{kJ mol}^{-1} \\ &Ag^0_{(nano)} + \frac{1}{2}H_2S_{(aq)} = \frac{1}{2}Ag_2S_{(s)} + \frac{1}{2}H_{2(g)} \quad \Delta G'_r = -12.83 \ \text{kJ mol}^{-1} \ - \ \Delta G^0_{f(AgNPs)} < 0 \ \text{kJ mol}^{-1} \end{aligned} \tag{13}$$

Consequently, it is possible that under strict anaerobic conditions, nanosilver can be sulfidized without free silver ion release. Indeed, during anaerobic sludge digestion and anaerobic glucose degradation, no silver ion release was observed even at the nanosilver concentration of 40 mg L^{-1} (Yang et al., 2012). However, in anaerobic wastewater facilities and other anaerobic scenarios nanosilver could be transformed to Ag_2S steadily (Chen et al., 2013; Kaegi et al., 2013; Lombi et al., 2013). The kinetics of nanosilver sulfidization under strict anaerobic conditions or on which timescales this reaction occurs remains to be determined.

4. Aggregation of silver nanoparticles in aquatic environments

4.1. Mechanisms of nanosilver aggregation

Aggregation refers to the formation of nanosilver clusters in suspension. Size-based $\Delta G_{f(AgNPs)}$ needs to be calculated to determine whether the aggregation of silver nanoparticles is thermodynamically favorable, just as it was calculated to predict whether nanosilver dissolution is thermodynamically feasible under certain circumstances. As mentioned above, since $\Delta G_{f(AgNPs)}$ increases as particle size decreases, the ΔG_r of nanosilver aggregation is negative. Consequently, the aggregation process of nanosilver is thermodynamically favorable.

To describe the thermodynamic interactions between nanosilver in aquatic environments, classic Derjaguin–Landau–Verwey–Overbeek (DLVO) theory may apply (Eastman, 2010; Hotze et al., 2010; Huynh and Chen, 2011; Li et al., 2012; Stebounova et al., 2011; Wiesner and Bottero, 2007). This theory quantitatively describes the potential energy of the repulsive force (V_R) due to electric double-layer repulsion, and the potential energy of the attractive interaction (V_A) due to van der Waals attraction (Dwivedi et al., 2015; Stumm and Morgan, 1995).

Assuming silver nanoparticles are ideally spherical, V_R can be expressed in Equation (14) (Eastman, 2010; Hunter et al., 2001;

Verwey and Overbeek, 1999; Wiese and Healy, 1970):

$$\begin{aligned} V_R^{\psi} &= 2\pi\,\varepsilon\, r_{AgNPs}\,\psi_0^2 \ln\left(1 + e^{-\kappa H}\right) && \text{if } \kappa\, r_{AgNPs} > 10 \\ V_R^{\sigma} &= -2\pi\,\varepsilon\, r_{AgNPs}\,\psi_0^2 \ln\left(1 - e^{-\kappa H}\right) && \text{if } \kappa\, r_{AgNPs} > 10 \\ V_R^{\sigma} &= V_R^{\psi} \cong 2\pi\,\varepsilon\, r_{AgNPs}\,\psi_0^2\; e^{-\kappa H} && \text{if } \kappa\, r_{AgNPs} < 5 \end{aligned} \tag{14}$$

where V_R^{ψ} is the interaction between silver nanoparticles under constant potential (J), V_R^{σ} is the interaction between silver nanoparticles under constant charge (J), ε is the relative dielectric constant of the solution (around 79 at room temperature for water), ψ_o is the surface potential of nanosilver (V), H (= d - $2r_{AgNPs}$) is the shortest interaction distance between two silver nanoparticles (nm), d is the distance between the centers of two closest silver nanoparticles (nm), and κ is the reciprocal of the Debye double layer thickness (nm^{-1}). Alternatively, if $(H/r_{AgNPs})^2 << 1$, the overall V_R can be simplified to Equation (15) (Hiemenz and Rajagopalan, 1997):

$$V_R = \frac{64\pi\, N\, r_{AgNPs}\, k_B\, T}{\kappa^2}\left[\tanh\left(\frac{z\, e\, \psi_0}{4k_B\, T}\right)\right]^2 e^{-\kappa H} \tag{15}$$

where N is the number-based nanosilver concentration (# nm^{-3}), k_B is the Boltzmann constant (1.38×10^{-23} J K^{-1}), z is the electrolyte valence or charge number (#), and e is the elementary charge (1.60×10^{-19} C).

V_A between spherical silver nanoparticles can be expressed by Equation (16) (Croll, 2002; Eastman, 2010; Stebounova et al., 2011):

$$V_A = -\frac{A_{eff}}{6}\left[\frac{2}{s^2-4} + \frac{2}{s^2} + \ln\left(\frac{s^2-4}{s^2}\right)\right] \cong -\frac{A_{eff}\, r_{AgNPs}}{12H} \tag{16}$$

where A_{eff} is the Hamaker constant (J), and s (= $d/r_{AgNPs}\cdot A_{eff}$) increases when the particle size of nanosilver decreases. For instance, when r_{AgNPs} in water decreases from 100 nm to 1 nm, A_{eff} increases from 37 zJ to 80 zJ (Pinchuk, 2012).

The net total potential energy (V_T) among silver nanoparticles is the sum of V_A and V_R (i.e., $V_T = V_A + V_R$). A negative V_T value indicates that the attractive force is dominant while a positive V_T value indicates that the repulsive force is dominant. V_T is critical in determining the stability of silver nanoparticles in aquatic environments. The stability ratio (W) is the ratio of 1) the aggregation rate due to pure Brownian motion (the "fast" aggregation rate) to 2) the rate of Perikinetic aggregation when the inter-particle and hydrodynamic interactions are absent (the predicted aggregation rate) (Kuo and Hsu, 1999; Ma et al., 2005). It can be calculated using V_T (Equation (17)) (Hahn et al., 2011):

$$W = 2r_{AgNPs}\int_{2r_{AgNPs}}^{+\infty} \frac{\exp\left(\frac{V_T}{k_B\, T}\right)}{d^2}\,\mathrm{d}d \tag{17}$$

W can be used to estimate the aggregation potential of a silver nanoparticle suspension: suspensions with larger W values are more stable than the ones with smaller W values. For instance, if $W = 10^6$, only one out of 10^6 collisions between silver nanoparticles can be successful and produce larger particles (Stumm and Morgan, 1995), suggesting that the suspension is very stable. On the other hand, the stability ratio W should always be seen in combination with the particle concentration. Particles in a fully destabilized system (i.e., $W = 1$) will not aggregate if the collision probability is too low (i.e., concentration is too low).

