A critical review on silver nanoparticles: from synthesis and applications to its mitigation through low-cost adsorption by biochar

Md Anwarul Islam, Mohan V. Jacob, Elsa Antunes*

College of Science and Engineering, James Cook University, Townsville, QLD 4811, Australia

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* Corresponding Author: Elsa Antunes (elsa.antunes1@jcu.edu.au)

Abstract

Silver nanoparticles are one of the most beneficial forms of heavy metals in nanotechnology applications. Due to its exceptional antimicrobial properties, low electrical and thermal resistance, and surface plasmon resonance, silver nanoparticles are used in a wide variety of products, including consumer goods, healthcare, catalysts, electronics, and analytical equipment. As the production and applications of silver nanoparticles containing products increase daily, the environmental pollution due to silver nanoparticles release is increasing and affecting especially the aqueous ecosystem. Silver nanoparticles can kill useful bacteria in soil and water, and bioaccumulate in living organisms even at low concentrations from 10^{-2} to 10 µg/mL silver can show antibacterial effect. On the other hand, the maximum silver discharge limit into freshwater is 0.1 µg/L and 3.2 µg/L for Australia and the USA, respectively. To reduce its toxic consequences and meet the regulatory guidelines, it is crucial to remove silver nanoparticles from wastewater before it is discharged into other water streams. Several technologies are available to remove silver nanoparticles, but the adsorption process using low-cost adsorbents is a promising alternative to mitigate silver nanoparticle pollution in the bulk stage. As one of the low-cost adsorbents, biochar produced from the biomass waste could be a suitable adsorbent. This review focuses on collating the latest evidence on silver nanoparticle production, applications, environmental consequences, and cost-effective technological approaches for silver removal from wastewater.

Keywords: Adsorption; Biochar; Environmental pollution; Nano silver; Nanoparticles

1 Introduction

Silver nanoparticle (Ag NP) is an important innovation in nanotechnology. Unique physicochemical and strong antimicrobial properties make silver nanoparticles suitable for numerous applications [1-3]. Particularly biomedicines, medical devices, functional textiles, cosmetics, food packaging, food supplements, odour-resistant items, electronics, household appliances, dental amalgam, water disinfectants, paints, and room spray [4, 5]. Therefore, increasing demand has led to a rise of silver nanoparticles' production. Worldwide, the total estimated production of silver nanoparticles was about 500 tonnes per year in 2009, while expecting an increase of approximately 900 tonnes by 2025 [6-10].

Silver ion and metallic silver nanoparticles are both hazardous to living organisms and aquatic ecosystems [11]. Ingestion of silver may cause health risks by metabolising and depositing in subcutaneous fat [12, 13]. Silver ion in the water system is classified as a hazardous material by the World Health Organization (WHO), the U.S. Environmental Protection Agency (USEPA), Australia, and Germany [12-14]. Further, wastewater generating from manufacturing processes and usage of these products are contaminated with silver nanoparticles and/or silver ions [15-18]. Therefore, it is important to remove either form of silver from the wastewater before discharging the effluent into the natural environment [19, 20].

The concentration of silver nanoparticles or silver compounds in wastewater varies depending on the wastewater generating points. In Malaysia, concentrations of silver nanoparticles found in sewage treatment plant (STP) vary between 0.13 and 20.02 mg /L [9], in Canada up to 1.9 µg/L [21], and in Germany between 0.32 and 3.05 µg/L [22]. Wastewater treatment plant (WWTP) with primary treatment processes, such as screening, precipitation, coagulation, and followed by biological treatment can remove most of the silver nanoparticles and silver compounds [20, 22, 23]. However, wastewater treatment facilities, which have no preliminary or primary treatment process, can be impacted by silver toxicity and may lead to a discharge of contaminated effluents [24, 25] as silver ions have a negative influence on bacteria dominant aerobic treatment processes [6, 26-28]. Even low

concentrations of silver (ng/L) are toxic and still representing a real threat to the environment for the long run [29, 30].

In terms of economic feasibility, easy operation, and sustainability, adsorption is a promising method to remove low concentrations of heavy metals including silver and other precious metals from wastewater [31-34]. Adsorption is the adhesion of atoms, ions, or molecules to the surface of a substrate by chemical or physical interactions [34]. Silver adsorption study by using a low-cost adsorbent has gained substantial interest in recent years [12, 35]. Several studies are found on silver removal using different adsorbents, but just a few research has been done so far on the application of biochar to remove silver from an aqueous solution [34, 36]. However, biochar produced from biomass might bring the breakthrough [37].

The present review made an effort to analyse the progress on silver nanoparticles application, consequences, and mitigation of its environmental toxicity by adsorption. To our best knowledge, this is the first review on silver nanoparticles from the synthesis processes to their environmental mitigation.

2 Silver nanoparticles synthesis

Metallic silver is a naturally available soft, white, lustrous rare element with high thermal and electrical conductivity [38-40]. Silver nanoparticles are a special form of metallic silver having less than 100 nm size in at least one dimension which offers silver nanoparticles a high surface area to volume ratio [3, 7]. Silver nanoparticles can be produced by several methods, such as physical and chemical processes as shown in Figure 1 [41]. Each process has some advantages and disadvantages in terms of process complexity, particle size distribution, stability, applications of Ag NPs, and cost.

In the physical process, metallic solid silver is firstly evaporated in a furnace by conventional heating or electrical arc discharge and then condensed as nanoparticles [42]. Uniform particle size, narrow particle size distribution, and uniform shape of Ag NPs can be produced by changing the thermal or ac

power, and arc discharge [43]. The common drawbacks of this conventional process are the high energy consumption, heating up the surrounding environment, and a long time to achieve thermal stability [44]. However, laser ablation is one of the most used physical processes where the metal plate absorbs a laser impulse to produce a plasma phase of silver atoms which form different particle sizes of silver nanoparticles by varying silver ions [45]. The cooling liquid medium allows condensation of nano drops of silver and finally high purity and desirable silver nanoparticles are produced by this process [46]. The laser ablation process produces pure Ag NP colloids as there is no use of chemicals in the solution.

Spray pyrolysis (thermal decomposition) is another physical method by which monodisperse Ag NPs in poly (vinylpyrrollidone) matrix can be produced without any reducing agent [47]. In this process, an aqueous solution of $AgNO_3$, and dextran or polyvinylalcohol (PVA) is first injected into an electrically heated horizontal tubular reactor [48], and then the solution is ultrasonically atomised and carried out from the reactor by nitrogen gas which protects the Ag NPs from oxidation [49, 50]. Silver nanoparticles can be also produced from direct silver metal sputtering into a liquid medium (glycerol and water). The silver nanoparticles produced from metal sputtering were spherical with a uniform particle size distribution with an average diameter of approximately 3.5 nm [51]. Another potential production method for silver nanoparticles is the emulsion detonation synthesis using precursors such as silver salts or metal particles [52]. In summary, the physical processes require high energy and are costly, but produce silver nanoparticles with a narrow particle size distribution and are the most suitable methods to produce a large volume of Ag NPs in a form of powder [44].

Chemical processes are the most common and simple methods to produce Ag NPs. Controlling particle growth in order to produce small spherical Ag NPs with narrow particle size distribution is one of the main challenges of this method. Chemical synthesis methods of silver nanoparticles often use three main components: metal precursor, reducing, and stabilizing agents. Silver nanoparticles are mainly produced from the reduction [53] of silver salts such as silver nitrate ($AgNO_3$), silver perchlorate

117 ($AgClO_4$), and silver tetrafluoroborate ($AgBF_4$). Commonly used reducing agents are ethylene glycol
118 ($C_2H_6O_2$), ethanol (C_2H_5OH), glucose ($C_6H_{12}O_6$), sodium borohydride ($NaBH_4$), hydrazine (N_2H_4), and
119 sodium citrate ($C_6H_5Na_3O_7$) [41, 53]. During the chemical synthesis of silver nanoparticles, it is also
120 essential to use some sort of stabilising agents to stabilise the nanoform of silver by avoiding the
121 aggregation of freshly prepared nanoparticles. For instance, polyvinyl pyrrolidone (PVP),
122 polysaccharide, polyvinyl alcohol (PVA), polyethylene glycol (PEG), chitosan, oleylamine, and gluconic
123 acid [41, 54]. Formation of initial nuclei and the subsequent growth of nuclei are the most important
124 processing stages to determine the uniformity of size and shape of Ag NPs, which can be controlled
125 by the reaction conditions, such as pH, reaction time, silver salts, reducing agents, and capping
126 chemicals [55, 56]. Chemical process is more suitable to produce highly monodispersed and shape
127 specific Ag NPs [57, 58].
128 Some researchers have successfully used selective plant extract or living organisms as a reducing agent
129 to replace synthetic chemicals. Using plant extract in the chemical reduction process is often termed
130 as biological reduction or eco-friendly or green manufacturing process of silver nanoparticles [41, 54,
131 59]. Recently, this biological pathway is gaining high interest because of a potential lower
132 environmental impact compared to other chemical processes [60, 61]. Biological method is not only
133 simpler and low-cost, but also has a lower environmental impact due to the elimination of toxicity
134 from the unreacted synthetic chemicals and their disposal [62, 63]. Ag NPs produced from the green
135 synthesis route are less likely to aggregate in the cell biological environment, which helps Ag NPs in
136 their biomedical applications [64].

