Review: Issues of Silver Nanoparticles in Engineered Environmental Treatment Systems

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Abstract Silver nanoparticles (AgNPs) have been developed and broadly used for various applications, especially biocidal purpose. This could lead to contamination of AgNPs in engineered environmental treatment systems. This review conveys basic knowledge of AgNPs including synthesis techniques, fate, contamination and toxicity mechanism. The work emphasizes on the influence of AgNPs on the wastewater treatment and environmental remediation system performances. AgNPs could be synthesized using physical or chemical methods. After production or utilization, AgNPs distribute in the wastewater treatment and remediation systems via wastewater and excess sludge. Toxicity of AgNPs including cell surface defection, cell metabolism inhibition and protein damage by AgNPs, released silver ions or reactive oxygen species is reviewed. In the engineered environmental treatment systems, silver (ions and particles) may influence chemical and biological processes. For the chemical processes, silver species are able to lessen the process performance by chemical interaction while silver could be toxic to organisms in biological processes and fail the process performance later on. Previous works presented inconsistent results on influence of AgNPs to the engineered environmental treatment systems because of difference in AgNP properties, tested conditions and environmental conditions.

Keywords Remediation · Nanosilver · Silver zerovalent · Wastewater treatment

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1 Introduction

Silver is a metal which has been known for long time to be useful for medical, industrial and household applications, such as biocides, electrical conductors, currency coins and ornaments. Recently, silver was also synthesized in nanosize (1–100 nm), called silver nanoparticle (AgNP). AgNPs are broadly used because of their higher effectiveness compared to traditional silver particles (Ray et al. 2009; Rai et al. 2009; Guzman et al. 2012).

AgNPs have been applied for biocidal purpose in various applications, such as a medical household, and

industrial applications (Ray et al. 2009; Rai et al. 2009; Abou El-Nour et al. 2010; Arvizo et al. 2012). For medical application, AgNPs have been applied for disinfection and therapeutics, such as infected burn and wound reduction, medical device sterilization, tumour therapy and cardiovascular implants (Atiyeh et al. 2007; Tian et al. 2007; Chen and Schluesener 2008; Rai et al. 2009; Chaloupka et al. 2010; Arvizo et al. 2012). AgNPs are also incorporated in daily life products, such as apparel, cosmetics and plastics because of their antimicrobial property (Benn and Westerhoff 2008; Blaser et al. 2008; Chaudhry et al. 2008; Kokura et al. 2010). Moreover, in the industrial sector, AgNPs are used as sensors and a component in biosensors (McFarland and Van Duyne 2003; Ren et al. 2005; Zheng et al. 2008). Also, the particles have been applied in water and wastewater treatments, such as for pesticide and bacterial removals (Lv et al. 2009; Wu et al. 2010; Dankovich and Gray 2011; Manimegalai et al. 2011). This leads to a large amount of the AgNP utilization. Blaser et al. (2008) claimed that the biocidal silver use increased from 30 up to 230 t/year for global plastic and textile industries in 2004 and 2010, respectively. It was also reported that up to 15 % of total silver in the form of monovalent silver ions (Ag^+) or AgNPs could be released from biocidal plastics and textile into water. The fate of AgNPs related to textiles and plastics was discussed in a study by Blaser et al. (2008). This may lead to silver of approximately 190–410 t/year entered to wastewater treatment plant. Another recent study confirmed that AgNPs were released from AgNP-coated socks during washing process (Benn and Westerhoff 2008). Accumulative silver mass of up to 2 mg from 100 to 500 mg of socks was detected after washing for four times. Based on a large amount of AgNP utilization and the AgNP release information from the earlier studies, AgNPs are likely to be spread and might cause a problem in aquatic, terrestrial or atmospheric environments in the near future (Blaser et al. 2008; Lapresta-Fernández et al. 2012).

The engineered environmental treatment systems related to silver fate are wastewater treatment and site remediation which receive AgNPs from wastewater and sludge, respectively. Biological treatment processes (biological wastewater treatment and bioremediation) could be substantially influenced because AgNPs damage microorganisms in the systems leading to failure of the treatment. Thus far, there was no published review focusing on the influence of AgNPs to the engineered environmental systems. Previously, review studies mainly concentrated on AgNP syntheses, applications and toxicities (Sharma et al. 2009; Abou El-Nour et al. 2010; Durán et al. 2010a, b; Marambio-Jones and Hoek 2010; Arvizo et al. 2012; Guzman et al. 2012; Reidy et al. 2013; Levard et al. 2012; Bondarenko et al. 2013; Magdolenova et al. 2014). From previous works, it was clear that AgNPs are toxic to microorganisms, plants and animals; however, the particles are very useful and likely remain as an important composition in daily life products in the long run. Therefore, along with the development of AgNP-containing products, knowledge of AgNP fate in the engineered environmental treatment systems is also needed. This study emphasizes on the issues of AgNPs on the engineered environmental treatment systems including the wastewater treatment system (WWTS) and environmental remediation system (ERS). The work also includes information of AgNP synthesis, utilization, fate, contamination, toxicity mechanism and potential AgNP control techniques. This work should assemble the knowledge related to AgNPs and give perspective to deal with the influence of AgNPs in the future.

2 AgNP Synthesis, Utilization and Contamination

2.1 AgNP Synthesis

Several synthesis methods have been developed to achieve desired characteristics (sizes, shapes and surfaces) (Choi and Hu 2008; Durán et al. 2010a, b; Marambio-Jones and Hoek 2010). The AgNP synthesis methods could be divided into two approaches including physical and chemical approaches.

Physical Approach This approach comprised evaporation/condensation and irradiation. For the evaporation/condensation, silver ion solution is vaporized into a carrier gas and then cooled for nucleation and nanoparticle formation (Baker et al. 2005). Another technique, irradiation, AgNPs are produced by irradiating (laser, microwave or ionization) silver solution. The particle size could be controlled by variation of irradiation time and laser power (Amendola et al. 2007). The physical approach uses minimal or no chemicals, but the approach consumes a lot of energy and time (Abou El-Nour et al. 2010).

Chemical Approach The chemical approach is the most common technique to synthesize silver materials (Marambio-Jones and Hoek 2010). This approach comprises electrochemical reduction, photochemical reduction and chemical reduction techniques (Murray et al. 2005; Maretti et al. 2009; Marambio-Jones and Hoek 2010). The most common synthesis method is chemical reduction technique. Ag^+ in a solution is reduced by a reducing agent (such as sodium borohydride and sodium citrate) and formed silver atom (Ag^0) (Hsu and Wu 2007). The Ag atoms agglomerate and become particles. Also, a capping agent (such as surfactant) might be used to stabilize AgNPs. Lately, a biochemical approach which applies extracts from organisms as reducing agents and/or capping agents was developed. It is similar to chemical reduction method but use extracts from organisms (microorganisms and plants) as reducing agents and/or capping agents. The well-known biological extracts used for AgNP synthesis are proteins, amino acids and polysaccharides (Sharma et al. 2009; Marambio-Jones and Hoek 2010).

