RESEARCH ARTICLE
doi: 10.2306/scienceasia1513-1874.2020.097

ScienceAsia 46 (2020): **697–705**

Biosynthesized silver nanoparticles from shoot and seed extracts of *Asphodelus tenufolius* for heavy metal sensing

Marya Siraj[a], Zafar Ali Shah[a], Sami Ullah[b], Hamida Bibi[c], Muhammad Suleman[a], Afia Zia[a], Tariq Masood[a], Zafar Iqbal[a], Mudassar Iqbal[a,*]

[a] Department of Agricultural Chemistry, The University of Agriculture Peshawar, 25120 Pakistan
[b] Department of pharmacy, University of Peshawar, 25120 Pakistan
[c] Department of Soil and Environmental Sciences, The University of Agriculture Peshawar, 25120 Pakistan

*Corresponding author, e-mail: mudassariqbal@aup.edu.pk

Received 19 Nov 2019
Accepted 14 Oct 2020

ABSTRACT: Biosynthesis of silver nanoparticles (AgNPs) was achieved by treating the aqueous extract of shoots and seeds of *Asphodelus tenufolius* Cav with 1 mM silver nitrate solution at 30 °C. The synthesized AgNPs were characterized through UV-Vis spectroscopy, Fourier Transform Infra-Red Spectroscopy and Scanning Electron Microscopy. The absorption maxima of shoot AgNPs was 444 nm and seed AgNPs was 448 nm. The FTIR spectral analysis showed a distinct peak stretching at 1380 cm^{-1} was clearly visible for both seed and shoot extract mediated AgNPs, and this was not present initially in crude extract of both samples. The SEM analysis confirmed the size (shoot = 58.2 nm and seed = 51.6 nm) of extract mediated AgNPs and shape (spherical and poly-dispersed) of the synthesized AgNPs. Both the synthesized AgNPs were stable at acidic pH 5.5 to fairly basic pH 9. Increase in acidity to pH 3.5 caused complete decomposition. The Metal (Cu, Ni, Co and Zn) sensing of different metal salt solutions (1 mM) confirmed the effect of copper salts (250 µl/ml of AgNP solution) on both shoot and seed AgNPs while shoot AgNPs showed effect against Zn salt. This research can open a new domain for the detection of various heavy metals in aqueous solution through simple colorimetric determination.

KEYWORDS: green synthesis of nanoparticles, eco-friendly silver nanoparticles, heavy metal detection, colorimetric analysis

INTRODUCTION

Nanotechnology is a versatile field of the modern research era. It deals with smaller size of particles (except viruses) ranging approximately from 1 to 100 nm following a proper strategy and manipulation of their structural chemistry [1]. Within this size range, all the properties (chemical, physical and biological) of an atom or their combine molecular form bring fundamental changes. Novel applications of nanoparticles and nanomaterials in various chemical, physical and biological industries are growing rapidly [2] due to their completely new and/or enhanced physical and chemical properties based on size, distribution and morphology. Metal nanoparticles have enhanced functions as compared to bulk particles and have been investigated due to enhanced catalytic [3], optical [4], electronic [5], water treatment [6] and various biomedical [7] and biological [8] properties including antimicrobial [9] and enzymatic [10] activities. Recently, superparamagnetic iron oxide nanoparticles were synthesized, and surface modification was performed for a better interaction with cells in diagnostic or therapeutic applications [11]. Benyettou and coworkers have developed target specific silver nanoparticles for dual drug delivery of doxorubicin and alendronate to control cancer cells [12].

Biocompatibility of metal nanoparticles synthesized via chemical methods is an issue as it leads to the NP with toxic materials adsorbed on the surface and may have an adverse effect in application [13]. The green synthesis of metal nano particles has attained much attention recently as an ecofriendly and cost effective alternate to chemical and physical methods [14–17]. This process involves the reduction of ionic metal through various biomolecules and enzymes present in living cells and later the stabilization of NPs by both inter and intracellular biomolecules [18]. Biogenic synthesis of silver nanoparticles using various fungal extracts has also shown appreciable effects against plant pathogenic microbes [19]. Researchers have used various plant extracts for the biosynthesis of a variety of metal nanoparticles. Sharma and coworkers have reported AgNPs using polysaccharides as capping and stabilizing agents with potent antimicrobial activities [17]. Abalkhil et al [20] have reported the synthesis of bactericidal AgNPs using *Aloe vera*, *Portulaca oleracea* and *Cynodon dactylon*.