137 Silver nanoparticles can also be synthesized by electrochemical cell methods where a silver anode
138 dissolves gradually. Under the electrolysis conditions, produced silver ions are reduced at the platinum
139 cathode, and subsequently a colloidal suspension of silver nanoparticles is produced [65, 66]. Silver
140 nanoparticles are produced by photochemical methods by using electromagnetic radiation. In this
141 process, ultraviolet and visible lights are used. The reduction is carried out by the silver ions which are
142 produced by the irradiation of the solvent molecules [2, 67].

Ag NPs are also produced by mechanical ball milling (mechanical process), which is a top-down physical process. The silver nanoparticles are produced by grinding coarse silver particles (usually microparticles) that are placed in a ball mill and subjected to high-energy collision from ceramic balls. [68]. The final size of Ag NPs depends on the size of the ceramic balls, milling time, and concentration of silver particles in the mill. However, solid powder of silver salts such as silver nitrate can also be milled with an organic reducing agent (i.e. lignin, plant extracts) by ball mill and produced Ag NPs, this process is often classified as a mechano-chemical process [69, 70]. Mechanical ball milling is advantageous for its low energy consumption, simplicity, and high potential for mass production of Ag NPs [69]. A representation of the production methods is presented in Figure 1 while Table 1 summarises the main processing conditions, properties, and applications of Ag NPs for the most used production methods.

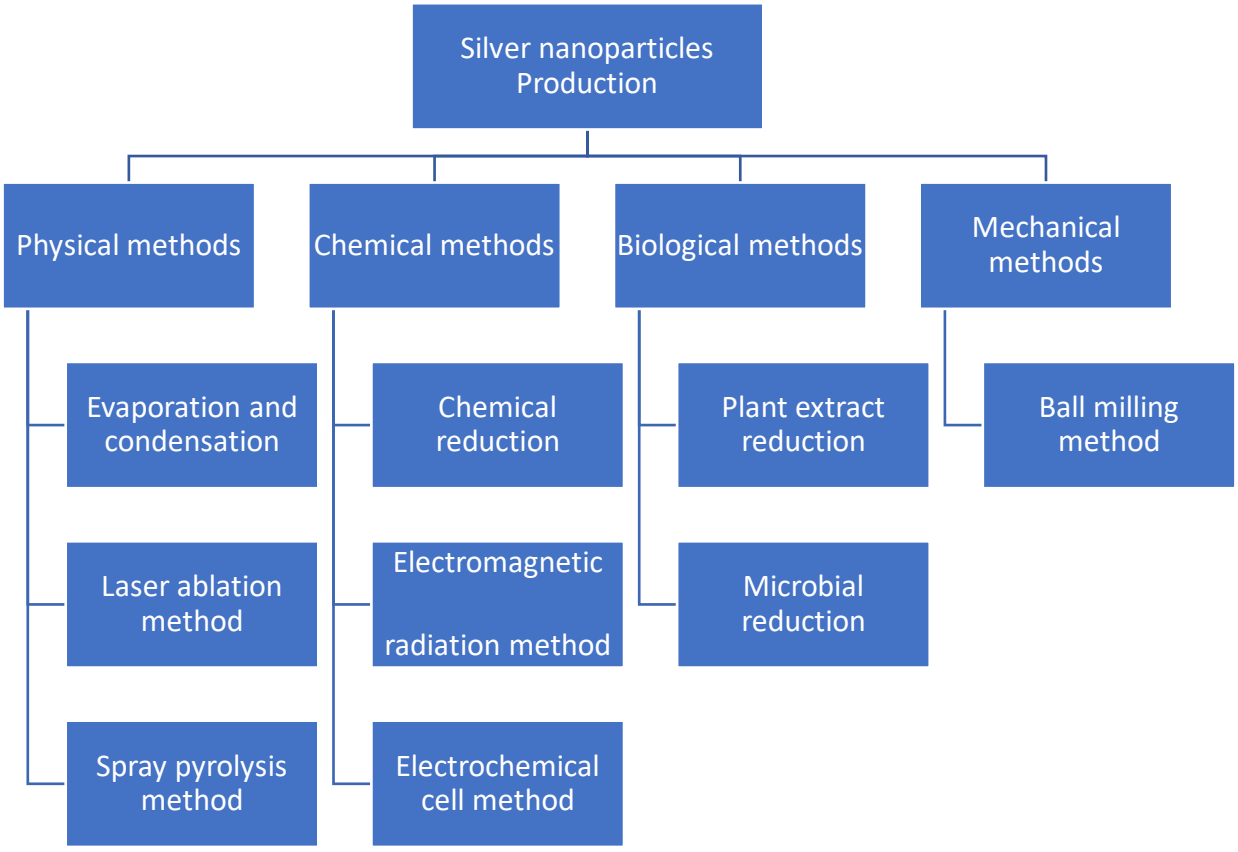

Figure 1. Main silver nanoparticles production methods.

156 Table 1. Few examples of shape-specific Ag NPs synthesis methods, properties, and their applications.

Method	Process	Reagents and Conditions	Properties of Ag NPs	Application of Ag NPs	Reference
Physical Methods	Laser ablation	Precursor = Silver 99.99% Laser ablation at 355 and 532 and 1064 nm light and laser power 12 mJ/pulse for 30 min	Size : 10 - 30 nm Shape: Spherical	Electronic devices, catalyst	[71]
		Precursor = Silver 99.99% Laser ablation at 532 nm light and laser power 0.34 J/pulse for 5 min	Size: 2 - 5 nm Shape: Spherical	Electronic devices, catalyst	[72]
Chemical Methods	Chemical reduction	Precursor = Silver chloride (0.01 M) Reducing agents = hydrazine hydrate (0.1M) Capping agent = 2% PVA pH 8–9 by ammonia at room temperature	Size: 10 - 60 nm Shape: Spherical or pseudo-spherical	Biomedical science (anti-bacterial)	[55]
		Precursor = Silver nitrate (10 mM) Reducing agents = $NaBH_4$ (8 mM) in NaOH (0.125 M) Capping agent = trisodium citrate (100 mM) silver seeds are instantly irradiated with a 70 W sodium lamp for 2 hours	Size: 4 - 5 nm Shape: Triangular / nanoprisms	Plasmonic and sensing, analytical devices, photovoltaics, molecular detection	[73]
		Precursor = Silver nitrate (95 mM) Reducing agents = hydrochloric acid in ethylene glycol (3mM) Capping agent = 2% PVP at 130°C for 10 hrs	Size: 50 ± 5 nm Shape: Nanocubes	Cysteine sensing, analytical devices	[74]
		Precursor = Silver oxide Reducing agents = NA as reaction supports oxidation reduction growth at 200 - 300°C	Size: 40 - 55 nm Shape: Nanorods	Plasmonic and sensing, analytical devices	[75]
		Precursor = Silver nitrate (0.1 M) Reducing agents = Trisodium citrate (0.1 M) Capping agent = Formaldehyde (1.5 M) Irradiated by MW(650 W, 2.45 GHz) for 1 min	Size: 24 - 132 nm Shape: Spherical	Anti-bacterial	[76]
		Precursor = Silver nitrate (0.25 mM) Reducing agent = Starch Capping agent = cetyl trimethyl ammonium bromide (0.2 M) at 40°C temperature for 12 hrs	Size: ~ 60 nm Shape: Hexagonal	Plasmonic and sensing, analytical devices	[77]
		Precursor = Silver nitrate (15 mM) Reducing agent = Starch Capping agent = Cetyl trimethyl ammonium bromide (0.1 M) at 27°C temperature for 20 hrs	Size: ~ 40 nm Shape: Flower-shaped	Analytical devices (SERS), catalysis	[77]
		Precursor = Silver nitrate Reducing agent = $NaBH_4$ Capping agent = trisodium citrate and ascorbic acid electrochemical cell process at room temperature	Size: 2 - 5 nm diameter and 2 - 4 µm length Shape: Nanorods and nanowires	Plasmonic and sensing, analytical devices	[78]

Biological methods	Biological reduction by plant extracts	Precursor = Silver nitrate (20 mM) Reducing agents = fresh extract of Artichoke (Cynara scolymus L.) flower heads pH 7 at 40°C temperature	Size: 30 - 80 nm Shape: Spherical	Electronic applications	[60]
		Precursor = Silver nitrate (1.0 mM) Reducing agents = turmeric powders at room temperature	Size: 5 - 35 Shape: Spherical and quasi-spherical	Agricultural and food industries	[79]
		Precursor = Silver nitrate (1.0 mM) Reducing agents = S. mammosum extract pH 9 by NaOH at 35 (± 1)˚C temperature for 30 minutes	Size: 10 - 14 nm Shape: Spherical	Biosensor	[80]
		Precursor = Silver nitrate Reducing agents = Quercetin (QUC,3,3Q,4Q,5,7-pentahydroxyflavone) (50 mM) at pH 7	Size: 5 - 8 nm Shape: Spherical	Biosensor	[81]
		Precursor = Silver nitrate (0.1 M) Reducing and capping agents = Orange Peel Extract Irradiated by Microwave (700 W) for 15 min	Size: 1 – 56 nm (95% < 30 nm) Shape: Spherical	Anti-bacterial	[82]
		Precursor = Silver nitrate (2.0 mM) Reducing agent = saffron (Crocus sativus L.) wastages extract Ultrasonic irradiation at room temperature for 3 hrs	Size: 12 - 20 nm Shape: Spherical	Anti-bacterial	[83]
	Microbial reduction	Precursor = Silver nitrate (3.5 mM) Reducing agent = Airborne bacteria (Bacillus sp.) Nutrient agar containing silver nitrate solution is incubated at room temperature for 7 days	Size: 5 - 15 nm Shape: Spherical	Anti-bacterial	[84]
		Precursor = Silver nitrate (3.5 mM) Reducing agent = fungus (C. Cladosporioides) Fungi and nutrient containing silver nitrate solution is incubated at 27°C temperature for 78 hrs	Size: 10 - 100 nm Shape: Spherical	Anti-bacterial	[85]
		Precursor = Silver nitrate (0.1 g/L) Reducing agent = Bacillus licheniformis at pH 8 Incubated at 27°C temperature for 24 hrs	Size: 10 - 80 nm Shape: Spherical	Anti-bacterial	[86]