This chemical approach can use various chemicals and easily modifies the method to accomplish target properties. However, the approach deals with many hazardous chemicals such as poly(ethylene glycol) used as a reducing agent (Marambio-Jones and Hoek 2010). Biochemical technique is a greener synthesis, but the biological reaction rate sometimes is slow.

2.2 AgNP Fate and Contamination

AgNPs are new components in real practice; therefore, fate and contamination of AgNPs are not well-understood. The published information mostly were estimated from computer models and detected from laboratory or pilot results (Blaser et al. 2008; Benn and Westerhoff 2008; Kaegi et al. 2010; Kim et al. 2010). Li et al. (2013) reported that treated effluent from nine municipal WWTSs in Germany containing AgNPs of 12 ng L^{-1} could estimate AgNP load of 4.4 g day^{-1} for the WWTS with 520,000 t day^{-1}.

The fate of AgNPs related to textiles and plastics was discussed in a study by Blaser et al. (2008). It was reported that the silver residues from many countries in Asia, North America and Europe generally went to solid waste management and retained in solid waste landfill. The rest of silver residues (approximately 190–410 t year^{-1}) passed to WWTSs and distributed to natural water and soil (Table 1). Otherwise, a small

Table 1 Calculated amount of silver from global textile and plastic industries in each environmental medium

Environmental medium	Amount of silver	
	t year^{-1}	%
WWTSs	190–410	100.00
Natural receiving water (from treated wastewater)	20–130	11.53–31.70
Soil (from wastewater treatment sludge for agricultural purpose)	80–190	42.10–46.34
Atmosphere (from solid waste incineration smoke)	8–17	4.06–4.21

Silver entering solid waste landfill is neglect

portion of silver (8–17 t year^{-1}) could be released to the atmosphere via stack gas from solid waste incineration (Table 1). Based on the silver flow mentioned above, the potential AgNP fate in the environment including the engineered environmental treatment systems is presented in Fig. 1.

It is noticed that after passing the processes, AgNPs may change their form (Fig. 1) (Nowack 2010). Normally, redox reaction and pH play an important role on Ag speciation (Levard et al. 2012). In the presence of oxygen, AgNPs are likely to dissolve to Ag^+ while silver sulphide particles (Ag_2S) are found in anaerobic condition. Low pH in the environment promotes Ag dissolution. For example, Fabrega et al. (2009) reported that a suspension of commercial AgNPs (with diameter sizes of 30–50 nm) at pH of 0.5 was completely dissolved whereas the dissolution of AgNPs at pH of 6 to 9 was only between 1 and 2 %. This could be explained by the chemical reaction shown in Eq. (1). Lower pH results in higher H^+ leading to higher dissolution.
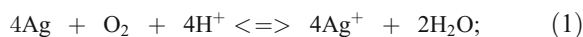
$$4Ag + O_2 + 4H^+ <=> 4Ag^+ + 2H_2O; \quad (1)$$
$$\Delta DG_{298}° = -11.25 \text{ kJ/mol}$$

Also, the size of AgNPs plays an important role of Ag dissolution. Angel et al. (2013) found that the dissolution rate of nanosize silver particles (diameter sizes of 14–15 nm) was 20 times more than that of the microsize silver particles (at diameter sizes of 2.0–3.5 μm).

Recently, Kim et al. (2010) found nanosized silver sulphide particles (Ag_2S) in sludge from an AgNP-contaminated wastewater treatment plant in USA. It was implied that AgNPs could change their form to be Ag^+ and Ag_2S. Later, Kaegi et al. (2011) confirmed that most AgNPs precipitated as Ag_2S in the non-aerated

Fig. 1 AgNP fate in environment
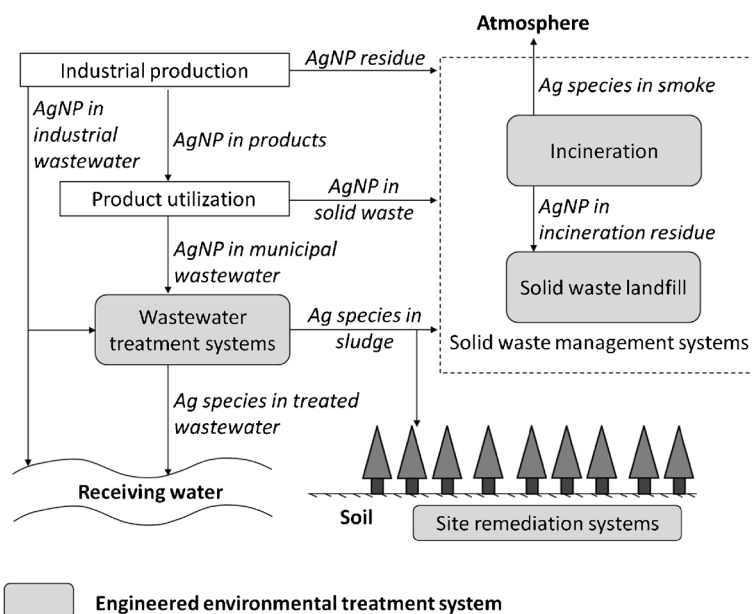
wastewater treatment tank. This resulted in Ag_2S suspended in the treated effluent or sorbed onto sludge. It is noticed that the solubility product constant of Ag_2S (5.92×10^{-51}) was much less than those of Ag in other forms such as silver chloride (1.77×10^{-10}), silver sulphate (1.20×10^{-5}), silver carbonate (8.46×10^{-12}) and silver oxide (4.00×10^{-11}) (Levard et al. 2012). Therefore, it could be said that the reduced sulphur such as in wastewater influents, AgNPs, are likely to dissolve and precipitate as Ag_2S and remain stable sorbed on sludge.

Table 2 is a summary of silver contamination related to AgNPs from previous works. Earlier, the silver contamination was predicted based on information of life cycle analysis (Blaser et al. 2008; Mueller and Nowack 2008; Gottschalk et al. 2009; Musee 2010). Most studies reported the contamination in terms of total silver due to uncertain magnitude of Ag transformation varying based on AgNP characteristics. Recently, the silver contamination in forms of AgNP and Ag^+ was able to be detected (Mitrano et al. 2011; Hoque et al. 2012). Different silver concentrations detected in the studies were caused by AgNP-incorporated technology used in each product, wastewater collection and treatment systems, and wastewater compositions (Table 2) (Benn and Westerhoff 2008; Kim et al. 2010; Nowack 2010; Hoque et al. 2012). It is noticed that modelled Ag contamination was much higher than that of measured Ag concentration. It was reported that Ag contamination

in wastewater treatment effluent, sludge and river of up to 18 μg L^{-1}, 39 mg/kg and 148 ng L^{-1}, respectively, was modelled (Blaser et al. 2008). In practice, Ag contamination in nanograms per litre level was detected in WWTS and river (Mitrano et al. 2011; Hoque et al. 2012). This indicates that Ag may retain in early stage of product (containing Ag) life cycle leading to low Ag contamination in WWTS and river.