Asphodelus tenuifolius also known as onion weed is commonly available in agricultural fields. It is known to possess various potent metabolites such as triterpenoid glycoside [21], various sterols [22], naphthalene and anthraquinone [23]. We can utilize these biomolecules as both reducing and stabilizing agents towards the synthesis of silver nanoparticles. This could generate ecofriendly nanomaterial with very minimum toxicity. We hypothesize the use of these AgNPs for the estimation of heavy metals present in aqueous medium through colorimetric determination. Heavy metals are of major concern for the environment and consequently for living organisms. These metals are readily soluble in aqueous medium and can enter food and feed chain of human and animals. Their early estimation is of prime importance to avoid health issues and various fatal diseases. Determination of heavy metals requires expensive equipment such as atomic absorption spectrophotometer and inductively coupled plasma spectrophotometer. Besides this, sample pretreatment and preparation is also of major concern to the environment as it requires energy and the use of various toxic chemicals. This work was designed to develop robust and cost effective method for the determination of heavy metals in aqueous medium using silver nanoparticles prepared via green synthesis through the shoot and seed extracts of *Asphodelus tenuifolius*. The results of this research could help in the development of biosensors for determination of heavy metals.

MATERIALS AND METHODS

All chemicals used in the research were of analytical grades. Freshly prepared double distilled deionized water was used for the preparation of various salt solutions as well as for the synthesis of AgNPs.

Collection and pre-treatment of *Asphodelus tenuifolius*

The mature plant samples of *Asphodelus tenuifolius* Cav were collected during April 2017. The aerial part (shoots) and seeds of *Asphodelus tenuifolius* Cav were selected for silver nanoparticle synthesis. Both shoots and seeds were washed with 2% aqueous mercuric chloride solution and distilled water to remove microbial load and dirt particles. The plant samples were oven dried at 70 °C for 48 h and ground using an electric grinder (THOMAS-Wiley LABORATORY MILL, Model no. 4) to obtain a powder.

Extraction and fractionation of *Asphodelus tenuifolius* Cav

The powdered sample (250 g) of shoots and seeds was subjected separately to cold extraction with absolute ethanol at room temperature for 72 h, followed by filtration initially using muslin cloth to separate bigger particles and later using filter paper (Whatman no. 1) to obtain the clear liquid extract. The extracts of both shoots and seeds were concentrated under reduced pressure using rotary evaporator to obtain crude extract (30 g each). The non-polar fractions were excluded through fractionation using n-hexane.

Synthesis of silver nanoparticles

Syntheses of silver nanoparticles were carried out at room temperature by treating 1 mM aqueous silver nitrate ($AgNO_3$) solution separately in different ratios (v/v; 1:1, 1:2, 1:10, 6:1 and 10:1) with the ethanol extracts of both shoots and seeds. The biomolecules present in the extract served as reducing (Ag^+ to Ag^0), capping as well as stabilizing agent for the synthesis of AgNPs [24]. The change in colour of reaction solution was observed within 1 h from light to dark brown, which is a primary indication of AgNP formation.

Characterization of silver nanoparticles

The absorbance spectra of synthesized AgNPs from both shoots and seeds of *Asphodelus tenuifolius* were analyzed using UV-Vis spectrophotometer (Optima sp3000+, Japan) through wavelength scan (200 nm–1000 nm) at a resolution of 1 nm, and scanning electron microscopy images were taken using JEOL JSM 5910 SEM instrument. The AgNP samples were extracted through centrifugation (10 000 rpm for 10 min), followed by loading onto aluminium plated coated with gold grids and drying at reduced pressure. FTIR measurements of synthesized AgNPs were studied by (Prestige-21 spectrophotometer; Shimadzu, Japan) in the range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} using KBr pellet method.

Metal sensing through colorimetric properties of AgNPs

The cationic effect of various heavy metals as follows: Cobalt (Co^{2+}), Zinc (Zn^{2+}), Copper (Cu^{2+}) and Nickel (Ni^{2+}) on synthesized silver nanoparticles (1 mM solution) of these metals were added separately (0–250 µl/ml) to both shoot and seed AgNP solution under continuous stir. Their effect was studied through UV-Vis spectra by taking pure extracts of shoots and seeds as blank. The effect was also compared by examining distilled water against synthesized AgNPs through UV-Vis spectrophotometer.