157

158 Physicochemical properties of Ag NPs depend largely on the production process and reducing or
159 capping agents used. Each of the synthesis methods produces a colloidal solution of Ag NPs with a
160 specific size and shape. Ag NPs can be produced in a variety of shapes such as nanospheres, necklaces,
161 nanobars, nanocubes, nanoprism, bipyramids, nanostars, nanowires, triangular, hexagonal, nanorice,
162 and flower-shaped [53, 77, 87]. However, according to Table 1, the spherical shape is the most
163 common shape obtained from many of the synthesis processes. Morphology of Ag NPs determines
164 the efficiency of their end application [77]. For example, triangular / nanoprisms shapes are suitable
165 for biosensors, Surface Enhanced Raman Spectroscopy (SERS), and Metal-Enhanced Fluorescence
166 (MEF) [8]. In electronic circuit printing and catalytic usages Ag NPs size is more important than shape,
167 ultrafine particles with a size ranging from 2 nm to 8 nm are appropriate for these applications [71].

168 Crystallinity is also an important property of Ag NPs. A higher degree of crystallinity of Ag NPs shows
169 a high quality of SPR by doubling the dephasing time of localized surface plasmons [88]. A study also
170 suggests that single crystalline Ag NPs showed three times higher response than polycrystalline Ag
171 NPs on absorption cross-section of N719 dye [89]. X-ray diffraction data of produced Ag NPs reveals
172 that the face centred cube crystalline structure are (111), (200), (220), and (311) lattice planes [90,
173 91].

174 Stability of the colloidal solution of Ag NPs often depends on Zeta potential [92, 93]. Zeta potential is
175 defined by the charge of the particles in a colloidal system [94]. In general, a minimum value of ±30
176 mV zeta potential is required for a stable colloidal system [95]. Ionic nature or polarity of capping
177 agents or stabilising agents can also influence the physicochemical behaviour of the colloidal solution,
178 such as zeta potential [96].

179 In summary, each production method has some advantages and some disadvantages. Depending on
180 the applications, Ag NPs are required to have different shape and purity. For instance, laser ablation
181 method is suitable to produce Ag NPs for electronics use where purity is one of the most important
182 properties. However, this physical method may not be suitable for other applications because of its

high production cost. Similarly, considering the low environmental impact, green synthesis (biological) methods are promising, but for cheap and bulk production of Ag NPs, pure chemical routes are cost-effective where the synthetic chemicals are used as reducing and stabilising agents. Ag NPs produced from the green synthesis method have less aggregation behaviour than the Ag NPs produced from direct chemical synthesis, thus retains higher toxicity for a longer time [64]. However, a requirement in terms of the shape of Ag NPs may dictate the selection of the synthesis method.

3 Applications of silver nanoparticles

Silver nanoparticles have numerous applications in: healthcare, consumer products, information, and communication technology (ICT), food industry, environmental health, and agriculture sectors [38, 41, 54]. Figure 2 shows the main nano silver applications, 30% of silver nanoparticles are used in medical products, 25% in paints and coatings, 15% in functional textiles, and 15% in cosmetics or personal care products [97].

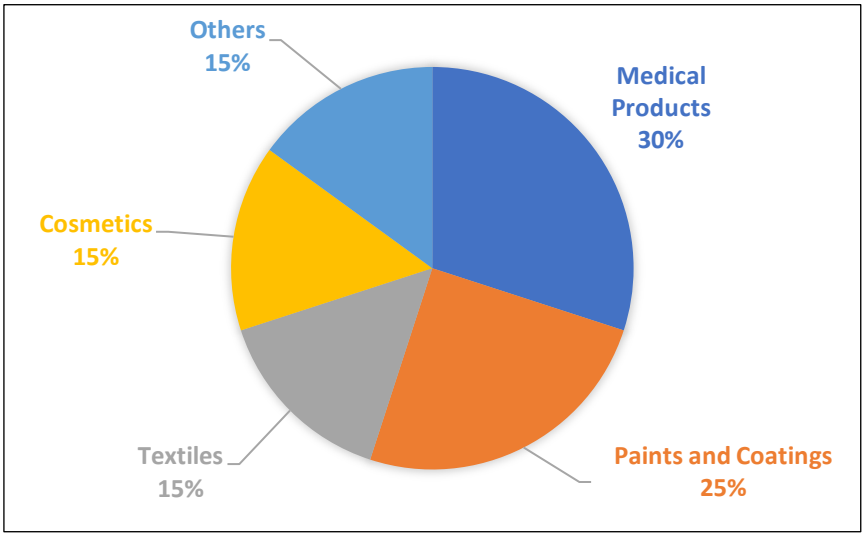

Figure 2. Major applications of silver nanoparticles [97].

Before the discovery of antibiotics, silver compounds were widely used to treat wounds or burns [98, 99]. As infection or diseases caused by bacteria, viruses, or fungi can lead to critical conditions for any patient regardless of age and gender, it is important to prevent any possible microbial activity in a

wound. Due to silver's unique antimicrobial properties to fight viruses [100], bacteria, and fungi, silver nanoparticles have been used in diverse healthcare products such as antimicrobial dressing/bandages, wound care products, breathing tubes, and catheters [54, 101, 102]. Ag NPs are also used in various implantable medical devices, for instance, Ag NPs deposited polymeric composite coatings (single or multi-thin layer) on dental implants, contact lenses, orthopaedic implants, and cardiovascular implants [103-105]. Direct deposition of Ag NPs on surgical equipment and titanium implants is also a common practice [106-108]. Silver nanoparticles have good potential to be also used as antitumor agents to treat human lung cancer cells [109, 110]. Also, Ag NPs have proven inhibitory effect on HIV1 (human immunodeficiency virus) cells [111-113].

Antibiotic resistance is one of the greatest concerns raised by health experts and WHO [114-116]. Particularly, whether antibiotics fail to destroy microorganisms to control the infection or to treat a wound [117]. In those cases, silver nanoparticles containing medication can be beneficial [118-120]. Recent studies have also revealed a synergetic effect of silver nanoparticles when applied with selective antibiotics, such as penicillin G, amoxicillin, erythromycin, vancomycin, and clindamycin [3, 4, 38, 54].

Furthermore, silver nanoparticles have good optical properties such as Surface Plasmon Resonance (SPR), which makes nano silver suitable to be used in biosensors, diagnostics, drug delivery, and imaging [7, 121]. Other examples of applications include analytical sensors in Surface Enhanced Raman Spectroscopy (SERS) [8], Metal-Enhanced Fluorescence (MEF), in immune sensing of biological probes and biological markers where nanoparticles are used [122].

Silver nanoparticles are abundantly used as an ingredient in many consumer products, such as cosmetics, soaps, pastes, antimicrobial textiles, and plastic coatings [123]. The main reason may be the intrinsic antimicrobial effect of silver nanoparticles, even when present in low concentrations [102]. For instance, silver-containing deodorants or socks (functionalized textiles) help to diminish bacterial growth on the skin [117]. In addition, due to very low electrical resistivity [8] and increased

stability, silver nanoparticles are used in electronics products such as high conductive pathways, transistors, photonic and antireflective materials, and optical fibres [1, 2, 124].

Preservation of packed foodstuff is still challenging as bacteria or fungi can grow during the storage period. Silver nanoparticles are used in packaging containers and wrapping consumables to prevent and/or control food spoilage and extend the shelf-life [4, 125]. On the other side, organic preservatives are available and widely used in full processed foods; however, they are not suitable for semi-processed foods as they can be converted into toxic substances under various food processing conditions such as high temperature [54]. A few food supplements also contain silver nanoparticles in low concentrations that are safe to humans, but sufficient to kill microorganisms [54, 126].

Drinking water must also be free from any form of microorganisms. Therefore, the disinfection of potable water is as equally important as filtering. Silver nanoparticles have been used in membrane filters to disinfect drinking water [127, 128]. Similarly, silver nanoparticles are used in the filter of a heating, ventilation and air conditioning (HVAC) system to disinfect air [54, 129].

Silver nanoparticles are also used as a catalyst for several chemical processes, in particular its photocatalytic behaviour allows silver nanoparticles to catalyse several chemical reactions, such as hydrogenation of organic compounds and some oxidation reactions [7, 130, 131]. However, some researchers claim that the high surface area and surface energy dominate the catalysis process [1, 8].