Thermodynamic analysis is important to understanding whether a nanosilver suspension is stable or whether it tends to aggregate. However, thermodynamics alone cannot predict how quickly the nanosilver aggregation will occur. To better understand the nanosilver aggregation process, aggregation kinetics needs to be quantified. Generally speaking, nanosilver aggregation will follow a second-order reaction kinetics (Equation (18)) (Croll, 2002; Eastman, 2010):

$$-\frac{dN_t}{dt} = k_a\, N_t^2 \quad \text{or} \quad \frac{1}{N_t} = \frac{1}{N_0} + k_a\, t \tag{18}$$

where t is the reaction/aggregation time (min), k_a is the second-order aggregation rate constant (mL #$^{-1}$ min^{-1}), and N_0 and N_t are the number-based silver nanoparticle concentrations at time zero and t (# mL^{-1}), respectively. The half-life of nanosilver aggregation ($t_{1/2}$) dependents on N_0 and can be expressed as $t_{1/2} = 1/(k_a \cdot N_0)$. For the early stage aggregation, k_a is inversely proportional to N_0 (Equation (19)) (Chen and Elimelech, 2006; Huynh and Chen, 2011):

$$k_a \propto \frac{\lim_{t\to 0}\left(dD_{h,t}/dt\right)}{N_0} \tag{19}$$

where $D_{h,\,t}$ is the hydrodynamic diameter of silver nanoparticles at time t (nm). k_a can also be simply expressed as $k_a = \alpha \cdot \beta$, where α is a dimensionless sticking coefficient (or the attachment coefficient), and β is a mass transport coefficient (mL #$^{-1}$ min^{-1}) (Huynh and Chen, 2011; Stumm and Morgan, 1995).

To estimate the nanosilver aggregation rate, it is essential to obtain the values of α and β. The physical meaning of α is the ratio of the rate at which silver nanoparticles attach to the rate at which silver nanoparticles collide. Thus, α equals the reciprocal of W (Elimelech et al., 1995; He et al., 2013; Li et al., 2012). β is the aggregation rate constant under diffusion-limited conditions or favorable (non-repulsive) aggregation conditions (Holthoff et al., 1996; Huynh and Chen, 2011; Li et al., 2012). This largely physical factor can be determined theoretically (Buffle and van Leeuwen, 1993; Wagner et al., 2014).

4.2. Influencing factors of nanosilver aggregation

Numerous environmental factors affect the aggregation process of AgNPs, but among them, pH significantly influences the stability of a nanosilver suspension (Baalousha, 2009; Badawy et al., 2010; French et al., 2009; Keller et al., 2010; Musee et al., 2014). Theoretically, when the solution pH equals the pH_{PZC} of nanosilver, the pH corresponding to the point of zero charge (Ibanez et al., 2007) of nanosilver, both the net surface charge and mobility of silver nanoparticles have zero value, resulting in the smallest W value (unity value). At this point (i.e., pH = pH_{PZC}), the degree of stability of a nanosilver suspension is minimal and larger aggregates form easily (French et al., 2009; Stumm and Morgan, 1995). In general, the larger the absolute difference between the solution pH and the pH_{ZPC} of AgNPs (i.e., $|pH - pH_{ZPC}|$), the more stable the AgNP suspension (Mukherjee and Weaver, 2010). However, in natural aquatic environments, the impacts of pH on the stability of nanosilver suspension are very complex. For instance, in the pH range of 2–10, pH minimally impacted the aggregation of PVP coated nanosilver, but pH change in the same range significantly influenced the aggregation of branched polyethyleneimine (BPEI) coated nanosilver (Badawy et al., 2010), suggesting that surface coating can also affect nanosilver aggregation. It should be noted that in aerobic aquatic environments, the surface of AgNPs is likely covered with a very thin layer of silver compounds such as Ag_2O and Ag_2S (Dwivedi et al., 2015; Kumar and Münstedt, 2005; Levard et al., 2013a, 2012; Maurer-Jones et al., 2013). Thus, the pH_{pzc} values of nanosilver surface layers significantly affect nanosilver

aggregation as well. Therefore, more work is necessary to understand the complex aggregation process of nanosilver in natural aquatic environments.

Increases in ionic strength can significantly increase the aggregation rate of AgNPs (Badawy et al., 2010; Chambers et al., 2014; Christian et al., 2008; Delay et al., 2011; Levard et al., 2012). This response to ionic strength was found in many other metallic/metal oxide nanoparticles, such as nano-scale zero valent iron (NZVI) (Saleh et al., 2008), zinc oxide nanoparticles (nanoZnO) (Bian et al., 2011; Domingos et al., 2013), and titanium dioxide nanoparticles (nanoTiO_2) (French et al., 2009). For instance, the hydrodynamic diameters of 20-nm nanosilver in solutions with conductivities of 30 $\mu S\ cm^{-1}$ and 150 $\mu S\ cm^{-1}$, increased by 1.7 fold and 3.3 fold over time, respectively (Alva et al., 1991; Dolling and Ritchie, 1985; Harmon et al., 2014). In addition, one study concluded that nanosilver aggregates steadily at high ionic strength solutions, regardless of how the nanosilver surface is modified (Stebounova et al., 2011). On the other hand, another study found that even a relatively small reduction of ionic strength could substantially increase the stability of nanosilver suspension (Römer et al., 2011). Finally, the impact of ionic strength on the aggregation of nanosilver is more significant for particles with smaller size (Harmon et al., 2014).

As the pH_{ZPC} of AgNPs is estimated to be 2.0 (Sadowski et al., 2008), under normal aquatic conditions the AgNPs are generally negatively charged (Huynh et al., 2014; Stuart et al., 2014; Stumm and Morgan, 1995; Tugulea et al., 2014). In addition, most silver nanoparticles might have anions on the surface (e.g., Cl^- and citrate ions) that can provide a negative charge (Dunn et al., 2009; Liu et al., 2010; Stevanović et al., 2012). Based on the Schulze–Hardy rule (Jenny and Reitemeier, 1935; Verrall et al., 1999), cations can reduce the stability of nanosilver suspensions by compressing the electric double layer, eliminating the surface charge, and removing the repulsive energy (V_R). Not surprisingly, therefore, aggregation of nanosilver is very significant in solutions with high concentrations of divalent cations such as Mg^{2+} and Ca^{2+} (Zhang et al., 2012). These divalent cations do not bind specifically to nanosilver, particularly when nanosilver is pristine (i.e., without any capping agents or adsorbed anions). However, they can still efficiently eliminate or neutralize the surface charge of AgNPs through the charge neutralization and/or the electrical double layer compression mechanisms (Baalousha et al., 2013; Chandrakanth and Amy, 1998; Ho et al., 1997). On the other hand, monovalent cations such as K^+ and Na^+ can also enhance the aggregation of nanosilver, but they are much less effective in screening its surface charge than divalent ones (Akaighe et al., 2012; Chen and Zhang, 2012; Li et al., 2010; Mukherjee and Weaver, 2010). For instance, one study revealed that the critical coagulation concentrations (CCCs) of nanosilver [naked, citrate-coated, and sodium dodecyl sulfate (SDS)-coated] in the electrolytes of sodium chloride (NaCl), sodium nitrate ($NaNO_3$), and calcium chloride ($CaCl_2$) were 40 mM, 30 mM, and 2 mM, respectively (Li et al., 2010, 2012). Similarly, other research found that the CCCs of nanosilver in NaCl, $CaCl_2$, and magnesium chloride ($MgCl_2$) solutions, were 47.6 mM, 2.1 mM, and 2.7 mM, respectively (Huynh and Chen, 2011).