3 AgNP Toxicity and Resistance

3.1 Toxicity and Resistance Mechanism

Numerous previous studies have evaluated the toxicity of AgNPs to microbial, plant or animal cells (Lok et al. 2006; Choi et al. 2008; Damm et al. 2008; Marambio-Jones and Hoek 2010; Guzman et al. 2012; Lapresta-Fernández et al. 2012). AgNPs could damage the cells by themselves or by Ag^+ and/or reactive oxygen species (ROS) created by AgNP oxidation (Choi et al. 2008; Asharani et al. 2009; Marambio-Jones and Hoek 2010). The Ag dissolution followed an Eq. (1) described in earlier section.

This Ag dissolution significantly occurred in aerobic condition (Yang et al. 2013). Based on Gibbs free energy which was less than zero ($\Delta G° < 0$), this reaction is a spontaneous reaction (Levard et al. 2012; Yang et al. 2013). During the dissolution, ROS may be created.

Table 2 Summary of silver contaminations related to AgNPs

Silver detected form	Contaminated concentration	Environmental medium	Location	Reference
Total Ag (model)	2–18 μg L^{-1} 39 mg kg^{-1} 148 ng L^{-1}	WWTS effluent Sludge River	Switzerland	Blaser et al. (2008)
AgNP (model)	0.002–0.004 μg m^{-3} 0.03–0.08 μg L^{-1} 0.02–0.1 μg kg^{-1}	Air Receiving water Soil	Switzerland	Mueller and Nowack (2008)
AgNP (model)	22.7, 8.3, 11.2 ng kg^{-1} year^{-1a} 1,581, 662, no record ng kg^{-1} year^{-1a} 0.8, 0.1, 0.7 ng L^{-1a} 42.5, 21, 38.7 ng L^{-1a} 1.7, 1.6, 1.9 mg kg^{-1a} 952, 195, 1,203 ng kg^{-1} year^{-1a} 0.008, 0.002, 0.021 ng m^{-3a}	Soil Sludge treated soil Surface water WWTS effluent WWTS sludge Sediment Air	Europe, USA, Switzerland	Gottschalk et al. (2009)
Total Ag	145 μg-Ag L^{-1}	Rain contaminated by AgNP-containing paint during initial runoff event	Switzerland	Kaegi et al. (2010)
AgNP (model)	7.8–306.6 kg year^{-1} 6.2–184.2 kg year^{-1} 0.003–0.619 μg L^{-1}	Wastewater WWTS Aquatic ecosystem	Johannesburg, South Africa	Musee (2010)
Dissolved silver (dAg) AgNP	520, 60 ng L^{-1b} 200, 100 ng L^{-1b}	WWTS influent, WWTS effluent	Boulder, CO, USA	Mitrano et al. (2011)
AgNP	1.90 ng mL^{-1} Not detectable at detection limit of 0.8 ng mL^{-1}	WWTS effluent Lakes and river	Ontario, Canada	Hoque et al. (2012)
AgNP	<12 ng L^{-1}	WWTS effluents	Germany	Li et al. (2013)

[a] Data of Europe, USA and Switzerland, respectively

[b] Data of WWTS influent and WWTS effluent, respectively

These three species (AgNP, Ag$^+$ and ROS) could: (i) damage cell wall, membrane and components including DNA and (ii) inhibit cell metabolism. Generally, biological cells correlated to the engineered environmental treatment systems are microorganisms, especially bacteria. Consequently, in this review, the mechanism of AgNP toxicity to microorganisms is focused on.

Damage of Cell Wall, Membrane and Components AgNPs could attach to cell membrane, penetrate into and damage the cells. This action varied based on microbial species. Mostly, Gram-positive bacteria had higher resistance to AgNPs compared to Gram-negative bacteria (Jung et al. 2008; Guzman et al. 2012). The previous results suggested that the Gram-positive bacteria had much thicker peptidoglycan in cell surface layer than the Gram-negative bacteria resulting in high tolerance of AgNP toxicity (Jung et al. 2008; Guzman et al. 2012).

Silver (AgNPs and Ag$^+$) was likely to bind/attach to proteins containing sulphur at the cell surface (Morones et al. 2005; Hwang et al. 2008). Another explanation was about electrostatic attractive force (Raffi et al. 2008; Dasari and Hwang 2010). The positively charged particles could easily attach onto the microbial cells which normally are negatively charged. The particles then interact with the cell membrane and cause broken walls and membranes. Some portion of cellular content disappear thereafter (Smetana et al. 2008). The activated sludge during nitrification process in presence of AgNPs (5 mg L^{-1}) was studied (Giao et al. 2012). The cell envelope was obviously damaged and cellular content released.

Inhibition of Cell Metabolism and Damaging of DNA Silver ions could interact with enzymes involving respiration in the microbial cells (Marambio-Jones and Hoek 2010; Lapresta-Fernández et al. 2012). Silver had high affinity to react with thiol groups (−SH) of respiratory proteins locating at the cell membrane (Durán et al. 2010a, b; Marambio-Jones and Hoek 2010). Silver ions could also inhibit ATP synthesis and phosphate uptake and increase DNA mutation. ROS could endorse intracellular oxidative stress (Yang et al. 2013). Furthermore, free radicals could damage membrane lipids resulting in membrane collapse, protein malfunction and DNA damage (Mendis et al. 2005; Nel et al. 2006; Choi et al. 2008; Marambio-Jones and Hoek 2010).

Even though AgNPs were likely to dissolve in aqueous solution, the portion of Ag^+ varied from 0.1 % to up to more than 90 % of dissolution (Lok et al. 2007; Choi et al. 2008; Liu and Hurt 2010; Sotiriou and Pratsinis 2010; Hou et al. 2012; Dobias and Bernier-Latmani 2013). The Ag dissolution rate depends on several factors including the particle size, particle surface and environmental conditions such as pH or salt concentrations. Some previous works reported low Ag dissolution (0.1 to 4.0 % of total Ag) found that AgNP toxicity was higher than that of Ag^+ (Lok et al. 2007; Choi et al. 2008; Liu and Hurt 2010; Hou et al. 2012). The degree of AgNP toxicity compared to Ag^+ was inconsistent. For example, Lok et al. (2007) found that AgNP toxicity in *Escherichia coli* was approximately 1,000 times higher than that of Ag^+ whereas Choi et al. (2008) reported that AgNP toxicity in nitrifying microorganisms was twice higher than Ag^+. However, this information obviously indicated that AgNPs themselves were also toxic to microorganisms.

Contrarily, some other studies presented that toxicity of AgNPs was from Ag^+ only (Navarro et al. 2008; Sotiriou and Pratsinis 2010; Levard et al. 2012; Yang et al. 2013). Since AgNP might affect the cell surface and components, Ag^+ also reacts inside the cells. The difference of results could be due to a high Ag dissolution (up to 90 %) which took place in the latter cases leading to insignificant toxicity of AgNPs. Currently, direct toxicity mechanism of AgNPs was proved to be the cell surface damage by microscopic imaging. No exact mechanisms of action on the functional genes (or protein) involved in the direct AgNP toxicity and resistance mechanisms were proposed. The continued work

on these mechanisms to microorganisms should be conducted.