Functional textiles often contain silver nanoparticles that are embedded in textiles, but the washing process releases most of the silver nanoparticles [132, 133]. However, silver leaching from the textiles during the washing cycle is driven by several factors, such as nanoparticle size, water quality, hardness, detergent quality, and attachment of silver nanoparticles within textiles [134]. A study in Norway found that washing machines using a ‘nano-wash’ feature can release silver nanoparticles or silver ions up to 11 µg/L into the water during its operation [132].

Building materials, including paints, contain silver nanoparticles to protect against microbial activity [123]. Figure 3 demonstrates the wide variety of silver nanoparticle applications discussed in previous paragraphs.

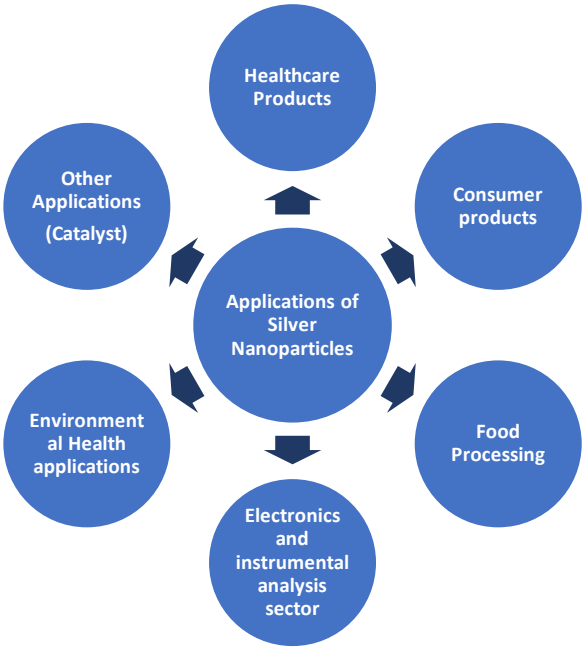

Figure 3. Main applications of silver nanoparticles.

4 Consequences and chemical transformation

The environmental and human health consequences of growing production and extensive use of silver nanoparticles are inevitable [135]. Different production methods produce toxic residues and some of them are even carcinogenic and can cause allergic reactions or bioaccumulate on aquatic organisms [3]. In contrast, ultimately all silver nanoparticles enter into the aquatic environment either through Wastewater Treatment Plant (WWTP) or Sewage Treatment Plant (STP) with the discharged effluents as can been seen in Figure 4 [7, 123]. For instance, many consumer products and healthcare products release silver nanoparticles that enter the aquatic environment through the sewage disposal system. Biosolids from WWTPs and STPs and the ash/residue from Waste Incineration Plant (WIP) have been applied in agriculture as soil amendments, from where silver can leach out and enter again into the surrounding environment [20]. Silver nanoparticles used in building materials can run off and

accumulated in the soil [3]. Figure 5 shows that the estimated nano silver flow and the discharge in the aquatic system after wastewater treatment is 13% of total production [136]. Therefore, the study on the toxic effect on organisms and ecosystems gained substantial interest among researchers in recent years.

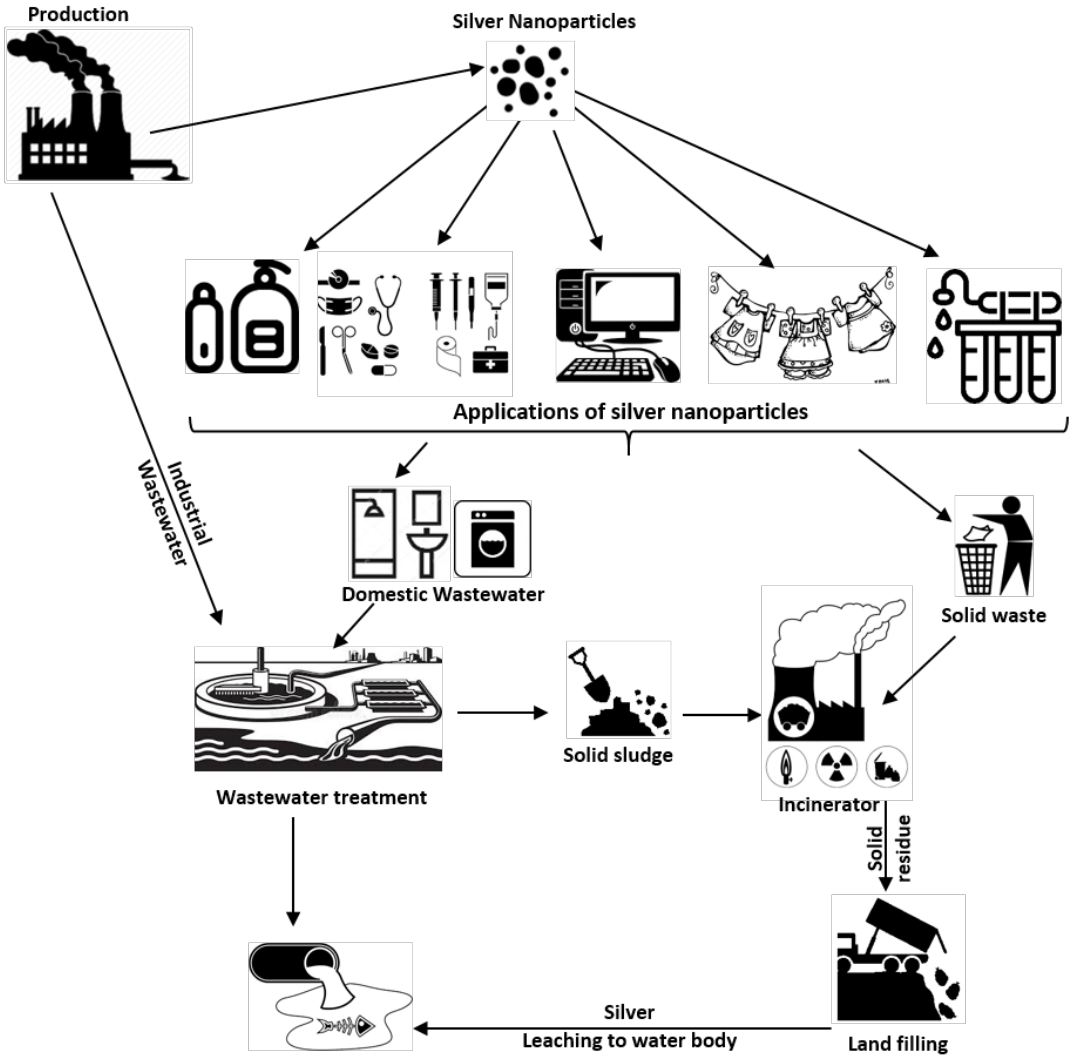

Figure 4. The life cycle of silver nanoparticles.

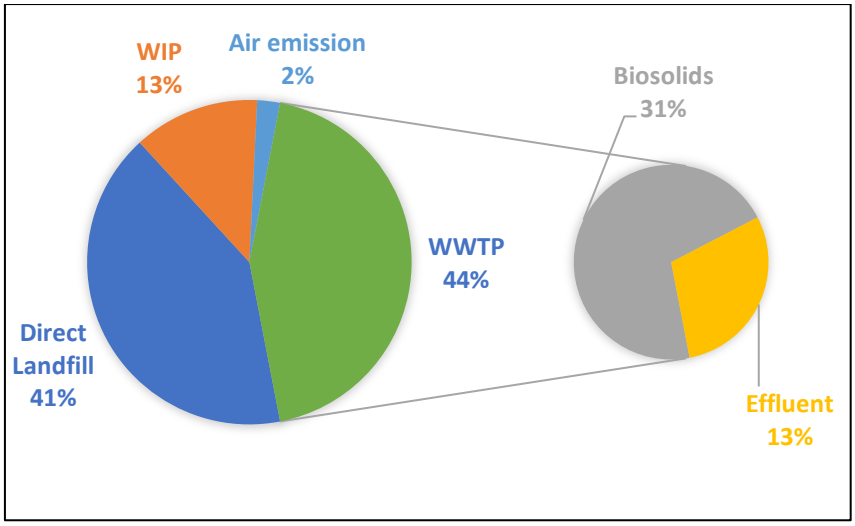

Figure 5. Global material flow for silver nanoparticles [136].

When the silver nanoparticles come to the open surface water environment, the interaction between Ag NPs and other natural organic materials (NOM), such as fulvic and humic acids create a coating on the surface of Ag NPs and subsequently settled as sediments [137-139]. These coated Ag NPs are analogous to the protein corona [10, 140]. This transformation often contributes to change the aggregation behaviour and toxicity of Ag NPs [141].