Certain organic substances (e.g., surfactants and/or NOM) can induce a charge to the surface of nanosilver, increase the repulsive energy among AgNPs, create a thin surface film, and hence increase the stability of nanosilver suspension (Kennedy et al., 2012; Leo et al., 2013; Liang et al., 2013; Zhang et al., 2009). For instance, humic acids (HA) from a river at 10 mg L^{-1} could cause disaggregation of nanosilver by forming a nano-scale film on its surface (Fabrega et al., 2009). NOM from lakes and ponds showed similar effects (Chinnapongse et al., 2011; Delay et al., 2011). In addition to NOM, many synthesized organic materials can serve as capping agents or stabilizers and increase the stability of AgNPs by "covering" the particle surface, hence reducing the effective collisions among AgNPs (Fayaz et al., 2010; Mafuné et al., 2000; Tao et al., 2008). These chemicals include SDS (Sharma et al., 2009), PVP (Kvitek et al., 2008; Sintubin et al., 2009; Yin et al., 2003), 3-(aminopropyl) trimethoxysilane (APS) (Pastoriza-Santos and Liz-Marzán, 1999), citrate (MacCuspie, 2011), PVA (Choi et al., 2010), and Daxad 19 (Sondi et al., 2003).

Furthermore, other factors such as initial AgNP concentration, initial particle size (Römer et al., 2011; Zhang et al., 2011a), UV light exposure, and oxidization conditions, would have an impact on nanosilver aggregation as well. For instance, one study found that because of the oscillating of electrons at resonant conditions, UV light from sunlight could irreversibly induce nanosilver aggregation (Cheng et al., 2011). Another study revealed that compared with anaerobic conditions, aggregation of nanosilver in oxygenated water was 3–8 times faster, indicating that dissolved molecular oxygen can also significantly affect nanosilver aggregation (Zhang et al., 2011a).

Of course, the homoaggregation (or autoaggregation) of nanosilver discussed above is an experimental artifact due to exceedingly high initial nanosilver concentrations in the absence of other particles (surfaces). In a natural aquatic environment homoaggregation of nanosilver is very unlikely because nanosilver typically has very low concentrations in such environments (Gottschalk et al., 2009, 2013; Mueller and Nowack, 2008) and is vastly outnumbered by a great variety of natural colloids (e.g., clays, iron hydroxides, and metal sulfides). Since in natural water bodies the heteroaggregation between nanosilver and other particles/surfaces likely dominates (Praetorius et al., 2014; Quik et al., 2014), more work is needed to better understand the aggregation behaviors of nanosilver in real aquatic environments.

In addition to dissolution and aggregation, another important physicochemical process that can significantly affect the environmental fate and antimicrobial activities of nanosilver is its transport in saturated and unsaturated porous media (e.g., vadose zone) (Sirivithayapakorn and Keller, 2003a; Tian et al., 2010). In porous media, nanosilver will not only directly interact with the aquatic phase but also with the solid–water interfaces (SWI) and/or the air–water interfaces (AWI) (May et al., 2012; Saiers and Lenhart, 2003; Schijven and Hassanizadeh, 2000; Torkzaban et al., 2008). Consequently, the physicochemical behavior of nanosilver and its interactions with microbes in porous media would be much different from those in an aquatic environment.

Migration behaviors or transport dynamics of nanosilver in porous media are controlled by factors such as the water chemical properties (e.g., pH and ionic strength), interstitial velocity, properties of nanosilver (e.g., size, shape, charge, and coating agent), nanosilver aggregation characteristics, and surface properties of the media (McCarthy and Zachara, 1989; O'Melia et al., 1997; Seymour et al., 2013; Sirivithayapakorn and Keller, 2003b; Wagner et al., 2014). Among them, the surface properties of both porous media and nanosilver are very important parameters that affect the transport of nanosilver in porous media. For instance, one study found that when the environmental pH was less than the pH_{PZC} of nanosilver, the affinity of nanosilver for the porous medium of uncoated silica glass beads was much lower than that for a hematite coated surface (Lin et al., 2011). It was also reported that the attachment efficiencies of PVP and gum arabic coated nanosilver on octadecylichlorosilane (OTS) coated glass beads respectively were 4 and 2.5 times greater than that of the uncoated beads (Song et al., 2011). Furthermore, the deposition of nanosilver on a porous medium could be favored by dissimilar surfaces (e.g., nanosilver is coated by polymers while the porous medium is not) (Lin et al., 2012). A detailed discussion of the transport of nanosilver in

porous media is beyond the scope of this review and can be found elsewhere (Flory et al., 2013; Goldberg et al., 2014; Kanel et al., 2015; May et al., 2012; Mittelman et al., 2013; Ren and Smith, 2013; Taghavy et al., 2013; Xiao and Wiesner, 2013; Yang et al., 2014c).

5. Antimicrobial mechanisms of silver nanoparticles

5.1. Silver ion release and the toxicity of nanosilver

The scientific community still debates the actual antimicrobial mechanisms of nanosilver, especially whether it has "particle-specific" antimicrobial effects (Behra et al., 2013; Eom and Choi, 2010; Hackenberg et al., 2011; Maurer et al., 2014; Yu et al., 2013). Furthermore, it is doubtful whether nanosilver is more toxic than silver ions (Hansen and Baun, 2012) at the same overall silver concentrations. However, it is generally accepted that silver ion release is the predominant antimicrobial mechanism of silver nanoparticles (Calder et al., 2012; Kennedy et al., 2012; Kittler et al., 2010; Lok et al., 2007; Neale et al., 2013; Radniecki et al., 2011), which can be viewed from different perspectives.

Many studies have shown that in a system where nanosilver is present, the released silver ions are almost exclusively responsible for its overall toxicity (Choi et al., 2008; Colman et al., 2012). For instance, to discriminate the biological effects of free silver ions and ion-free nanosilver, nanosilver was stored under argon gas (AgNP-Ar) and oxygen gas (AgNP–O_2) separately before being applied to cultures of human skin keratinocytes (HaCaT). Since AgNP-Ar started releasing silver ions only after contacting the cells while AgNP–O_2 already released silver ions during storage and generated more free silver ions, the former showed significantly lower toxicity (Ahlberg et al., 2014). On the other hand, compared with Ag^+-rich silver nanoclusters, Ag^0-rich silver nanoclusters showed much higher cellular toxicity to human neonatal foreskin fibroblast cells (strain BJ) in that the latter underwent more rapid Ag^+ release and subsequent reactive oxygen species (ROS) generation (Setyawati et al., 2014). In addition, it was revealed that silver ion release mainly mediated the toxicity of nanosilver to many microorganisms, such as *Nitrosomonas europaea*, *Chlamydomonas reinhardtii*, and *Sphaerium corneum* (Arnaout and Gunsch, 2012, Navarro et al., 2008; Völker et al., 2015). Another study even found that the toxicity of nanosilver (sizes 20 nm, 40 nm, 60 nm, and 80 nm) towards different microorganisms could be fully explained by silver ion release or nanosilver dissolution (Ivask et al., 2014).