Some microorganisms (such as *Salmonella* sp. and *Chromobacterium violaceum*) could tolerate some toxic substances such as AgNPs and Ag^+ naturally (Durán et al. 2010a, b; Marambio-Jones and Hoek 2010). Most previous works involving the AgNP-resistant cultures (such as *Fusarium*, *Enterobacteria*, *Pseudomonas*, *Cyanobacteria*, *Bacillus*, *Aspergillus* and *Geobacter*) focused on the use of the strains for the AgNP biosynthesis (Parikh et al. 2008; Suresh et al. 2010; Saravanan et al. 2011). Most previous works emphasizing mechanism of silver resistance was on silver ion (Gupta et al. 2001; Silver 2003). The silver ion resistance was encoded in both chromosome and plasmid genes, such as *sil* and *agr* gene series in *Salmonella* sp. and *E. coli*, respectively (Gupta et al. 2001; Silver 2003). These microorganisms brought Ag^+ out by pumping H^+ into the cells resulting in Ag-resistant property (Gupta et al. 2001; Silver 2003). This presented mechanism should take place for Ag^+ dissolving from AgNP. Thus far, there were only a few published studies focusing on AgNP (in particle form) and cell resistance mechanism (Khan et al. 2011; Giao et al. 2012; Miller et al. 2013). The previous works found that microorganisms could tolerate AgNPs likely because of physical protection by exopolymeric substances (EPS) from the cells (Khan et al. 2011; Giao et al. 2012). In terms of molecular biological mechanism, no substantial impact of AgNPs on antibiotic resistance gene was found in an anaerobic digester in California, USA (Miller et al. 2013). However, numerous factors could influence this mechanism; the continued work on this point is recommended to fill in the knowledge gap on Ag toxicity.

3.2 Toxicity Influencing Factors

Factors influencing toxicity could be divided into two main groups: (i) AgNP properties and (ii) environmental conditions. AgNP properties related to in vitro toxicity included physical properties (size, shape, crystallinity and surface charge) and chemical properties (surface coating, elemental composition and solubility). For physical properties, AgNPs synthesized to different shapes (such as truncated triangular, spherical and rod-shapes) had different active facets (Pal et al. 2007; Carlson et al. 2008; Choi and Hu 2008; Somasundaran et al. 2010; El Badawy et al. 2011). AgNPs with a {111} lattice plane as the basal plane (like truncated triangular

shape) showed the highest biocidal property compared to others. It was reported that *E. coli* was completely inhibited by the truncated triangular AgNPs with Ag content of 10 $\mu g\ L^{-1}$ while the spherical AgNPs of 500 to 1,000 $\mu g\ L^{-1}$ caused 100 % inhibition for the same culture (Pal et al. 2007). For size, it is obvious that the particles at smaller size had higher surface area resulting in higher biocidal activities.

In chemical property point of view (surface coating, elemental composition and stability), among various AgNP synthesis methods, several reducing and capping agents and synthesis techniques were applied and resulted in different particle surface properties (Kvitek et al. 2008; El Badawy et al. 2011; Suresh et al. 2012). These properties significantly affected the microbial cell surface and membrane causing cell death or malfunction. Moreover, the factors also influenced AgNP stability; more particle stability (less aggregation) led to more toxicity (Suresh et al. 2012; Whitley et al. 2013).

Another important factor, environmental conditions such as pH, light, ionic strength, salinity, organic matter (OM) and DO, affected the AgNP toxicity (Lok et al. 2007; Choi and Hu 2008; Choi et al. 2009; Gao et al. 2009; Nel et al. 2009; Dasari and Hwang 2010; Lushchak 2011). The pH close to the isoelectric point and OM (including natural OM and EPS released during cell lysis) could stimulate AgNP aggregation resulting in lower toxicity. For DO and light, these parameters promoted ROS attributing to higher AgNP toxicity. In addition, DO concentration also endorsed AgNP dissolution magnitude (to Ag^+) which resulted in Ag toxicity (Yang et al. 2013). It was shown that in anaerobic sludge digestion system (DO less than 0.5 $mg\ L^{-1}$), AgNPs of up to 40 $mg\ L^{-1}$ did not inhibit the treatment system since there was no oxidative dissolved Ag^+ released (Yang et al. 2012). Natural chemicals related to ionic strength and salinity (such as cysteine ligands and chloride) influence both AgNP dissolution and re-precipitation. These factors could either promote or decrease the AgNP toxicity. In presence of divalent cations related to hardness and alkalinity (such as calcium carbonate), toxicity of AgNPs apparently decreased (Zhang et al. 2012). Figure 2 presents relationship of AgNP toxicity influencing factors.

Based on the information from previous works, cytotoxicity caused by the above factors has been inconsistently presented. For example, Choi and Hu (2008) reported that the AgNP sizes (9–21 nm) significantly affected the toxicity level of nitrifying microorganisms.

Another study by Suresh et al. (2012) found that the sizes did not influence AgNP toxicity but the particle surface (coating type such as a poly(diallyldimethylammonium) surface coat, a peptide surface coat and an oleate surface coat) played an important role on cytotoxicity. The inconsistent results were due to the varying tested AgNPs and environmental conditions performed by each research group. In this context, it could state that toxicity mechanism and toxicity influencing factors could be generally described as mentioned above but exact prediction needs to be estimated case by case.

4 Influence of AgNPs to Engineered Environmental Treatment Systems

Based on the fate of AgNPs shown in Fig. 1, the engineered environmental treatment systems including wastewater treatment and site remediation could be influenced by AgNPs. The particles could enter WWTSs via municipal and industrial wastewater while AgNPs may go to contaminated sites via WWTS sludge applied for site remediation such as the sites with biostimulation process. A previous work found that in Germany, WWTS sludge of 30 % was applied as fertilizer (Schlich et al. 2013). It was also reported the AgNP-contaminated soil of 0.0015 mg/kg dry soil after sludge application. The engineered environmental treatment systems generally comprise physical, chemical and biological processes.

Physical Processes The physical processes normally apply for preliminary and primary treatments to remove debris, grit and large particles, such as screening, sedimentation, flocculation and filtration. Since the physical processes are gravity and/or size separation processes, the physical processes should not be obviously disturbed by AgNPs (small and light weight).

Otherwise, these processes may be able to remove some portion of AgNPs sorbed on the large particles (Brar et al. 2010). The particles (mono-dispersed particles or aggregates) could attach on general particles in the wastewater, but opportunity of aggregation and attachment depends on wastewater characteristics such as alkalinity, natural organic matter (NOM) and solids concentration (Huang and Wang 2001; Li et al. 2010). Huang and Wang (2001) reported that solid concentration played a role on metal removal. Both solids and

Fig. 2 Relationship of AgNP
toxicity influencing factors
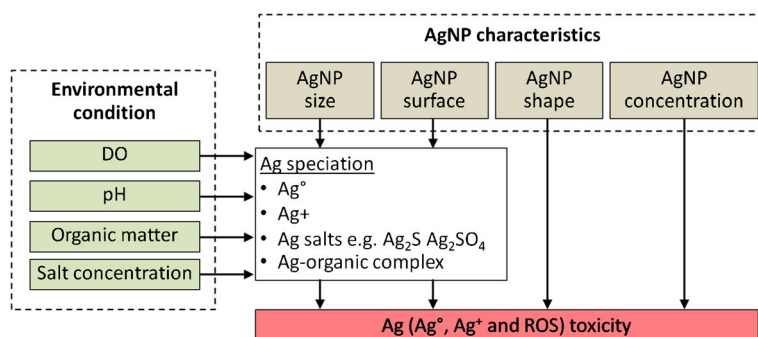
metal are simultaneously removed in the primary clarifier. Li et al. (2010) found that fulvic acid of 4.5 mg L^{-1} promoted AgNP aggregation. In addition, Levard et al. (2012) reported that AgNP surface (coated and uncoated) played an important role on AgNP aggregation but the influence was different. The particles coated with polyvinylpyrrolidone and citrate were well-stabilized AgNPs (less aggregation) compared to the uncoated one (Kvitek et al. 2008; Huynh and Chen 2011). For this treatment unit process, minimal efficiency (approximately 10 %) of AgNP removal by the physical process (simulated primary clarifier by jar test) was reported (Hou et al. 2012).