However, silver in wastewater is a mixture of silver nanoparticles, nanoparticle aggregates of silver sulphide and silver ions [142]. Over time, chemical transformation often occurs including oxidation, reduction, dissolution and/or sulfidation [7, 123, 143]. Nevertheless, the dissolution of silver nanoparticles depends on several factors including the type of surface coating of Ag NPs and surrounding water parameters, such as pH, dissolved organic matter (DOM), dissolved oxygen (DO), coexisting electrolytes, hardness, particle size and exposure time [144-146]. Due to its ionic behaviour, silver ions can bioaccumulate in the organism through cell membrane ion transporters [123]. In contrast, DOM can lead to the reduction of silver ion (Ag^{+}) into silver (Ag^{0}) nanoparticles under the sunlight [143, 145, 147]. Therefore, both phenomena demonstrate a direct impact on the aquatic ecosystem. In acidic condition, silver nanoparticles produce silver ions as demonstrated by reactions (1) and (2) [3]:

288 $4Ag_{(s)} + O_{2(aq)} + 4H^{+}_{(aq)} = 4Ag^{+}_{(aq)} + 2H_2O_{(l)}$ (1)

289 $Ag_2S + 2H^{+} \rightleftharpoons 2Ag^{+} + H_2S_{(aq)}$ (2)

290 However, recent studies suggest that the aggregation rate of Ag NPs is directly proportional to the
291 concentration of cations (e.g. Na^{+}, Ca^{2+}) and the presence of humic acid (DOM) expedites the
292 aggregation [148, 149]. Despite the low concentration of DOM in seawater Ag NPs still show a higher
293 aggregation rate because of the concentration of the cations in the seawater [148]. This aggregation
294 of Ag NPs not only decreases the rate of silver ion (Ag^{+}) release, but also helps to decrease the toxic
295 effect of Ag NPs [150, 151]. However, other researchers suggested that both pH and electrolyte
296 density are mostly responsible for the aggregation, and the presence of DOM inhibits the aggregation
297 because of the biomolecular corona effect [64].

298 Ag NPs having higher specific surface area show a higher dissolution rate thereby higher toxicity than
299 Ag NPs having low surface area regardless of particle shape [152]. However, the surface area often
300 depends on the shape of the particles. A study suggests that truncated triangular Ag NPs have more
301 antibacterial property to the gram-negative organisms than Ag NPs with other shapes [153]. However,
302 another study shows that human alveolar epithelial cells were strongly affected by the wire-shaped
303 Ag NPs, whereas spherical Ag NPs showed no effect [154]. Optical properties are also influenced by the
304 geometrical shape of the particles, but further investigation is required to better understand the
305 impact of the particle shape on other usages of Ag NPs [45].

306 Silver nanoparticles can contaminate air from the HVAC filters where they are used. These airborne
307 silver nanoparticles can be inhaled by humans [3]. However, researchers showed that the potential
308 routes of exposures are mainly oral, inhalation or transdermal [8, 41]. It is reported that overexposure
309 to silver nanoparticles causes severe skin decolouration to bluish grey (argyria) in humans [41].
310 However, specific toxicity to humans is yet to be explored [155]. Quantification and comprehensive
311 risk assessment of ecotoxicity need to be carried out.

Silver nanoparticles can be adsorbed by plant species that are growing in soil amended with mostly silver-containing biosolids. In WWTP, usually, silver nanoparticles and silver nitrate ($AgNO_3$) are converted into Ag_2S according to reaction (3) [156, 157] which has low bioavailability in the soil [158].

$$4Ag + O_2 + 2HS^- \rightleftharpoons 2Ag_2S + 2OH^- \quad (3)$$

Silver intake by plant root (wheat, rape) was increased by high concentration of Cl^- in soil, but plant growth was not impacted [159, 160]. However, as the silver is adsorbed by plants, consumption of fresh produce loaded with silver compounds may pose a health risk to humans. Additionally, the toxicological studies on phytoplankton (e.g. *Hydrilla Verticillate*), zooplankton (e.g. Daphnia Magna), fish (e.g. zebrafish, rainbow trout, Japanese medaka) showed clear ecotoxicity by silver nanoparticles in different environmental conditions [161, 162]. Therefore, silver bioaccumulation in fish and plant species can be transferred into the entire food chain [30].

Capping/stabilising agents or chemical coatings have not only direct influence on the particle size, shape, and aggregation behaviour, but also, they have a vital role in dissolution and induced cytotoxicity [163]. These coatings are fundamental for the final application. For instance, chitosan derived polysaccharide coated Ag NPs demonstrate significant antimicrobial property without showing any toxicity to eukaryotic cells [164]. On the other hand, PEG-coated Ag NPs demonstrated a higher dissolution rate than PVP coating [165]. However, the dissolution of any coating or capping agents also depends on the surrounding environment [166].

5 Silver Toxicity

Several studies found that silver nanoparticles show toxicity to bacterial growth, cell-based in vitro systems, algae, fishes [4, 167], water plants and the human reproductive system [2]. Even though many of those studies have been done under controlled laboratory conditions, a short duration of time, and with a relatively higher concentration of silver ions than the real-life situation. Additionally, the natural aquatic ecosystem has a complex dynamic among the inhabitants, surrounding environment, other nanoparticles, and pollutants, and chemical transformation of the different forms

of silver at their extremely low concentration (ng/L to µg/L) over a long period of time. Therefore, detail environmental and health risks associated with silver nanoparticles in a realistic situation are yet to be done [30]. However, recent studies prove that a concentration as low as 10^{-2} to 10 µg/mL silver has shown antibacterial activity [61, 168].

The toxicity of silver nanoparticles can be explained by various mechanisms. The majority of silver toxicological studies show the elemental silver (Ag^0) and monovalent silver (Ag^+) are the most common forms of silver that have demonstrated toxicity. However, the toxic effect of silver is determined by the amount of free silver ion released from the silver substrates [38]. Elemental or zero-valent silver can enter into cells, and react with oxygen to produce toxic silver ions and reactive oxygen species (ROS), which can cause DNA damage [169, 170].

Human exposure to silver nanoparticles can occur through skin contact with silver nanoparticles containing products, food that contains or in contact with silver nanoparticles packaging, disinfected drinking water, swimming pools and antifouling, nasal and throat sprays, and other forms of medicines [4, 41]. If the silver ion is ingested by a human, it is deposited in the subcutaneous fat cells [12, 13]. Excessive exposure can cause argyria in which human skin turns greyish blue [117, 171]. Silver can also inhibit Na^+ and Cl^- uptake which may lead to failure of electrolyte balance in body fluid [33]. Airborne silver nanoparticles can enter the lungs and cause chronic health problems, which can become serious for people with preconditions such as asthma or chronic obstructive pulmonary diseases [172].

Silver ion oxidises thiol group of enzymes, thus interrupts the electron-transport chain and DNA reproduction. Ag^+ can also directly interact with DNA [41] and denature DNA and RNA [7]. However, in some cases, the dissolution of silver nanoparticles into silver ions may produce reactive oxygen species (ROS) which can deactivate microorganisms [30, 173]. Therefore, silver nanoparticles are usually more toxic than silver ions in the same environment. Figure 6 summarises the different routes of exposure of silver nanoparticles in the environment, including human exposure.

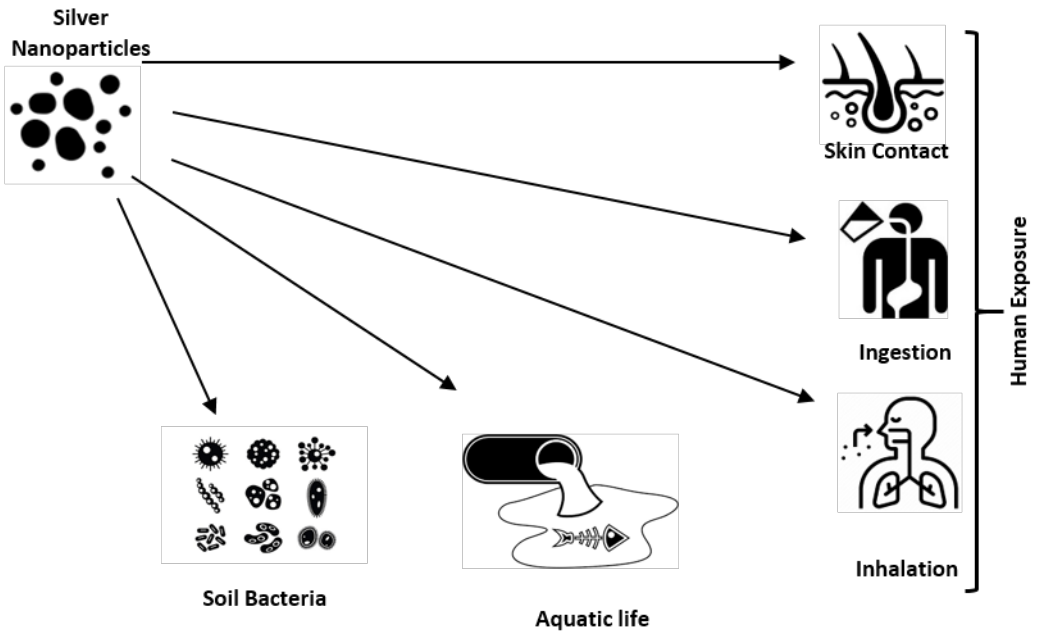

Figure 6. Route of exposure of silver nanoparticles.

Recent studies have demonstrated that all forms of Ag NPs toxicity are size-dependent instead of shape or morphology. Particle size less than 20 nm is more toxic than other larger particle size of Ag NPs [174, 175]. Because smaller particle size offers a higher specific surface area which increases the rate of Ag^{+} release.