This conclusion is also rooted in the findings that nanosilver has negligible or even no "particle-specific" impacts on cells, indicating that silver ion release is the main antimicrobial mechanism of nanosilver. For instance, under strict anaerobic conditions, PVP or PEG coated nanosilver (size 2.8 nm – 10.5 nm) did not release free silver ions and thus showed no inhibitory effect on the growth of *Escherichia coli* K12 strain (Xiu et al., 2012). Another study revealed that capped and purified nanosilver (size 30 nm – 60 nm) in the absence of ionic silver had no antimicrobial effect on *E. coli* (Sheehy et al., 2015). Similarly, other studies reported that nanosilver had only negligible or even no "particle-specific" biological effects on human cancer cell lines (De Matteis et al., 2015; Maurer et al., 2014) and *Caenorhabditis elegans* (Yang et al., 2011). In addition, the mixed-culture community of microbes during an anaerobic digestion process was not interrupted by nanosilver dosing even at a relatively high AgNP concentration (~ 40 mg L^{-1}) since no free silver ion was released under anaerobic conditions (formation of Ag_2S is possible) (Yang et al., 2012). Therefore, these results suggest that direct interactions between cells and silver nanoparticles will not suppress cellular functions in general (Lok et al., 2006), implying that silver ion release generally serves as the main antimicrobial mechanism of nanosilver.

Since silver ion release is the main antimicrobial mechanism of nanosilver in aquatic environments, environmental factors that can promote or suppress free silver ion release would facilitate or mitigate the toxicity of nanosilver (Dwivedi et al., 2015). For instance, the cell damage caused by nanosilver to several organisms, such as *E. coli*, *C. elegans*, *Raphidocelis subcapitata*, *Chydorus sphaericus*, *Danio rerio*, and *Daphnia magna*, could be alleviated by fulvic acids (FA), HA, and/or dissolved organic matter (DOM) because these organic substances can inhibit silver ion release (Cupi et al., 2015; Seitz et al., 2015; Wang et al., 2015; Yang et al., 2014b; Zhang et al., 2012). In addition, one study showed that under UV irradiation, perfluorocarboxylic acids (PFCAs) could significantly decrease nanosilver dissolution rate (as well as its aggregation and ROS generation) and hence reduce its toxicity to *E. coli* (Li et al., 2014). Similarly, alginate could even mute the toxicity of nanosilver towards *N. europaea* by binding to (or covering) the nanosilver surface and blocking its dissolution (Ostermeyer et al., 2013). Furthermore, because bovine serum albumin (BSA) can strongly chelate Ag^+, it has the potential to reduce the toxicity of nanosilver towards *N. europaea* even though it could facilitate silver ion release.

In addition to organic matter, many inorganic ions and/or ligands such as S^{2-} and Cl^- can strongly affect the toxicity of silver nanoparticles by altering silver ion release or availability. It is well known that the sulfidization of nanosilver significantly mitigates nanosilver toxicity, mainly because the formation of Ag_2S with extremely low solubility dramatically precipitates and reduces the bioavailability of Ag^+ (Levard et al., 2013a; Reinsch et al., 2012; Starnes et al., 2015). However, chloride might either decrease or increase the toxicity of nanosilver. AgCl precipitate dominates at low Cl/Ag ratios while soluble silver(I)-chloride complexes [i.e., $AgCl_x^{(x-1)-}$] dominate at high Cl/Ag ratios (Gupta, 1998; Ho et al., 2010; Li et al., 2010). As the toxicity of nanosilver is generally controlled by the concentration of dissolved $AgCl_x^{(x-1)-}$ (Levard et al., 2013b), the increased salinity (increased Cl/Ag ratios) could increase the toxicity of nanosilver to *Oryzias latipes* embryos (Kataoka et al., 2015). On the other hand, other researchers found that with increased chloride levels (fixed overall ionic strength), the concentration of $AgCl_x^{(x-1)-}$ increased in the nanosilver suspension while the toxicity of nanosilver to *E. coli* decreased, especially at low ionic strengths (e.g., 40 mM) (Chambers et al., 2014). This inconsistency could be explained by the fact that in such a system the silver(I)-chloride complexes are actually less toxic to *E. coli*. It is also possible that AgNPs in a solution with low or zero chloride concentration tend to form more fractal structures, providing more surface area for the interaction between cells and particles and facilitating the delivery of nanosilver to the cells (Chambers et al., 2014). Therefore, more studies are required to determine the impacts of chloride on the toxicity of nanosilver, particularly in natural aquatic environments.

Inorganic ions can also affect the antimicrobial activities of nanosilver through generating ionic strength. For instance, the increase in ionic strength at a constant chloride level significantly increased the toxicity of nanosilver to *E. coli* cells. As silver ion release from nanosilver is more significant at higher ionic strengths (constant chloride level), the increase in the toxicity could be explained by the enhanced nanosilver dissolution (and decreased fractal dimension, which could increase the bioavailability of nanosilver) at higher ionic strengths (Chambers et al., 2014).

Furthermore, physical factors such as sunlight irradiation can affect the toxicity of nanosilver by altering silver ion release. For instance, sunlight irradiation could facilitate the surface oxidization of nanosilver, enhance nanosilver dissolution (silver ion release), magnify ROS generation, and then increase the toxicity of AgNPs to

a fish cell line (George et al., 2014). Similarly, one study showed that sunlight irritation significantly increased the toxicity of nanosilver to several natural aquatic bacterial strains by facilitating ROS release in the presence of HA (Dasari and Hwang, 2010). In contrast, in another study (Cheng et al., 2011), nanosilver suspension was pre-treated with sunlight irradiation for several days, which irreversibly induced and facilitated nanosilver aggregation. The aggregation, in turn, significantly mitigated the antimicrobial activities of AgNPs to plant *Lolium multiflorum* seeds by reducing the silver ion release rate (Levard et al., 2012; Nel et al., 2006; Yang et al., 2011). The inconsistency between these two studies might be explained by the fact that in the second study (Cheng et al., 2011) nanosilver was exposed to sunlight before being applied to the seeds of *L. multiflorum*, rendering aggregation the main factor that altered the toxicity (ROS was either generated in small amounts or the generated ROS had already degraded before the nanosilver treatment). However, in the first study (Dasari and Hwang, 2010), enhanced nanosilver dissolution and ROS generation were the main factors that increased the toxicity of nanosilver.

Finally, the widely-observed particle size- and morphology-dependent toxicity of nanosilver (Agnihotri et al., 2014; Choi and Hu, 2008; Pal et al., 2007; Silva et al., 2014; Sotiriou and Pratsinis, 2010) to microorganisms might be an indirect phenomenon, as silver ion release is significantly affected by the particle size as well as the morphology of nanosilver (Liu et al., 2010; Stoehr et al., 2011; Zhang et al., 2011b). For instance, smaller nanosilver tends to release silver ions faster than larger ones and hence is more toxic while nanosilver aggregation could strongly reduce its toxicity by increasing the particle size (Gliga et al., 2014; Hoheisel et al., 2012; Liu et al., 2014a; Scown et al., 2010; Shang et al., 2014; Xiu et al., 2012). Overall, these findings suggest that silver ion release is plausibly the major antimicrobial mechanism of nanosilver.