Physical processes for ERSs include the application of physical techniques such as in situ grouting, soil washing and air sparging/air stripping. The physical processes are only physical separation, such as the in situ grouting is to restrict the pollutants by cement wall or containment. Hence, the physical processes should not be visibly influenced by AgNPs. It is noticed that the particles could physically attach to soil on the top soil layer (Bradford et al. 2009; Coutris et al. 2012).

Chemical Processes The chemical processes involving chemical reactions, such as adsorption, coagulation, ion exchange and precipitation, target for reducing small particles or dissolved solids. Silver may compete with other particles (with similar surface charge) in the chemical processes resulting in lower treatment efficiency. Figure 3 is a schematic diagram of potential reactions related to AgNPs. Reactions including dissolution/oxidation, precipitation, sulphidation, complexation, aggregation, attachment/adsorption and sedimentation (physical process) may take place. AgNPs could dissolve or oxidize and convert to Ag$^+$. Along with the oxidation, ROS may be created. These dissolution and oxidation are important processes which normally occur

in all WWTSs (Lok et al. 2007; Choi et al. 2008; Liu and Hurt 2010; Hou et al. 2012). The reaction may decrease the amount of oxidizing agent (such as O$_2$ or H$_2$O$_2$) in the systems.

Precipitation and sulphidation (precipitation by sulphide) form Ag-insoluble species, such as Ag$_2$S. It was reported that AgNPs directly and indirectly precipitated as Ag$_2$S which are less toxic and more stable (highly insoluble) compared to AgNPs as shown in Fig. 3 (Kim et al. 2010; Liu et al. 2011). These reactions depended on wastewater characteristics such as pH, DO, NOM concentration and ionic strength. For sulphidation of AgNPs, this chemical reaction arises in incomplete anaerobic treatment systems with slight oxygen concentrations. In aerobic environment, sulphur normally is in sulphate and sulphite forms (mainly sulphate) which were proven to be non-reactive with AgNPs (Liu et al. 2011). But oxygen was still needed for sulphidation of AgNPs. During the indirect sulphidation of AgNPs, oxygen was used for oxidizing AgNPs to Ag$^+$ and Ag$^+$ then precipitated by reactions with H$_2$S or HS$^-$ to Ag$_2$S. For the indirect sulphidation of AgNPs, the reaction was solid–fluid heterogeneous reaction. This is the conversion of particles (AgNPs) to particles (Ag$_2$S) via oxysulphidation (Liu et al. 2011). It is likely that in WWTS, some portion of AgNPs may be continuously dissolved along with the wastewater treatment train. Therefore, both direct and indirect sulphidation could take place. This is an important reaction for AgNP toxicity reduction and immobilization.

Sedimentation of silver could be associated by AgNP aggregation. Attachment/adsorption bound Ag species to solids, such as debris and biosolids (Kiser et al. 2010). These reactions are important processes to remove Ag from the wastewater; however, Ag in biosolids could be toxic to microorganisms as mentioned in the previous section (details on the effect to biosolids in the WWTSs
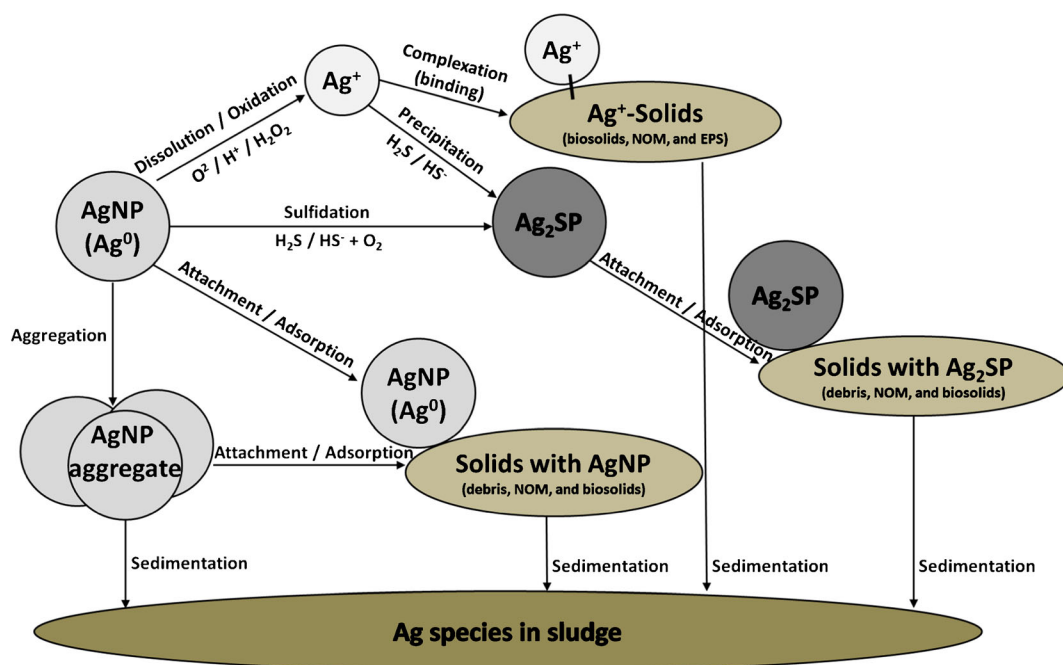
Fig. 3 Schematic diagram of potential reactions related to AgNPs

presented in later section). In practice, AgNPs are likely to contaminate the environment at low concentration. The AgNP concentrations in WWTS of 2–18 µg L^{-1} were estimated (Blaser et al. 2008). In this context, AgNPs may not greatly impact the chemical processes. On the other hand, the chemical processes could reduce or detoxify AgNPs contaminated wastewater via sulphidation, complexation and sorption.

Another process, photolysis (UV irradiation), is used for disinfection (approximately less than 100 mJ/cm^2) or organic degradation (approximately 1,000 mJ cm^{-2}). It is known that UV irradiation was applied for AgNP synthesis (Cuba et al. 2010; Gorham et al. 2012). The technique reduces Ag$^+$ to Ag metallic form. In the presence of UV radiation, photolysis could promote AgNP aggregation (Cuba et al. 2010). Moreover, as mentioned earlier, some portion of AgNP could be dissolved to Ag$^+$. In photolysis process, these ions could be reduced to be Ag particles. Therefore, it is likely that photolysis process may aid to control AgNPs. On the other hand, AgNPs at high concentration in the waste-water treatment system could absorb UV light and re-duce the system performance.