Stability of silver nanoparticles

The stability of synthesized AgNPs was evaluated by exposing them to various pH (2–14) for 10 min using 0.1 M HCl and 0.1 M NaOH aqueous solutions, varying temperature (30 °C, 50 °C and 60 °C) for 30 min and varying concentration of 1 mM aqueous NaCl solution (0–250 µl/ml) for 72 h. The effect of each parameter was monitored through UV-vis spectrophotometer by comparing the spectra.

RESULTS AND DISCUSSION

Synthesis of nanoparticles

The ethanolic extract obtained from the shoots and seeds of *Asphodelus tenuifolius* were subjected to silver nanoparticle synthesis using 1 mM aqueous silver nitrate solution. Different ratios (v/v; 1:1, 1:2, 1:10, 6:1 and 10:1) of shoot and seed extracts with 1 mM aqueous silver nitrate ($AgNO_3$) were mixed at room temperature. The shoot and seed extract of *Asphodelus tenuifolius* Cav acted initially as reducing agent (Ag^+ to Ag^0) and then as stabilizing agent through capping the AgNP with the biomolecules present in the extract. For both reactions, 1:1 (v/v) ratio of extracts and 1 mM aqueous $AgNO_3$ at 30 °C have the better conversion of AgNPs, and the optimum pH for shoot and seed extracts are 5 and 6.4, respectively. The change in colour from yellow to dark brown was noticed, and UV-Vis absorption band peak of AgNPs at 444 nm (sharp) was observed for shoot extract mediated AgNPs while the seed extract mediated AgNPs gave absorption band (wide) at 448 nm (Fig. 1). The absorption band of synthesized AgNPs are in-line with the results obtained by Bar and co-workers [25]; they synthesized silver nanoparticles using seed extract of *Jatropa curcas* with characteristic surface plasmon absorption band at 425 nm. Similarly, Song and Kim [26] have reported the absorption spectrum band at 430 nm of AgNPs using various plant extracts.

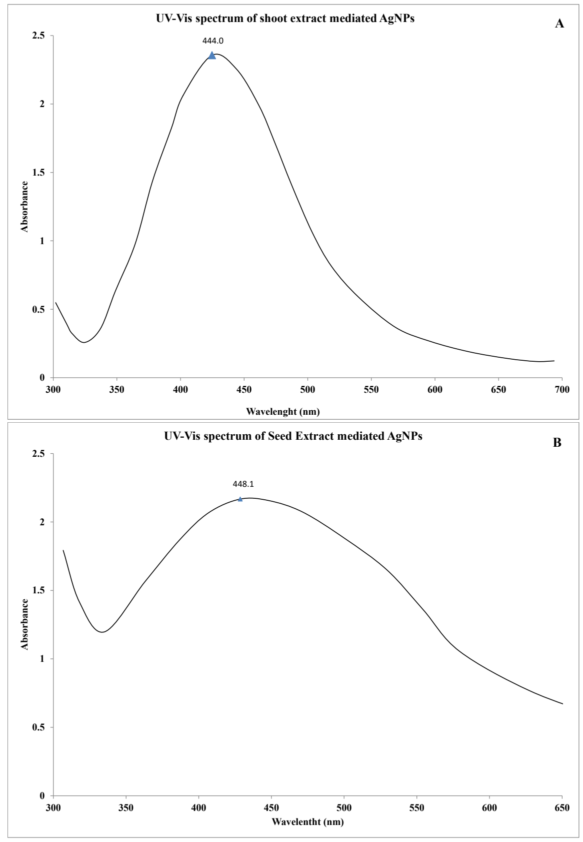

Fig. 1 UV-visible spectra of AgNPs synthesized using *Asphodelus tenuifolius*. (A) Shoot extract mediated AgNPs and (B) seed extract mediated AgNPs.

Fourier transform infrared spectroscopy

The FTIR spectra of the AgNPs synthesized using shoot and seed extracts from *Asphodelus tenuifolius* were recorded to identify the possible biomolecules responsible for Ag^+ reduction and capping for stabilization of resulted silver phyto-nanoparticles. The FTIR spectrum of shoot mediated AgNPs (Fig. 2B) showed prominent absorption bands at 3297, 2932, 2874, 1632, 1370, 1040 and 838 cm^{-1} as major peaks, similar to that of the seed extract mediated AgNPs (Fig. 2D) showing major absorption bands at 3312, 2928, 2857, 1740, 1652, 1569, 1386, 1153,1050, 999 and 841 cm^{-1} . For FTIR data, the comparison of both shoot and seed organic extracts showed an olefinic peak at 2150 cm^{-1} which disappeared in spectrum of shoot and seed extract mediated AgNPs. The absorption peak of 3350 cm^{-1} and 3312 cm^{-1} in the shoot and seed extracts,