5.2. Particulate nanosilver contribute evidently to the overall antimicrobial activities

Silver ion release from nanosilver dissolution may not be the exclusive toxicity factor of nanosilver. For instance, silver ion release could not fully explain the toxicity of nanosilver to *C. reinhardtii* (Navarro et al., 2008), *Arabidopsis thaliana* (Geisler-Lee et al., 2012), *Enchytraeus albidus* (Gomes et al., 2013), *Oncorhynchus mykiss* (Massarsky et al., 2014), and *N. europaea* (Yuan et al., 2013b). In addition, one study found that ionic silver and nanosilver had comparable toxicity towards *D. magna* and *Pimephales promelas*, indicating that the toxicity of nanosilver sometimes might be predicted using the total silver concentration (Hoheisel et al., 2012). Other research has shown that the toxicity of nanosilver could not be significantly inhibited by the addition of ligands under certain circumstances and silver ion release might be not the sole source of nanosilver toxicity (Kawata et al., 2009; Yue et al., 2015). These findings indicate that factors other than silver ion release, such as the surface properties of particulate nanosilver, also contribute to the overall toxicity of nanosilver. As an example, in one case, only ion-free silver nanoparticles showed toxicity to *D. rerio* embryos, but released silver ions did not (Asharani et al., 2008).

The role of particulate nanosilver in the overall toxicity of AgNPs can be viewed from the results of several different experiments. It is commonly found that nanosilver has much higher antimicrobial activities than free silver ions at the same total silver concentrations (Choi et al., 2008; Šiller et al., 2013; Sweet and Singleton, 2011; Yin et al., 2011), indicating that the intrinsic toxicity of particulate nanosilver cannot be neglected (Lubick, 2008). For instance, in an activated sludge system, nanosilver with a diameter of 5 nm had higher impacts on the microbial community structure/stability than silver ions, even though the former had a 20-fold lower total silver concentration, probably because nanosilver could deliver silver ions to microbes more efficiently (Yang et al., 2014d). Similarly, in landfill bioreactors treating municipal solid waste (MSW), methanogenesis was more sensitive to nanosilver than to silver ions (Yang et al., 2013a). In addition, at a fixed overall silver concentration, nanosilver showed more than 1000 times higher toxicity to *Pseudomonas putida* compared with $AgNO_3$. However, when only the ionic form ($AgNO_3$ or the Ag^+ released from nanosilver) was considered, nanosilver and $AgNO_3$ had very comparable antimicrobial efficiencies (Hachicho et al., 2014). It was also reported that nanosilver released from nanosilver coated socks was more toxic to *D. rerio* embryos than $AgNO_3$ (Gao et al., 2015). Furthermore, nanosilver at 40 mg L^{-1} could significantly inhibit the germination of *L. multiflorum*, but silver ions ($AgNO_3$) at the same concentration did not have this effect (Yin et al., 2011). As a result, these findings suggest that nanosilver is generally more toxic than silver ions and that particulate nanosilver is an important source of the overall toxicity of AgNPs.

The contribution of particulate nanosilver to the overall toxicity of AgNPs can be indirect. Nanosilver can penetrate into cells through endocytosis (internalization) and/or through the pores in the cell membrane (Fabrega et al., 2011; Milić et al., 2015) and undergo subsequent ionization or dissolution. Considering the small size of cells (Madigan et al., 2014), intercellular silver ion release can generate relatively high localized Ag^+ concentrations, which can effectively inactivate important cellular functions (De Matteis et al., 2015). This Trojan-horse type antimicrobial mechanism (Lubick, 2008; Palza, 2015; Park et al., 2010; Yang et al., 2012; Zook et al., 2011) is also found in several other engineered nanoparticles (Ettwig et al., 2010; Haroon et al., 2013; Palza, 2015; Weber et al., 2006). For instance, one study revealed that nanosilver (size 10 nm) could release silver ions both intracellularly and extracellularly, but only the intracellular Ag^+ release caused cytotoxicity to human lung cells, suggesting the existence of a Trojan-horse type effect (Gliga et al., 2014). Consequently, particulate nanosilver can contribute significantly to the overall antimicrobial properties of AgNPs through this Trojan-horse pathway, even though the detailed penetration process remains to be explored (Conner and Schmid, 2003; Hillaireau and Couvreur, 2009).

Furthermore, particulate nanosilver can contribute indirectly to the overall antimicrobial activities of AgNPs through affecting the silver ion release process. As discussed above, silver ion release is the main antimicrobial mechanism of nanosilver and factors that can affect silver ion release would also have an impact on the toxicity of nanosilver. Silver ion release is highly related to or even controlled by particle properties such as particle size, morphology, and surface coating (Agnihotri et al., 2014; Choi and Hu, 2008; Liu et al., 2010; Silva et al., 2014; Yu et al., 2013; Zhang et al., 2011b). As a result, particulate nanosilver may significantly impact the overall toxicity of AgNPs (Navarro et al., 2008; Wijnhoven et al., 2009) by affecting the nanosilver dissolution kinetics/process.

A handful of studies showed that nanosilver can also directly alter cell behavior and/or inhibit cell growth through a "particle-specific" pathway. For instance, toxicity of nanosilver to several Gram-negative bacterial strains (e.g., *E. coli* and *Pseudomonas aeruginosa*) was partially attributed to the direct interactions between the ion-free particles and important cellular components such as cell membranes and chromosomes (Morones et al., 2005). Another study found that nanosilver can penetrate into mouse erythroleukemia (MEL) cells and bind to RNA polymerase directly, resulting in deceleration of embryonic development (Wang et al., 2013b). On the other hand, when the direct contact (or close proximity) between AgNPs and *E. coli* cells was prevented, the antimicrobial activities of nanosilver could be mitigated (Huynh et al., 2014). Research has also indicated out that it is

unreasonable to rule out the "particle-specific" toxicity of nanosilver to *Eisenia fetida* (Gomes et al., 2015) and a gill cell line from *O. mykiss* (Yue et al., 2015).

However, released Ag^+ and ion-free silver nanoparticles could affect cells through different mechanisms/pathways (Loo et al., 2015). For instance, both ion-free nanosilver and the released silver ions contributed to the overall toxicity of AgNPs towards *E. fetida*, with Ag^+ mainly accumulating in the cytosol-containing fraction and ion-free particles mainly damaging granules and cell membrane compartments (Li et al., 2015). In addition, silver ion ligand 2,3-dimercaptopropanesulfonate (DMPS) could strongly inhibit the adverse effects of nanosilver on the activities of extracellular enzymes of beta-glucosidase and alkaline phosphatase by strongly complexing released Ag^+. Nonetheless, DMPS had no effect on the toxicity of nanosilver towards another enzyme (leucine aminopeptidase) because particulate nanosilver can modify the structure or obstruct the reaction center of this enzyme (Gil-Allué et al., 2015). These findings suggest that even though silver ion release is the main antimicrobial mechanism of nanosilver, the ion-free particles could still exhibit toxicity alone from a different mechanism.

It has been further proposed that silver nanoparticles and the released silver ions have comparable toxicity against *E. coli* when the initial particle size is relatively large and nanosilver dissolution is insignificant. However, for small nanosilver, where dissolution is significant, silver ion release from nanosilver dissolution is the most important element in its overall toxicity (Sotiriou and Pratsinis, 2010). Similarly, at low or high total silver concentrations, the main antimicrobial activities of nanosilver against *C. elegans* were silver ion release or "particle-specific" effects, respectively (Starnes et al., 2015). One study showed that the toxicity of $AgNO_3$ and nanosilver to *Pseudokirchneriella subcapitata*, *D. magna*, and *D. rerio* was highly species-dependent, suggesting that the biological effects of nanosilver might be a combination of the toxicity of ion-free nanosilver and released silver ions (Ribeiro et al., 2014).