Chemical processes for ERSs are the main remedia-tion process in practice. The processes involve the ap-plication of chemicals to immobilize or extract the pol-lutants off the soil and groundwater. There are several

techniques, such as pump and treat, surfactant enhanced aquifer remediation (to use surfactant to increase pollut-ant solubility before removal), chemical stabilization and chemical oxidation. In the terrestrial environment, Ag may be present in various forms. Silver has four oxidation states (0,+1, +2 and +3) and can exist in the forms of silver oxide, silver nitrate, silver halides (fluo-ride, chloride, bromide), silver sulphate, silver thiosulphate complexes and silver sulphide also. But Ag$^\circ$ and Ag$^+$ typically found in the environment (Purcell and Peters 1998). In ERSs, Ag species distrib-uting in the system should depend on the species in sludge.

All reactions which could occur in WWTSs may also take place in ERSs (Fig. 3). It was reported that the Ag species could sorb on soil (Ag fixation) but with differ-ent degrees of sorption based on soil organic content and AgNP surface (Coutris et al. 2012). It was found that AgNPs were well-retained in organic-rich soil (14 % organic content) by adsorption process. But the citrate-capped AgNPs (20 % extracted) was quite mobile in soil compared to uncoated AgNPs (1 to 3 % extracted) (Coutris et al. 2012).

Physical sorption of Ag$_2$S was believed. Silver ions are possible to sorb quicker and higher than AgNPs. Hou et al. (2005) reported that 88 % of Ag$^+$ (at 3 mg kg^{-1} soil) was sorbed on the top soil (0–2 cm). It

can be said that the sorbed Ag is an inactive (fixed) form. Therefore, among Ag^+, AgNPs and Ag_2S, AgNPs (with the lowest sorption) are possible to cause the most influence to the chemical process. Thus far, there was no report on direct effect of AgNPs to the chemical process performance.

Biological Processes The biological processes normally used for secondary or advanced wastewater treatment. The processes are to remove organic compounds and nutrients by microorganisms. Previously, it was reported that AgNPs in the contaminated wastewater after passing a simulated first clarifier (physical process) were removed to only 10 % (Hou et al. 2012). Therefore, microorganisms in the biological processes could be noticeably influenced by AgNPs leading to lower performance of the treatment systems. The examples of the affected systems were summarised in Table 3. It is noticed that the environmental studies mostly applied AgNPs with spherical shape at average size of 5–30 nm (Table 3). This is because the particles with this shape and sizes are likely to be used in commercial products, but for in the case of utilized AgNPs in other shapes such as triangular shape, the toxicity and influence should be higher than those of spherical AgNPs (information of shape-dependent toxicity is reviewed earlier). Based on the information in Table 3, the summary suggests that the biological processes could be either totally inhibited or uninhibited by AgNPs. The results from each study obviously vary.

In aerobic biological processes, chemolithotrophs are responsible for nitrification while heterotrophs are organic carbon oxidizers. Among the studies, AgNP affected chemolithotrophs and nitrification activities more than heterotrophs (Table 3). Nitrification is known as a sensitive process. This is because the nitrifying microorganisms are slow growing and sensitive to environmental stress, such as temperature, DO, pH and toxic substances. The nitrification inhibition could be due to the damage of cell surface and proteins by AgNPs, Ag^+ and ROS. As, ammonia monooxygenase and hydroxylamine oxidoreductase which are enzymes governing ammonia oxidation are located in the cell membrane and periplasm (Chain et al. 2003; Choi et al. 2008; Giao et al. 2012); therefore, AgNPs and Ag^+ not only damage the cell viability but also the nitrification process performance.

In the aerobic heterotrophic process, the AgNP toxicity action on aerobic heterotrophs was similar to

chemolithotrophs stated above. It was found either substantial or slight effects by AgNPs (Choi et al. 2008; Liang et al. 2010; García et al. 2012). These conflicting results could have two reasons as follows: The first reason is the difference in tested environmental conditions and cultures. For example, Choi et al. (2008) found the heterotrophic process inhibition of 55 % from the test with a synthetic wastewater containing AgNPs of 1 mg L^{-1} while García et al. (2012) reported slight inhibition from the test with AgNPs of 0.17 mg L^{-1}. The tested concentrations were much different (approximately six times). Additionally, the test with the low concentration of AgNPs may not significantly affect the microbial cultures leading to stable wastewater treatment performance. Another reason is different interactions of AgNPs in WWTSs. Numerous studies reported the difference of the AgNP dissolution or agglomeration magnitudes as stated in previous sections. For example, Wang et al. (2012) found the AgNP sorption of 88 % (the initial AgNP concentrations ranged from 0.5 to 1.5 mg L^{-1}) onto microbial sludge while Kiser et al. (2010) reported the AgNP sorption of 97 % at the initial AgNP concentrations of 0.5 to 0.6 mg L^{-1}. This could result in different biological performances. More sorption may cause more toxicity to microbial cells and less AgNP distribution in the WWTS. Also, in the long term, this may cause the accumulation of AgNP in return sludge resulting in lower wastewater treatment efficiency thereafter.

In the anaerobic heterotrophic process, theoretically, the AgNP toxicity action should be similar to chemolithotrophs and aerobic heterotrophs as stated above. However, there was a report of no to moderate effect of AgNP to the anaerobic biocoenoses (García et al. 2012; Yang et al. 2012). This may be due to the occurrence of AgNP sulphidation resulting in lower AgNP bioavailability. A good illustration of this situation is given by Yang et al. (2012). They studied the stable anaerobic treatment and microbial community from the experiment at the AgNP concentration of up to 40 mg L^{-1} (measured in total Ag form).

When suspended microbial cells and biofilm is compared, the cells in biofilm form performed much better than the suspended microbial cells in the test at AgNP concentration of 200 mg L^{-1} (Sheng and Liu 2011). This is because of the role of extracellular polymeric substances and physical protection by the layer of the cells. The result suggested that the microorganisms themselves have their own protection system. However,