6 Regulation

Silver nanoparticles can be released from silver-containing products to wastewater during the production process or after use. Scientists have warned about the widespread use of Ag NPs, in-vitro studies have demonstrated a high toxic effect on aquatic organisms and the possibility to be environmentally persistent [176, 177]. This growing concern raises awareness among the regulatory bodies and policymakers around the world to control the usages of silver nanoparticles and to ensure the appropriate treatment of wastewater. However, the regulation guidelines provide a maximum acceptable concentration of elemental forms of metals in surface water, groundwater, and drinking water. There is no separate guideline value of discharge for nanoform of silver or other metals in EPA, REACH (Registration, Evaluation, Authorization, and Restriction of Chemicals), EU, UK, Australia, and

New Zealand [178]. Despite the evidence of bioaccumulation and cellular toxicity, in vivo and environmental toxicity data of Ag NPs is insufficient for the short and long run. Thus, further investigation is necessary on the impact of Ag NPs under present and future exposure scenarios for both aquatic and terrestrial ecosystems. Nevertheless, all the regulatory bodies are researching detailed toxicity data to set a separate regulation for Ag NPs disposal limits. Regulatory bodies worldwide set the maximum allowable limit for silver; these values are presented in Table 2. The maximum limit for drinking water is 0.1 mg/L for the USA, Australia and Switzerland, while for Germany and China is 0.08 mg/L and 0.05 mg/L, respectively. The maximum limit for freshwater and marine waters is slighter lower than for drinking water and vary between 0.1 to 7.5 µg/L depending on the country regulation (Table 2).

Table 2. Permissible limits of silver in water according to various standards.

Country	Regulatory Body	Area	Maximum Limit	Reference
USA	National Secondary Drinking Water Regulations (NSDWR)	Drinking water	0.1 mg/L	[13, 179]
USA	U.S. Environmental Protection Agency (U.S. EPA)	Freshwater and saltwater	3.2 µg/L and 1.9 µg/L	[179]
USA	Toxicity Characteristic Leaching Procedure (TCLP)	Leachate as a hazardous waste	5.0 mg/L	[179]
Australia	ANZECC*	Freshwater and Marine waters	0.1 µg/L and 1.0 µg/L	[180]
Australia	NHMRC**	Drinking water guideline	0.1 mg/L	[14]
Canada	Canadian Water Quality Guidelines for the Protection of Aquatic Life	Freshwater and Marine waters	0.25 µg/L and 7.5 µg/L	[181]
Germany	German Federal Environment Agency (GFEA) (1990)	Drinking-water regulations	0.08 mg/L	[182]
China	National Standard of the People's Republic of China	Drinking water	0.05 mg/L	[183]
Switzerland	WHO	Drinking water	0.1 mg/L	[184]

* ANZECC: Australian and New Zealand Environment Conservation Council

** NHMRC: National Health and Medical Research Council

In this section, a global regulatory point of view on Ag NPs is discussed. **In the USA:** Different US federal agencies such as U.S. EPA, U.S. FDA, and U.S. NIOSH (National Institute for Occupational Safety and Health) work to regulate the environmental and public health impacts of Ag NPs [176]. According to the recent recommendation, NIOSH proposed the maximum exposure limit (REL) of 0.9 $\mu g/m^3$ for silver nanoparticles and 10 $\mu g/m^3$ for any other form of silver [185]. On the contrary, the US Conference of Governmental Industrial Hygienists sets the threshold limit values for metallic silver and soluble silver as 0.1 mg/m^3 and 0.01 mg/m^3, respectively [186]. However, the absence of effective methods for detail hazard assessment of Ag NPs makes regulation of Ag NPs a difficult task [187]. U.S. EPA and scientists elsewhere urged to develop a comprehensive risk assessment to further investigate the potential health and environmental impacts of all forms of nanomaterials [188].

In the European Union (EU): Like in the USA, the European Food Safety Authority (EFSA) is working to set a separate risk assessment followed by authorisation of nanomaterials. EFSA published a guidance report on risk assessment of the application of nanoscience and nanotechnologies in the food and feed chain in 2018. According to that guidance report, EFSA pointed out that the existing authorisation process is not adequate to cover the safety aspects of a nanomaterial or a corresponding non-nanomaterial [189]. However, the Joint Research Centre (JRC) published a NANoREG framework for the safety assessment of nanomaterials policy document to make a common ground to understand the environmental health and safety (EHS) aspects of nanomaterials under the current European regulatory framework focused on REACH [190]. REACH Regulation 1907/2006 focuses on both applicability and regulatory acceptance of nanomaterials and conventional or bulk substances. Nevertheless, these guidance documents suggest to take specific approaches for Ag NPs to carry out further risk assessment and uncertainty analysis for future recommendations [191, 192].

In Australia: Despite the growing scientific concern on some nanomaterials which may pose potentially serious health and environmental impacts, the regulatory bodies are yet to place a separate guideline for the nanomaterials in food and agriculture. Food Standards Australia New

Zealand (FSANZ), TGA (Therapeutic Goods Association), APVMA (Australian Pesticide and Veterinarian Medicines Association), and Department of the Environment are working together to assess the public and environmental health and safety of nanomaterials. However, a comprehensive regulation of any nanomaterials and their environmental release control measures have not been addressed yet [193].

7 Mitigation

In previous sections, the consequences of silver nanoparticles were discussed. This section focuses on gathering and discussing the potential solutions to mitigate silver pollution as well as the impact on the ecosystem. In recent years, several treatment processes have been explored by researchers. Sequencing Batch Reactor (SBR) [194], activated sludge process [195], anaerobic treatment, membrane filtration, reverse osmosis, and ion-exchange can remove most of the silver nanoparticles and silver compounds from wastewater. However, simplicity of operation and cost-effectiveness lead to investigating suitable sustainable alternatives such as adsorption. Several studies have been carried out on different adsorbents such as activated carbons, clays, biowaste materials, cellulosic materials, zeolites, graphene, and biochar. The adsorption capacity of an adsorbent depends on several physicochemical factors, such as specific surface area (BET), pore size, pore-volume, and surface functional groups [196]. More specifically, specific surface area and surface functional groups are the two most relevant contributors to physical and chemical adsorption respectively [197, 198]. The advantages and disadvantages of these various types of adsorbents are discussed in the following sub-sections.

7.1 Activated Carbon

Activated carbon is the most popular carbonaceous material used for numerous applications including wastewater treatment, drinking water purification, air and gas filtration, catalysts, catalyst support, hydrometallurgical processes, and gas mask for personal protection [199]. In general, activated carbon has a very high specific surface area between 200 to 2,500 m^2/g [200, 201] and high pore volume,

439 which makes this adsorbent suitable for adsorbing a wide range of organic and inorganic pollutants
440 including silver. Activated carbon is one of the widely used commercial adsorbents for air and water
441 purification [33].

442 Activated carbon can be produced from coal (mineral carbon) or agricultural waste biomass or
443 naturally available abandoned lignocellulose materials [26, 202]. The production process involves
444 either physical or chemical activation to convert biomass into activated carbon [203, 204]. In both
445 processes, carbonisation is carried out at a temperature from 300°C to 600°C and activation at around
446 500°C to 900°C in an inert environment [202, 205]. Chemical activation demands an excessive amount
447 of chemicals from 1:1 to 1:6 for the mass ratio of feedstock to activating agent [206, 207]. While
448 physical activation requires CO_2 or steam, chemical activation requires the use of inorganic salts and
449 acids such as $ZnCl_2$, K_2CO_3, HNO_3, H_2SO_4, H_3PO_4, KOH, or NaOH [205, 208].

450 Finely porous structure and hydrophilic surface functional groups are key characteristics that make
451 activated carbon a good adsorbent [209]. The electrostatic interaction between functional groups
452 present in the activated carbon and ionic species such as silver ion is responsible for high adsorption
453 [210]. For instance, oxygen anions (O^{2-}) present in the activated carbon forms a bond with silver ions
454 to produce Ag_2O. However, chemical modification of activated carbon introduces strong acidic groups,
455 and increases the density of total surface functional groups, such as –CHO, =CO, –COOH, $–SO_3H$, thus,
456 increases adsorption capacity [33, 211]. As shown in Table 3, chemical modification of activated
457 carbon by sodium hydroxide treatment can double the silver adsorption capacity, even in a short
458 contact time [33]. As presented in Table 3, all experiments are favourable at room temperature and
459 for low initial concentration of silver. Low concentration acid solution (e.g. HNO_3) can be used for silver
460 recovery from the used adsorbents [211]. Adsorption of silver nanoparticles on activated carbon
461 depends largely on the conversion of silver nanoparticles into silver ions [212].

462 Table 3. Summary of silver adsorption capacity by different types of adsorbents from aqueous solution (mainly silver nitrate solution).