Form the aforementioned analysis, it can be concluded that both silver ion release and particulate AgNPs might be responsible for the overall toxicity of nanosilver, but perhaps through different pathways (Bondarenko et al., 2013; Fabrega et al., 2009; Gil-Allué et al., 2015; Laban et al., 2010; Meyer et al., 2010; Suresh et al., 2010). More work is thus needed to distinguish the toxicity mechanisms and the specific toxicity contribution of each species *in vivo*, when both are simultaneously present in the same biological system. This research seems very challenging, considering all the efforts that have been made so far to decipher the different biological effects of Ag^+ and ion-free AgNPs.

5.3. ROS generation is another important antimicrobial mechanism of nanosilver

The excellent antimicrobial activities of nanosilver can also be explained by its capability for ROS generation under aerobic conditions (Baker et al., 2014; Foldbjerg et al., 2011, 2015, 2009; Limbach et al., 2007; Mafuné et al., 2000). During the nanosilver dissolution process in oxygenated water, ROS can be generated as intermediates (Hwang et al., 2012b; Liu and Hurt, 2010; Zhang et al., 2011b). The released Ag^+ can also induce ROS generation (Choi and Hu, 2008; Foldbjerg et al., 2009; Park et al., 2009). Nevertheless, the effectiveness of generating ROS by silver ions would be much lower than that by nanosilver (Batchelor-McAuley et al., 2014; Loo et al., 2015).

ROS as strong oxidants generated by nanosilver, regardless of the specific pathway, can seriously damage cell components, such as proteins, lipids, and nucleic acids (Cooke et al., 2003; Ercal et al., 2001; Hwang et al., 2008; Kovacic and Somanathan, 2010; Li et al., 2015; Piao et al., 2011). Using recombinant bioluminescent *E. coli* strains as subjects, one study showed that the ROS [mainly superoxide radicals ($\cdot O_2^-$) but not hydroxyl radicals ($\cdot OH$)] generated by nanosilver could cause significant protein/membrane damage (Hwang et al., 2008). Another study reported that ROS (e.g., $\cdot O_2^-$, $\cdot OH$, and H_2O_2) played an important role inactivating *E. coli* by damaging cell membranes (Loo et al., 2015). It was found that when a human hepatoma cell line HepG2 was pretreated by an antioxidant, the inhibition of nanosilver through oxidative stress was absent, proving that ROS generation is one key antimicrobial mechanism of nanosilver (Kim et al., 2009; Kim and Ryu, 2013). In addition, the inhibitory effects of nanosilver on mixed-culture nitrifying bacteria were well correlated with the amount of photocatalytic intracellular ROS generated through the endogenous processes (Choi and Hu, 2008). Furthermore, the toxicity of nanosilver towards both microbes and mammalian cells could be enhanced though the addition of H_2O_2 (Ho et al., 2010), indicating that ROS are actively involved in the antimicrobial activities of nanosilver.

5.4. The cell membrane appears to be the main biological target of nanosilver

Regardless of the agent (silver nanoparticles, silver ions, or ROS) through which nanosilver exhibits its antimicrobial activities, it is important to investigate how it affects cells. Generally speaking, nanosilver exposure can significantly damage cellular structures (such as cell membranes and cell walls), components (such as nucleic acids, lipids, and proteins), and/or important cellular functions (such as metabolic activities) (Hackenberg et al., 2011; Li et al., 2011; Siripattanakul-Ratpukdi and Fürhacker, 2014; Yu et al., 2013; Zhao and Wang, 2012). In particullar, the cell membrane/wall might be the main biological target of nanosilver.

Proteins are dominant components of a cell membrane and usually carry out indispensable cellular functions (Madigan et al., 2014; Spector and Yorek, 1985). Silver, especially silver ions, can bind strongly to sulfur (thiol)-containing proteins or enzymes (Levard et al., 2012; Liau et al., 1997; Rai et al., 2009) and inhibit enzymatic activities (Braydich-Stolle et al., 2010; Gordon et al., 2010; Lee and Lee, 1990). In addition, surface charged nanoparticles might alter the organization and local state of lipids or the structure of phospholipid membranes (Badawy et al., 2010; Dawson et al., 2009; Eastman, 2010; Stumm and Morgan, 1995; Wang et al., 2008). For example, the surface charge of nanosilver has a significant impact on its toxicity to *E. coli* where a higher attraction between the bacterial surface and the nanosilver (due to higher absolute surface charge differences between them) yields a higher inactivation efficiency (Silva et al., 2014). Furthermore, compared with subcellular structures/components (e.g., nucleic acids), the cell membrane/wall will have more opportunities to interact with nanosilver (Moo-Young et al., 1996) and is thus likely to be the first structure affected by nanosilver (Neal, 2008). Consequently, the cell membrane/wall is significantly involved in the toxicity mechanism of nanosilver and might be the main biological target of nanosilver attack.

Indeed, research has shown that nanosilver can seriously damage the structure and functions of a cell membranes/wall. For instance, due to its high reactivity and high affinity for sulfur-containing cell membranes, nanosilver can efficiently generate pores in an *E. coli* cell wall and alter cell membrane permeability (Gogoi et al., 2006). One study found that nanosilver treatment could damage an *E. coli* cell wall, leaving a significant accumulation of nanosilver on the cell membrane, which significantly increased the membrane permeability. This subsequently caused an efflux of

important cellular components from the cell, which, in turn, resulted in cell death (Sondi and Salopek-Sondi, 2004). Nanosilver associated ROS generation might also be responsible to some extent for cell membrane damage because ROS could seriously destroy the integrity of the cell membranes of several pathogentic strains such as *Staphylococcus aureus* and *P. aeruginosa* (Priester et al., 2014; Su et al., 2009).

In addition, nucleic acids (i.e., DNA and RNA) might also be affected by nanosilver. Nanosilver, released silver ions, and/or generated ROS could be internalized by cells (De Matteis et al., 2015; Hashimoto et al., 2014) and difunctionalize nucleic acids (Buffet et al., 2014; Eom and Choi, 2010; Hackenberg et al., 2011; Likus et al., 2013; Yu et al., 2013). For instance, DNA damage/breakdown was widely detected from nanosilver treatment in human/mammalian cells (Ahamed et al., 2008; AshaRani et al., 2009; French et al., 2009; Guo et al., 2013; Piao et al., 2011; Singh et al., 2010). Silver ions can also cause DNA damage in both Gram-negative and Gram-positive bacteria (Feng et al., 2000) and prevent DNA proliferation/replication (Lansdown, 2002; Rai et al., 2009; Samuel and Guggenbichler, 2004). ROS generation is one very reactive and efficient mechanism in destroying DNA (Alarifi et al., 2014; Cadet and Wagner, 2013; Colin et al., 2014; Imlay and Linn, 1988; Rinna et al., 2015; Yang et al., 2009). Furthermore, both RNA polymerase activity and messenger RNA (mRNA) transcription can be inhibited by nanosilver, suggesting that the overall RNA activity is sensitive to nanosilver treatment at the transcriptional level (Rai et al., 2009; Wang et al., 2013b).