Table 3 Engineered environmental treatment systems affected by AgNPs

System description	AgNP size (nm)	Effect on system performance and lmicrobial community	Reference
Wastewater treatment systems			
Inhibitory effect by on the autotrophic and heterotrophic growth was determined	Applied size at 14 nm (active size at 200 nm)	Growth of autotrophic nitrifying organisms (86 %) was inhibited at AgNP of 1 mg L^{-1}.	Choi et al. (2008)
The study was to determine inhibition of nitrifying organism	9–21	Sizes of AgNPs played an important role to nitrifying organism growth inhibition The effective concentration of AgNPs causing 50 % inhibition was 0.14 mg L^{-1}	Choi and Hu (2008)
The research was to study the impact of ligands (Cl$^-$, SO$_4^{-2}$, PO$_4^{-3}$, EDTA^{-4} and S^{-2}) on AgNP toxicity to nitrification	6–24	Nitrification inhibition of 100 % occurred at AgNPs of 1 mg L^{-1}. Sulphide effectively reduced AgNP toxicity (by 80 %) Ammonia-oxidizing microorganisms were more sensitive than nitrite-oxidizing microorganisms	Choi et al. (2009)
Planktonic and biofilm activities from AgNP contaminated wastewater treatment were determined	15–21	Biofilms were four-time higher resistant to AgNPs compared to planktonic cells Silver ion was more toxic to *E. coli* because AgNPs were aggregated and resulted in lower toxicity	Choi et al. (2010)
Sorption of AgNPs onto activated sludge was studied	13	Sorption of AgNPs on glycoprotein from the HIV-1 viral lipid membrane (39 % removal) was reported Sorption, aggregation and sedimentation promoted AgNP removal of 97 %	Kiser et al. (2010)
Inhibitory effect from shock loading of AgNPs to autotrophs and heterotrophs was evaluated	1–29	AgNPs and Ag+(total Ag of 1 mg L^{-1}) inhibited nitrification for 41.4 and 13.5 %, respectively Silver significantly affected nitrifying microorganisms	Liang et al. (2010)
Effect of AgNPs on biofilm and planktonic pure culture in wastewater treatment was performed at AgNPs of 200 mg-Ag L^{-1}	<5	Biofilm microbial community was much more tolerant	Sheng and Liu (2011)
Effect of AgNPs on activated sludge process was studied	–	AgNPs did not present effect on WWTS performance. AgNPs of 88 % was removed during the treatment	Wang et al. (2012)
The work determined effect of AgNPs on aerobic and anaerobic wastewater treatment at AgNPs of 0.17 mg L^{-1}	30	AgNPs caused biogas production inhibition of 33 to 50 %	García et al. (2012)
Fate and impact of AgNPs (0.1–1.0 mg L^{-1}) in simulated wastewater treatment processes were determined	–	AgNPs of 90 % remained in the wastewater after simulated primary clarification while AgNPs were completely removed in sequencing batch reactor processes	Hou et al. (2012)
Impact of AgNPs on anaerobic glucose degradation and sludge digestion was studied at AgNPs of 40 mg L^{-1}	21	There was no significant difference in biogas and methane production between the sludge treated with AgNPs The microbial community which *Methanosaeta* and *Methanomicrobiales* were dominant remained unchanged	Yang et al. (2012)
Environmental remediation systems			
Effects of AgNPs on natural bacterial community in estuarine environment were studied at AgNPs of 0–1 mg L^{-1}	<100	AgNPs accumulated in the surface layer of the sediment (about 3 mm from top) No or little significant AgNP impacts on the prokaryotic abundance were detected	Bradford et al. (2009)

Table 3 (continued)

System description	AgNP size (nm)	Effect on system performance and lmicrobial community	Reference
Effect of humic acid on the AgNP cytotoxicity to aquatic bacterial community was studied at AgNPs of 0–5 μM	15–25	In river water, AgNPs were reduced to Ag^+ up to 33 % but humic acid could bind Ag^+ and reduce Ag^+ toxicity	Dasari and Hwang (2010)
Influence of AgNPs on arctic soil microbial diversity was investigated	20	AgNPs significantly reduced the recovery of 16S sequences (13–70 %) in orders of *Solirubrobacterales*, *Actinomycetales*, *Rhizobiales*, *Acidobacteriales* and *Clostridiales*	Kumar et al. (2011)
The work was to assess the colloidal stability and agglomeration of AgNPs in aquatic ecosystem	20	AgNPs partially agglomerated in the pond water. It was also found that NOM promoted colloidal stabilization	Chinnapongse et al. (2011)
The study was to compare soil-binding behaviour of silver nitrate, citrate-stabilized Ag NPs and uncoated Ag NPs in organic and mineral soils	5, 19	All types of silver were more mobile in the mineral soil than in the organic soil. Silver nitrate and citrate-stabilized Ag NPs were rapidly immobilized in soil	Coutris et al. (2012)

based on the AgNP effects to biological process presented in Table 3, it could be said that the biological process could be severely affected by AgNPs at parts per million level such as the results by Liang et al. (2010) and García et al. (2012). However, concern on AgNP contamination may focus on parts per billion level since the particles have been developed to improve antimicrobial effects. Therefore, in the future, the toxicity of AgNPs may be higher. Thus far, the exact biological wastewater treatment response mechanism to AgNPs is still inconclusive. The continued work on this point is needed.

For ERSs, biological processes are important for removing contaminants in soil or groundwater by organisms (microorganisms called microbial remediation and plants called phytoremediation). Normally, the processes are applied for degrading organic compounds to be less mobile or toxic, such as carbon dioxide and water.

The effect of AgNPs (and all other transformed species) to bioremediation processes is similar to that of WWTSs which are inconsistent as shown in Table 3 (Bradford et al. 2009; Kumar et al. 2011). This is mainly caused by different environmental conditions and microbial community tolerance. The studied conditions with OM or salt-rich environments are likely to lessen silver-biocidal ability leading to lower effects on the bioremediation performance (Bradford et al. 2009; Dasari and Hwang 2010). However, in ERSs, the microbial community is complex. Whether some microbial

cultures are sensitive and could not survive in the Ag-contaminated environment, this may affect ecosystems. For example, Kumar et al. (2011) reported that in arctic soil, bacteria under order of *Bacillales* were growing better in presence of AgNPs but *Bradyrhizobium*, a nitrogen-fixing species, was noticeably influenced. This situation could cause an impact on the nitrogen cycle at the arctic ecosystem.

5 Potential AgNP Control Alternatives

AgNP contamination control strategy could be accomplished in two ways: policies and technical alternatives. For policies, regulations, environmental standards (including concentration limits) or economic incentives could be set. In this review, the alternatives in technical point of view are focused.

Thus far, environmental standards could not be set since there were conflicting results of minimal inhibitory concentration (MIC) of AgNPs. This is because the particles prepared differently gave totally different MIC values. For example, Guzman et al. (2012) reported that MICs of AgNPs with diameter sizes of 8 to 50 nm (prepared by sodium citrate and hydrazine–sodium citrate reduction techniques) for microorganisms including *E. coli* CCM 3954, *Pseudomonas aeruginosa* CCM 3955, *Staphylococcus aureus* CCM 3953 and *S. aureus* MRSA ranged between 7 and 259 mg L^{-1}. Peetsch et al.

(2013) found that spherical silver-doped calcium phosphate nanoparticles had MIC of 1 to 3 mg L^{-1} for mammalian and prokaryotic cells while Debabrata and Giasuddin (2013) reported MIC of AgNPs in *Saccharomyces cerevisiae* at 48.51 mg L^{-1}. Based on these examples, it looks like that AgNP contamination (as mentioned in earlier section) may not reach to MIC. However, an environmental standard of AgNP contamination needs to be concerned.

USEPA has set the maximum contaminant level of silver at 100 μg L^{-1} for drinking water since 1990s. Although this USEPA standard is likely to apply for conventional Ag ($AgNO_3$ and AgCl) utilization, the value may not be able to apply for AgNP due to the difference of the material characteristics and uses. Currently, it is difficult to conclude an exact value for an environmental standard. But it is obvious that for nanomaterials including AgNPs, environmental standards need to be enforced urgently along with the rapid increase of the material use. Also, the standard should apply for each particle characteristics including particle size, shape and surface since they are main factors influencing the magnitude of toxicity and reaction in the environment.