Type of Adsorbents	Adsorbent	Pre-treatment / modification	Adsorption capacity (mg/g)	pH	Initial concentration of silver (mg/L)	Contact time	Temp (°C)	Reference
Activated Carbon	Colloidal carbon nanospheres (CNS)	Sodium hydroxide	152	3-9	0.098 - 202	6 min – 32 hrs	Room Temp	[33]
	Activated carbon (Norit® CA1)*	No	65	3-9	50 - 105	12 hrs	20	[212]
	Coconut shell activated carbon	Washed in deionized water	60 - 80	3 - 5	100 - 500	200 min	30 - 50	[213]
	Peat-based activated carbon**	Washed with water	37.2	1.5 - 4.5	120	5 hrs	25	[209]
Biowaste Materials	Trimercaptotriazine-functionalized polystyrene chelating resin	-	187.1	0.0	820	4 hrs	Room Temp	[214]
	Chelamine	-	129.4	6	20 - 700	24 hrs	22±0.5	[215]
	Thiourea-modified chitosan resin	-	406.6	4	1,698	4 - 12 hrs	25 - 55	[216]
	Chitosan	-	42.0	6	50	1 - 96 hrs	20±0.1	[217]
	Hexanedioyl thiourea chelating resin (HTR)	-	491.8	6.9	5,393 (0.05M)	12 hrs	20	[218]

	Ion-imprinted chitosan gel beads	-	89.2	5	353	1 - 48 hrs	25	[219]
Modified celluloses	Magnetic cellulose xanthate	-	166	1	10	5 min – 1 hr	Room Temp	[220]
	L-cysteine functionalized cellulose	-	66.67	6.9	160	1 - 10 hrs	25	[221]
	Mercerized coconut fiber	-	64.93	7.5	169.8	30 - 340 min	30±1	[222]
	Pristine coconut fiber	-	54.15	7.5	25.4	30 - 340 min	30±1	[222]
	Cellulose nanocrystals (CNC)	-	34.35	6.39	107.8	2 hrs	20	[223]
	Chitin nanocrystals (ChNC)	-	19.80	6.63	107.8	2 hrs	20	[223]
	Cellulose nanofibers (CNF)	-	15.45	5.45	107.8	2 hrs	20	[223]
Clays	Modified vermiculite	-	69.2	4	10,000	30 sec - 16 hrs	10 - 20	[224]
	Montmorillonite	-	63.29	6	200	1 - 5 hrs	25	[35]
	Calcined bentonite	-	61.48	-	50 - 200	3 - 120 min	Room Temp	[225]
	Hectorite	-	49.5	4	27	60 min	Room Temp	[226]
	Saponite	-	48.3	4 - 8	2,000	5 hrs	23	[227]
	Raw Vermiculite	-	46.2	4	10,000	30 sec - 16 hrs	10 - 20	[224]
	Perlite	-	8.46	6.5	5 - 50	2 hrs	20 - 50	[19]

Biochars	Biochar-supported nanoscaled zero valent iron (nZVI)	zero valent iron (nZVI)	745.5 and 534.5	-	25 - 300	24 hrs	22±0.5	[11]
	Bamboo biochar	No	640	-	0-3000	24 hrs	22±0.5	[12]
	Engineered biochar from biofuel residue	No	90.06	-	20.7	10 min - 24 hrs	Room Temp	[36]
	Vineyard biochar	No	88.9	5.0± 0.1	50 - 500	70 min	19±2	[198]
	Paulownia tree biochar	No	75.2	5.0± 0.1	50 - 500	70 min	19±2	[198]
	Tobacco biochar	No	72.5	5.0± 0.1	50 - 500	70 min	19±2	[198]
	Biochar produced from biosolids	No	41.5	-	100 - 1000	10 min - 45 hrs	22±2	[34]

463 * Citrate-coated silver nanoparticles
464 ** Silver sulphate media

Despite having a large specific surface area which mainly comes from the microporous structure (<2nm) [228, 229], activated carbon cannot utilise those pores to adsorb Ag NPs as Ag NPs are larger than the pore diameter of activated carbon. The main limitations of using activated carbon for silver removal are the activation mechanism, regeneration of activated carbon, and overall cost-effectiveness [203, 205, 230]. The chemical modification involves the additional usage of chemicals, which is not environmentally and economically sustainable. Another limitation is the low or acidic working pH (Table 3). Semi-treated wastewater, which is the input for activated carbon adsorption, exhibits neutral pH after coagulation. Acidification is initially required which uses extra chemicals to bring the pH down, then neutralising demands more chemicals to meet the discharge limit of pH, 6 to 9 [180, 231-233]. In addition, silver nitrate solution has been used to measure the adsorption capacity except for one case where a mixture of silver ions and silver nanoparticles were used, which would be a more realistic scenario of silver in wastewater. However, the selectivity of silver among other pollutants, and the possibility of scaling-up to a continuous process are yet to be explored.

7.2 Functionalised biowaste materials

Multiple researchers find that adsorbents having sulphur and nitrogen-containing groups can show a higher affinity to silver ion as both have lone pair electrons [234]. Therefore, absorbents functionalised by amino or thiol groups can have good silver adsorption efficiency from aqueous solution [235]. Grapefruit peel modified by urea to create an amino group-containing organic matrix refers as bio-template showed 72.33 mg/g silver adsorption from aqueous medium [234]. Functional groups primarily form silver complexes thereby higher adsorption is achieved. However, strong bond energy between adsorbent and silver ions does not allow full regeneration of the adsorption which negatively affects the feasibility of the process [234]. Adsorption performances of few functionalised biowaste materials are shown in Table 3, showing that chelating and chitosan resins demonstrated a high silver adsorption capacity while chitosan has the lowest adsorption rate. The main limitation of using resins

and chelating agents is that the initial concentration of heavy metals in secondary or semi-treated effluent has to be more than 100 ppm to make the treatment process workable and feasible [236].

7.3 Cellulosic materials

Cellulose is the most abundant natural polymer [237], which is made of D-glucose repeating units [238], a six-carbon ring, also known as pyranose [239]. Structurally cellulose contains several hydroxyl groups that have a substantial impact on adsorption behaviour towards a wide range of water pollutants such as heavy metals (silver, copper, gold, zinc, lead, iron and chromium), organic dyes, protein and pesticides [220]. Adsorption capacity and selectivity for a specific target pollutant can be enhanced by chemical and/or physical modification [240].

Silver along with other heavy metals adsorption studies by modified cellulose gained considerable interest in recent years. For instance, L-cysteine modified cellulose can provide three surface functional groups (– COOH, $–NH_2$, and –SH) which shows a high silver adsorption capacity 66.67 mg/g in a batch process and 41.23 mg/g in a continuous column method exhibiting high selectivity towards silver ion in a multiple metal ions environment and good reusability of the adsorption column [221]. Magnetic cellulose xanthate can show up to 166 mg/g silver adsorption capacity from an acidic solution with three cycle adsorption-desorption and has a huge advantage of easy magnetic separation after adsorption [220]. Magnetic celluloses often contain zero-valent iron atoms, which have reductive and complexation tendencies and therefore increase the adsorption capacity [241]. Adsorption behaviour of modified cellulose for silver removal from aqueous solution is summarised in Table 3, showing an adsorption capacity between 15 and 166 mg/g. Table 3 also indicates that cellulosic materials can work at neutral effluent pH which does not require extra chemicals to adjust pH. However, adsorbent modification requires usually a chemical treatment that can produce subsequent wastewater and increase the environmental impact of the overall process.

7.4 Inorganic adsorbents

Inorganic adsorbents such as zeolite and clay possess good adsorption property. Zeolites have a porous framework of crystalline hydrated aluminosilicates [242]. Common types of natural zeolites are clinoptilolite, stilbite, natrolite, analcime, mordenite, phillipsite, chabazite and laumontite. However, several zeolites are synthesised such as zeolites A, X, Y and ZMS-5 [243, 244]. Both natural and synthetic zeolites are widely used due to their unique high cation exchange property, molecular sieving, catalytic, and adsorption behaviour [242]. Natural zeolites have been used to remove heavy metal ions and ammonium ions for groundwater and wastewater [245]. Among natural zeolites, clinoptilolite is the most abundant and naturally available with a typical chemical formula of $Na_6[(AlO_2)6(SiO_2)30].24H_2O$, and has shown a silver adsorption capacity of 33.23 mg/g [246]. Chemical modification of zeolites enhances its adsorption capacity and extends the property to adsorb anions and organic pollutants from aqueous medium [242]. Although the application of zeolites for various heavy metals removal is well studied, very few research has been done on silver adsorption by zeolites. Synthetic zeolite produced from green tuff stone cake showed a maximum silver adsorption capacity of 118.6 mg/g while the H-Na-ZSM-5 zeolite showed 61.4 mg/g [236, 247].

Clay is another example of inorganic adsorbents that have been used for heavy metals removal from aqueous solution even at a low concentration due to a good adsorption capacity [248]. Clay is a mixture of silica, alumina, metal oxides, water, and other minerals. Scientists classify clays into different groups depending on the quality and minerals present in them, such as kaolinite, montmorillonite, saponite, illite, pyrophyllite, vermiculite and serpentine [249]. However, most of the clays contain anions and cations that give strong ion-exchange property to remove inorganic and organic pollutants from wastewater [250]. In contact with water, clays can produce negative charges which can undergo complex reactions with the positively charged species such as silver, copper, lead, mercury, zinc, chromium, cadmium, manganese and arsenic to remove them from their aqueous solutions [249, 251].

The main advantage of using clay as an adsorbent is naturally available on the earth's surface, low-cost, non-toxic and abundantly available [226]. Nevertheless, scientists urged for pre-treatment and modification of clay with metallic oxides, such as MnO_2, Al_2O_3, Fe_2O_3, TiO_2, Fe_3O_4, $MnFe_2O_4$, to increase the adsorption capacity and selectivity towards a specific heavy metal or pollutant [224]. Previous researchers demonstrated that modified clay exhibits better results than the natural clay (Table 3). For instance, modified vermiculite and raw vermiculite showed a silver adsorption capacity of 69.2 mg/g and 46.2 mg/g, respectively [224], and the pH dependency is moderate. Inorganic materials can work in a wide pH range from 4 to 8. However, the silver adsorption capacity by clays is significantly lower than other adsorbents.