To summarize, antimicrobial properties of nanosilver are mainly governed by the release of silver ions from nanosilver dissolution, which might be further explained by the generation of ROS. On the other hand, the direct or "particle-specific" effect of particulate nanosilver may also contribute to the overall toxicity of AgNPs. Many important cellular components (e.g., proteins, nucleic acids, and lipids) and critical processes (e.g., ATP-associated metabolism) (Hwang et al., 2012a; Krishnaraj et al., 2010; Rai et al., 2009) can be seriously damaged or inhibited by nanosilver. But among them, the cell membrane might be the main biological target of nanosilver treatment (Lok et al., 2006).

6. Future research directions

Great efforts have been made to study the properties and activities of silver nanoparticles in aquatic environments, ranging from their thermodynamic stability, dissolution pattern, and aggregation to their antimicrobial mechanisms. However, research is still needed to investigate the behavior and fate of nanosilver in water bodies as well as its interactions with microorganisms. Several critical questions have been raised regarding the fundamental physicochemical properties of nanosilver and its antimicrobial mechanisms in aquatic environments.

6.1. Thermodynamics of nanosilver in aquatic environments: what is the actual $\Delta G_{f(AgNPs)}$?

As discussed above, $\Delta G_{f(AgNPs)}$ is very important in determining the equilibrium concentrations of nanosilver and released silver ions in aquatic environments (assuming that the total silver concentration exceeds the solubility of nanosilver). If we can accurately determine the true $\Delta G_{f(AgNPs)}$, we can then precisely determine the real transformation, fate, and ecotoxicity of nanosilver in aquatic environments. This paper for the first time calculated the $\Delta G_{f(AgNPs)}$ in water based on the available data and showed large inconsistencies in the literature. Certainly, the overall $\Delta G_{f(AgNPs)}$ increases as particle size decreases since smaller particles have higher total surface area (Cai et al., 1998; Plieth, 1982; Verhoeven, 1975). However, the overall $\Delta G_{f(AgNPs)}$ cannot be solely predicted by the surface free energy, suggesting that it can be significantly affected by other factors. Current research still seeks to understand how factors such as particle morphology, coating method, and biochemical properties of an aquatic environment quantitatively affect the overall $\Delta G_{f(AgNPs)}$. This requires well-designed experimental work for determining the actual $\Delta G_{f(AgNPs)}$ in aquatic environments. A comprehensive theoretical discussion with respect to the contribution of each factor to the overall $\Delta G_{f(AgNPs)}$ should be performed as well.

6.2. What is the true nanosilver dissolution or silver ion release kinetics?

Silver ion release kinetics must be adequately evaluated to better understand the transformation and fate of nanosilver in aquatic environments. So far, almost all studies have used a pseudo-first-order kinetics to predict silver ion release from silver nanoparticles in aquatic environments. However, the pseudo-first-order kinetics does not adequately explain the experimental data (Fig. 2). This paper revised this model, proposed a two-stage model, and obtained better results (Fig. 2). The validation and applicability of this relatively new two-stage model should be further verified. As a majority of the experimental work with respect to silver ion release was performed in relatively simple aquatic solutions, information related to nanosilver dissolution in complex and/or real aquatic environments (e.g., real sewage) is very limited. Furthermore, it is not clear whether the available active surface of nanosilver, other factors being fixed, can solely determine its dissolution process (i.e., whether the nano-effect significantly affects the dissolution). More research should be performed to more accurately predict the silver ion release process in real aquatic environments.

6.3. Will the nanosilver dissolution process be facilitated by microorganisms?

Microbes or their activities can reduce silver ions to nanosilver (Kalimuthu et al., 2008; Nanda and Saravanan, 2009; Pugazhenthiran et al., 2009; Saifuddin et al., 2009; Shahverdi et al., 2007; Thakkar et al., 2010). However, it is totally unknown whether nanosilver can be oxidized by microorganisms (i.e., microbe facilitated nanosilver dissolution). Under aerobic conditions, certain microbes might perform dissimilatory oxidation of AgNPs. It is widely reported that ferrous-ion-oxidizing bacteria can oxidize ferrous ions (Fe^{2+}) to obtain energy for growth in the presence of dissolved molecular oxygen (chemolithotrophic reaction) (Emerson et al., 2010; Fortin et al., 1996; Madigan et al., 2014). It is also possible that certain microbes can oxidize nanosilver in oxygenated water for growth. In addition, under anoxic conditions, some denitrifiers may facilitate anoxic, nitrate/nitrite-dependent nanosilver oxidative dissolution at a circumneutral/realistic pH (Equations (11) and (12)) in nitrite/nitrate-rich aquatic environments (Ettwig et al., 2010; Haroon et al., 2013; Weber et al., 2006). Anaerobic ammonium oxidation (anammox) bacteria, which could oxidize ferrous ions in the presence of nitrate (Oshiki et al., 2013), might also be able to cause a nitrate dependent nanosilver oxidization. Furthermore, under strict anaerobic conditions, sulfate reducing bacteria (SRB) can obtain electrons by directly oxidizing zero-valent iron (Fe^0) to Fe^{2+} (Enning and Garrelfs, 2014) and generate much sulfide (Baumgartner et al., 2006; Muyzer and Stams, 2008). This process has the potential to facilitate silver ion release. As a result, SRB might be able to oxidize nanosilver under strict anaerobic conditions. Finally, one cannot rule out the possible anaerobic oxidization of AgNPs by phototrophs photoautotrophically (Hu et al., 2013; Jiao et al.,

2005; Tang et al., 2009). Such a microbe-facilitated process, if it exists, would be of environmental significance with respect to a better understanding of silver cycling in nature and the ecotoxicity of nanosilver.

6.4. What are the true antimicrobial mechanisms of nanosilver?

Many antimicrobial mechanisms of nanosilver against microorganisms have been proposed and tested (Marambio-Jones and Hoek, 2010; Tolaymat et al., 2010; Xiu et al., 2012; Yu et al., 2013). Perhaps all these mechanisms contribute to the overall antimicrobial activities of nanosilver to different extents and from different simultaneous mechanisms. As a result, the key point might not be finding the "absolute" or "universal" antimicrobial mechanism (Bondarenko et al., 2013), but determining each mechanism's contribution to the overall antimicrobial activities of nanosilver in different biochemical environments.

7. Conclusions

- $\Delta G_{f(AgNPs)}$ in aquatic environments cannot be solely determined by the surface free energy of nanosilver. In fact, many other factors such as particle morphology and coating methods can significantly impact $\Delta G_{f(AgNPs)}$. As a result, in the analysis of nanosilver's thermodynamic stability in aquatic environments, these factors should be carefully considered.
- $\Delta G_{f(AgNPs)}$ determines whether nanosilver can react with a certain electron acceptor or whether its dissolution under certain conditions can occur. More carefully-designed experimental work is necessary to determine the effects of size and other factors on nanosilver dissolution/aggregation processes under varying aquatic environmental conditions (e.g., whether dissolution of nanosilver is possible under anoxic and anaerobic conditions).
- Silver ion release from the dissolution of nanosilver is often described using a pseudo-first-order kinetic model. However, this model often fails to adequately explain the nanosilver dissolution process. Therefore, a two-stage model has been proposed here to better predict the kinetics of silver ion release under aerobic conditions.
- Antimicrobial properties of nanosilver are mainly governed by the release of silver ions from nanosilver dissolution. ROS generation during nanosilver dissolution further enhances its bactericidal effect. Particulate nanosilver might also contribute to the overall toxicity of AgNPs (e.g., through the "particle-specific" pathway).