The technical AgNP control alternatives have been considered recently. Table 4 summarises the control alternatives investigated earlier. Based on Table 4, natural/existing and modified/additional control techniques are proposed. It can be seen that the AgNP control alternatives could be divided into two main processes: chemical and biological processes. It is noted that the physical processes (gravity separation) may not be appropriate for AgNP removal except the case of AgNP macro-aggregates. For the chemical processes, precipitation and sorption are proposed based on previous investigations (Choi et al. 2009; Kim et al. 2010; Kiser et al. 2010; Elmachliy et al. 2011; Hou et al. 2012; Liu et al. 2011; Wang et al. 2012). Precipitation by sulphide is to convert Ag^+ and AgNPs to Ag_2S as referred in earlier section. Biosorption on biomass or plants was another efficient chemical process to remove silver species. To avoid toxicity from silver in later treatment processes, the additional precipitation or sorption (with non-aerated condition) tank before secondary treatment could be alternatives (Fig. 4).

Table 4 Potential AgNP control alternatives

Control technique	Reference
Natural/existing control techniques	
Transformation of AgNPs to Ag_2S has less toxicity and is more stable by anaerobic wastewater treatment systems with sulphur-rich environments	Kim et al. (2010)
Sorption on biomass during biological treatment process	Hou et al. (2012)
	Wang et al. (2012)
Modified/additional control techniques	
Addition of sulphide to form Ag_2S is less toxic and more stable in an aqueous solution	Choi et al. (2009)
	Liu et al. (2011)
Isolation of Ag-detoxifying species, such as *Chromobacterium violaceum* to augment in contaminated wastewater or soil	Durán et al. (2010)
Sorption on biomass in biological treatment process	Kiser et al. (2010)
	Khan et al. (2012)
Microwave radiation and plant biosorption as an additional (advanced) treatment	Elmachliy et al. (2011)

For the biological processes, Ag-detoxifying species, such as *C. violaceum*, were isolated for cell bioaugmentation (Durán et al. 2010a, b). Cell bioaugmentation, addition of pollutant-detoxifying microorganisms, is one of the efficient engineered environmental treatment techniques which could apply for both wastewater treatment and environmental remediation (Siripattanakul and Khan 2009). Alternatively, cell entrapment technique may apply for this situation. The technique is to immobilize microorganisms in a porous polymeric matrix. The technique was successfully applied for either removal of hazardous substances or minimization of hazardous substance-cell contact (Cassidy et al. 1996; Siripattanakul et al. 2008; Siripattanakul-Ratpukdi 2012). The technique may combine to bioaugmentation, called entrapped cell bioaugmentation. The combined technique is an efficient and economical alternative because the pollutant-detoxifying in the entrapped cell form can be reused. Figure 4 presents the application of cell bioaugmentation and cell entrapment for Ag (Ag^+ and AgNP) control. For ERSs, phytoremediation could apply for nanosize Ag similar to traditional metal remediation (Bech et al. 2002; Archer and Caldwell 2004).

Chemical processes

Biological processes
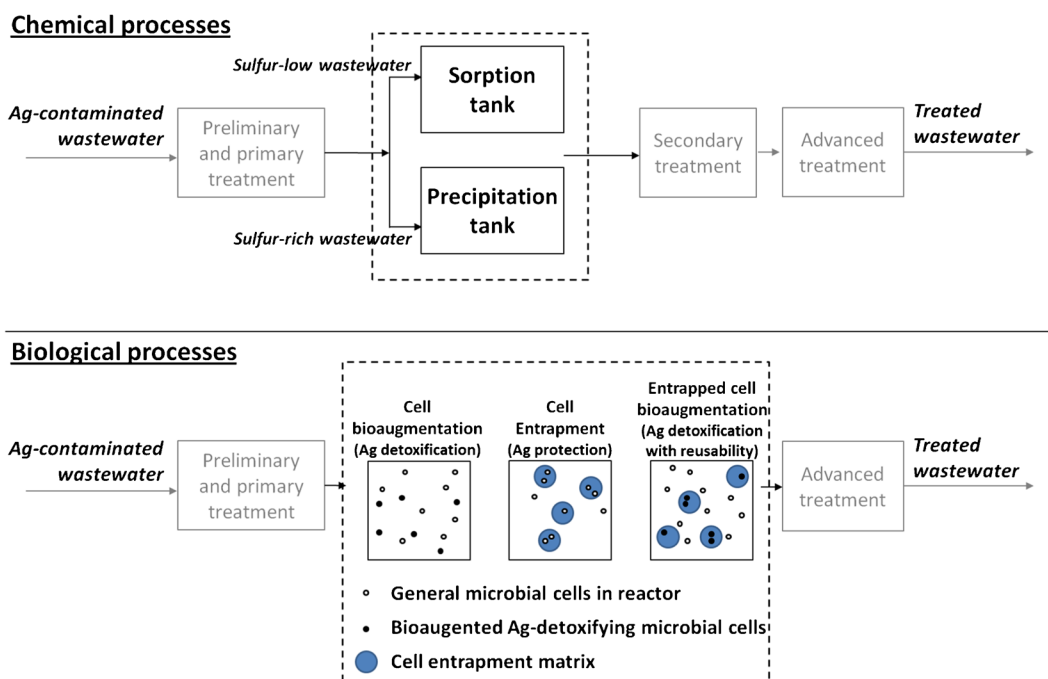
Fig. 4 Potential chemical and biological processes for Ag control in the wastewater treatment systems

6 Conclusion and Future Research Prospective

AgNPs have been developed to serve various applications. Also, influence of AgNPs in the environment including the engineered environmental treatment systems has been considered and studied lately. Numerous questions on AgNPs versus speciation, transport and influence mechanism to engineered environmental treatment systems arise. This is because a number of factors are involved in this issue. Thus far, the issue is critical because of its unpredictability.

AgNPs enter WWTSs and ERSs via wastewater and sludge, respectively. AgNPs could dissolve and re-precipitate definitely. Silver in nano- (and less) sizes (ions and particles) spreads over and deposits in the engineered environmental treatment systems. This circumstance could substantially influence the chemical and biological processes. For the chemical processes, Ag species are able to lessen the process performance by their substitution of chemical reaction components or as interference in chemical reaction. In biological processes, a role of Ag toxicity to biological organisms in the systems is considered at the milligram per litre level. This affects biological process performance. Up to now, potential AgNP control techniques are not well-proposed since Ag influence mechanisms are limited. However, the chemical processes (precipitation and sorption) and biological processes (cell bioaugmentation and cell entrapment) may be considered.

Further required works are listed as follows:

1. Fate of AgNPs in the engineered environmental treatment systems including AgNP dissolution, Ag re-precipitation, AgNP aggregation and sorption and interaction with chemical processes
2. Operating and environmental conditions affecting the system in presence of AgNPs such as hydraulic retention time, solid retention time, substrate concentration, biomass concentration, pH and temperature
3. Insight of AgNP influences mechanism on microbial community and microbial response (toxicity and resistance related to corresponded functional genes, enzymes and proteins).

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