7.5 Graphene

Graphene is a single atomic layer of sp^2-hybridized carbons, which are hexagonally arranged [252]. Graphene has drawn substantial scientific attention in recent years for its exceptional physical and chemical properties and multipurpose usages such as energy storage, hydrogen storage, nanocomposite and nanoelectronics [253]. The large theoretical surface area of approximately 2,630 m^2/g [254] favours graphene to be used as a promising adsorbent to remove pollutants from aqueous media. However, chemical modification helps to improve the surface properties and increase the density of oxygen functional groups [252]. For instance, triethanolamine modified graphene oxide showed silver ion adsorption capacity of about 410 mg/g after four cycles of reuse [255].

Nevertheless, graphene can aggregate irreversibly by π–π bonding and Van der Waals interactions to form graphite and consequently reducing its adsorption capacity and reusability [256]. The production cost of graphene is still high and its production processes may have a high carbon footprint. Recently, significant research has been carried out on the preparation of graphene containing biochar that has demonstrated good performance in adsorption of different pollutants [257].

7.6 Biochar

Biochar is the solid carbonaceous by-product from the pyrolysis of biomass, which consists of unconverted organic solids and ash, a mineral fraction of the biomass pyrolysis process [239, 258-260]. Depending on the potential use, pyrolysis parameters can be controlled to produce biochar with desired properties for a specific use. For instance, at a high temperature, volatile materials are removed quickly which results in high micro-pore volume in the biochar [261]. Micro-porous structure and a large surface area make biochar appropriate for diverse use such as soil quality enhancement and carbon storage [262-266], wastewater treatment [31, 34, 267-273], pesticide remediation [274], fuel and catalyst in energy recovery technologies [275, 276], activated carbon production [204, 277], removal of SO_2 and NO_x from flue gases [260].

Micro-pore volume is the main physical property defining the adsorption capacity of biochar. Surface functional groups are also important for the adsorption of certain pollutants. Pyrolysis temperature is the main processing variable impacting on both properties, surface functional groups decrease at high-temperature (> 600°C) while micro-pore volume increases with pyrolysis temperature [278]. The adsorption capacity of biochar is also affected by properties of contaminants such as ionic nature, polarity, and processing conditions [276]. Therefore, it is fundamental to understand the key biochar properties for adsorption of each compound or element and then define the biochar production. For instance, BET surface area, pore size, pore-volume, surface functional groups, surface charge, pH, and mineral components play a key role on adsorption [279, 280]. For example, pore size has an important influence on metal adsorption; biochar with small pore size cannot trap large adsorbate particles, regardless of their charges or polarity [279]. Oppositely, favourable polarity or surface charge allows adsorbate particles to enhance its contact with biochar.

Heavy metals (e.g. As, Cr, Cd, Hg, Pb) recovery by biochar is dominated by various mechanisms such as electrostatic interactions, cation exchange, complexation, reduction, and precipitation [279]. Silver adsorption is also driven by different mechanisms depending on the biochar quality and the

585 adsorption conditions. Chemical and/or physical modification is often carried out to increase the
586 density of surface functional groups or to add minerals, reducing agents and nanoparticles [279].
587 Surface functional groups such as –COOH, $–NH_2$, –OH have a strong influence on metal adsorption
588 capacity [281]. Biochar is often treated with alkali, reducing agents, oxidizing agents, carbonaceous
589 materials, metal ions, acid, steam and gas purging to modify its properties according to a specific use
590 [261].

591 Biochar has several added advantages compared to other similar adsorbents. For instance, relatively
592 low temperature and less chemically intensive process makes biochar less complicated and
593 inexpensive compared to activated carbon. Biochar production is an effective method for carbon-
594 sequestering from waste biomass, which would produce greenhouse gases by conventional disposal
595 (landfilling) [282]. Therefore, biochar has limited environmental footprints compared to activated
596 carbon.

597 The application of low-cost adsorbents to remove heavy metals, particularly modified biochar, has
598 attracted much attention in recent years [12, 35]. However, the low-cost sustainable modification and
599 application of biochar to mitigate silver nanoparticles pollution has not been well explored so far.
600 Table 3 compiles all projects where biochar was used for silver removal. According to Table 3, the
601 modification of biochar enhances adsorption efficiency to a great extent. For instance, biochar
602 supported nanoscale zero-valent iron (nZVI) showed up to 745.5 mg/g silver adsorption capacity [11].
603 The silver adsorption process by biochar can work under a wide range of initial concentrations at room
604 temperature. However, the pH dependency of the adsorption process has not been studied yet.

605 Firstly, data shown in Table 3 indicates that only one modification (by zero-valent iron) was studied.
606 Secondly, the pH dependency of the adsorption processes was not monitored and reported. Thirdly,
607 all the experiments were done on silver nitrate solution prepared with double distilled water except
608 one case. According to the literature, silver can be presented in various forms in wastewater, such as
609 silver nitrate, silver chloride, silver sulphide nanoparticles and silver nanoparticles. A study

610 demonstrated that the biochar can break the PHBV (polyhydroxybutyrate-co-valerate) composites
611 containing Ag NPs to release silver ions and eventually adsorb in a tropical soil environment [165].
612 Therefore, biochar adsorption should be tested for other silver forms that are available in aqueous
613 solutions.

614 In summary, the adsorption capacity of different adsorbents (Table 3) depends on the initial
615 concentration of silver, modification and/or activation of adsorbents, contact time and solution pH. In
616 general, biowaste materials and biochars are the type of materials with higher silver adsorption
617 capacity. The adsorption capacity of biowaste materials vary between 42 mg/g (for chitosan) and 407
618 mg/g for thiourea-modified chitosan, showing that the modifying agent/process plays a key role on
619 the adsorption capacity of adsorbents. This is also confirmed by the biochar adsorption results, the
620 biochar modified with the zero valent iron demonstrated the highest adsorption capacity of 745.5
621 mg/g. Bamboo biochar has also confirmed a high silver adsorption capacity, and is a promising low-
622 cost adsorbent for nano silver mitigation as well as for other contaminants.

623 # 8 Conclusions

624 Water pollution is the greatest threat to the entire ecosystem. Increasing the production and use of
625 silver nanoparticles are going to be an additional toxicity risk for the aquatic environment. Therefore,
626 it is crucial to develop an economically and environmentally feasible process to mitigate silver
627 pollution. Adsorption research has gained significant interest in recent years because of its cost-
628 effectiveness and suitability for bulk effluent treatment. The present review explored the
629 effectiveness of silver adsorption by different adsorbents.

630 Silver can be present in various forms in wastewater. For instance, silver nitrate, silver chloride, silver
631 sulphide nanoparticles, and silver nanoparticles. However, most of the research has been carried out
632 on silver nitrate which has not demonstrated the effectiveness of the process in a realistic
633 environment. Modified activated carbon shows good adsorption capacity under certain conditions,

634 such as low working pH. Activation mechanisms to produce activated carbon in order to enhance its
635 adsorption rate as well as regeneration processes to extend the adsorption cycles have been
636 investigated. However, these conditions make the treatment process more complex, more chemically
637 intensive, and cost-intensive. The selectivity of silver from other pollutants and the possibility of
638 scaling-up to a continuous process are yet to be explored.

639 Some of the functionalised organic/biowaste materials, such as resins and chelating agents can work
640 at a neutral pH. However, the initial concentration of silver has to be more than 100 ppm which is
641 impractical compare to the real-life situation where the silver ion concentration is less than mg/L level.
642 Cellulosic materials can also work at a neutral effluent pH and showed significant adsorption capacity,
643 but modification of these materials requires chemical treatment which can produce subsequent
644 wastewater. Inorganic adsorbents, such as zeolites and clay, demonstrated an adsorption capacity
645 significantly lower than the other adsorbents, but they can work under a wide range of pH: 4 to 8.
646 Another promising adsorbent, graphene, has drawn research interest recently, but susceptibility to
647 aggregate and to forming graphite is still a challenge to be further explored. Additionally, the current
648 production methods of graphene have a high carbon footprint due to the high energy demand which
649 again impacts on the production cost and environment.

650 Biochar has several advantages compared to other similar adsorbents. For instance, relatively low
651 processing temperature and no and less chemically intensive production processes make biochar a
652 low-cost adsorbent compared to activated carbon. Additionally, biochar production from biomass
653 waste helps to capture carbon rather than producing greenhouse gases. However, the low-cost
654 sustainable modification and application of biochar to mitigate silver nanoparticles pollution should
655 be further explored. A few key prospective areas of interests of silver removal may include, but are
656 not limited to:

657 • selection of appropriate biomass as the composition of biomass often drives the physical
658 and chemical properties of biochar

- low-cost modification of biochar to increase the adsorption capacity and to extend the reusability of used biochar
- assessment of the adsorption capacity under a realistic environment, especially the effect of other co-existing chemical compounds or elements
- experimentation on selectivity and recyclability
- scaling up of the adsorption process – from batch method to a continuous process
- in-depth cost study to demonstrate the economic viability of the overall process.

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