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List of abbreviations and symbols

T	Absolute temperature
AWI	Air-water interfaces
APS	3-(Aminopropyl) trimethoxysilane
Z	Amount of electron transferred
anammox	Anaerobic ammonium oxidation
M_{Ag}	Atomic weight of silver
V_A	Attractive interaction between silver nanoparticles
$\overline{\Delta G_{f(AgNPs)}}$	Average Gibbs free energy of formation of silver nanoparticles
A	Average number of silver atoms in each silver nanoparticle
HCO_3^-	Bicarbonate
k_B	Boltzmann constant
BSA	Bovine serum albumin
BPEI	Branched polyethyleneimine
C. elegans	*Caenorhabditis elegans*
$CaCl_2$	Calcium chloride
CO_3^{2-}	Carbonate
CO_2	Carbon dioxide
C. reinhardtii	*Chlamydomonas reinhardtii*
θ	Coefficient related to the properties of nanosilver
$C_{Ag^+(t)}$	Concentration of released silver ions from AgNPs at time t
CCC	Critical coagulation concentration
s	$d/r_{AgNPs} \cdot A_{eff}$
D. rerio	*Danio rerio*
D. magna	*Daphnia magna*
DLVO theory	Derjaguin–Landau–Verwey–Overbeek theory
Cl_2O	Dichlorine monoxide
DMPS	2,3-Dimercaptopropanesulfonate
DOM	Dissolved organic matter
d	Distance between the centers of two closest silver nanoparticles
$S_2O_4^{2-}$	Dithionite
E. fetida	*Eisenia fetida*
E	Electrode potential
E'	Electrode potential under biochemical standard state conditions
z	Electrolyte valence or charge number
e^-	Electron
S^0	Elemental sulfur
e	Elementary charge
$[O_{2(aq)}]$	Equilibrium concentration of dissolved molecular oxygen
$[Ag^+_{(aq)}]$	Equilibrium concentration of free silver ions
$C_{AgNPs(E)}$	Equilibrium concentration of nanosilver
$[H^+_{(aq)}]$	Equilibrium concentration of protons
K	Equilibrium constant
E. coli	*Escherichia coli*
FCC	Face-centered cubic
F	Faraday constant
Fe^{3+}	Ferric ion
Fe^{2+}	Ferrous ion
k	First-order reaction rate constant
FA	Fulvic acids
ΔG_r	Gibbs free energy change of a reaction
$\Delta G'_r$	Gibbs free energy change of a reaction under biochemical standard-state conditions
$\Delta G_{f(AgNPs)}$	Gibbs free energy of formation of nanosilver
$t_{1/2}$	Half-life
A_{eff}	Hamaker constant
HA	Humic acids
$D_{h,\ t}$	Hydrodynamic diameter of nanosilver at time t
H_2O_2	Hydrogen peroxide
H_2S	Hydrogen sulfide
$\cdot OH$	Hydroxyl radicals
$C_{AgNPs(0)}$	Initial silver nanoparticle concentration
V_R^{σ}	Interaction between silver nanoparticles under constant charge
V_R^{ψ}	Interaction between silver nanoparticles under constant potential

L. multiflorum *Lolium multiflorum*
$MgCl_2$ Magnesium chloride
β Mass transport coefficient
mRNA Messenger RNA
N_2 Molecular nitrogen
O_2 Molecular oxygen
MEL Mouse erythroleukemia
MSW Municipal solid waste
NZVI Nano-scale zero valent iron
$C_{AgNPs(t)}$ Nanosilver concentration at time t
AgNP-Ar Nanosilver stored under argon gas
AgNP–O_2 Nanosilver stored under oxygen gas
NIOSH National Institute for Occupational Safety and Health
NSDWR National Secondary Drinking Water Regulations
NOM Natural organic matter
V_T Net total potential energy among nanosilver
NO_3^- Nitrate
NO Nitric oxide
NO_2^- Nitrite
NO_2 Nitrogen dioxide
N. europaea *Nitrosomonas europaea*
N_2O Nitrous oxide
N Number-based nanosilver concentration
N_t Number-based nanosilver concentration at time t
N_0 Number-based silver nanoparticle concentration at time zero
OTS Octadecylichlorosilane
O. mykiss *Oncorhynchus mykiss*
$\%C_{AgNPs(E)}$ Percentage of silver nanoparticle concentration against total silver concentration at equilibrium
PFCAs Perfluorocarboxylic acids
PEL Permissible Exposure Limit
pH_{PZC} pH corresponding to the point of zero charge of nanosilver
PAOs Phosphorus accumulating organisms
PEG Poly(ethylene glycol)
PVA Poly(vinyl alcohol)
PVP Poly(vinyl pyrrolidone)
H^+ or $H^+_{(aq)}$ Proton
P. aeruginosa *Pseudomonas aeruginosa*
t Reaction time
ROS Reactive oxygen species
κ Reciprocal of Debye double layer thickness
ε Relative dielectric constant
V_R Repulsive force between silver nanoparticles
k_a Second-order aggregation rate constant
ΔE Shift in electrode potential
H Shortest interaction distance between two silver nanoparticles
AgCl Silver chloride
$AgCl_x^{(x-1)-}$ Silver(I)-chloride complexes
ρ_{Ag} Silver density
Ag^+ or $Ag^+_{(aq)}$ Silver ion
Ag_2O Silver monoxide
Nanosilver, AgNPs, or $Ag^0_{(nano)}$ Silver nanoparticles
$C_{AgNPs(t)}$ Silver nanoparticle concentration at time t
$AgNO_3$ Silver nitrate
$AgClO_4$ Silver perchlorate
Ag_2S Silver sulfide
SSD Silver sulphadiazine
$AgBF_4$ Silver tetrafluoroborate
$NaBH_4$ Sodium borohydride
NaCl Sodium chloride
SDS Sodium dodecyl sulfate
NaOCl Sodium hydrochloride
C_{NaOCl} Sodium hypochlorite concentration
$NaNO_3$ Sodium nitrate
SWI Solid-water interfaces
r_{AgNPs} Spherical radius of nanosilver
W Stability ratio
E^0 Standard electrode potential
ΔG_r^0 Standard Gibbs free energy change of a reaction
$\Delta G^0_{f(AgNPs)}$ Standard Gibbs free energy of formation of nanosilver
α Sticking (attachment) coefficient
SO_4^{2-} Sulfate
SRB Sulfate reducing bacteria
SO_3^{2-} Sulfite
SO_2 Sulfur dioxide
$\cdot O_2^-$ Superoxide radicals
ρ_{Ag} Surface free energy of silver
ψ_o Surface potential of nanosilver
$S_2O_3^{2-}$ Thiosulfate
$nanoTiO_2$ Titanium dioxide nanoparticle
TCLP Toxicity Characteristic Leaching Procedure
R Universal gas constant
U.S. EPA U.S. Environmental Protection Agency
Fe^0 Zero-valent iron
Ag^0 Zero-valent silver
$nanoZnO_2$ Zinc dioxide nanoparticle
nanoZnO Zinc oxide nanoparticle

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