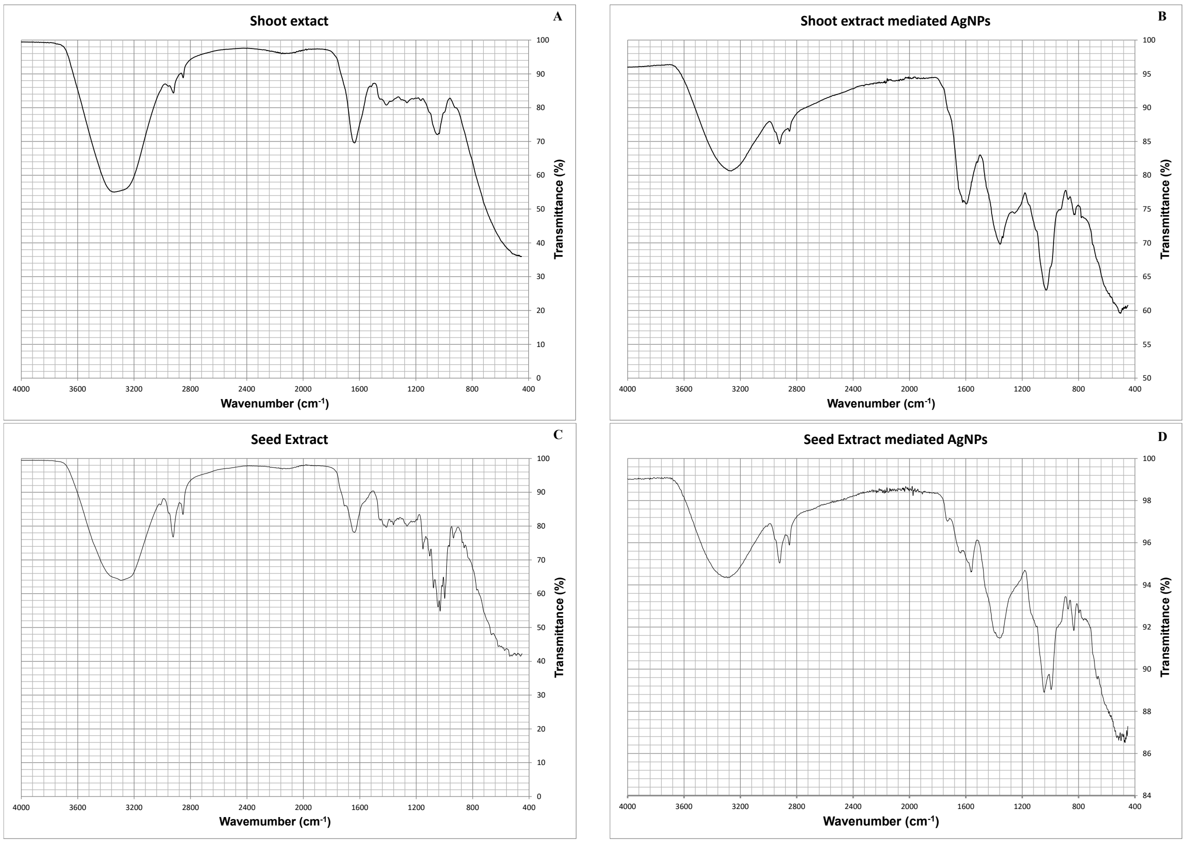

Fig. 2 FTIR spectra of *Asphodelus tenuifolius*: (A) shoot extract, (B) shoot extract mediated AgNPs, (C) seed extract and (D) seed extract mediated AgNPs.

respectively, indicated the O—H stretching vibration which shifted to 3297 cm^{-1} for both AgNPs. The absorption peaks in both organic extracts at 2858 cm^{-1} contributed to the O—H stretching vibrations of the –COOH functional group, shifting to 2874 cm^{-1} and 2557 cm^{-1} for the shoot and seed extract mediated AgNPs, respectively. It is evident from the spectrum that biomolecules with hydroxyl, alkene and carboxylic acidic functional groups took part in the synthesis of AgNPs. The shifting of bands indicated the interaction and participation of metal NPs with both seed and shoot extracts of *Asphodelus tenuifolius* and is presented in Table 1. The FTIR study provides evidence for the presence of various functional groups that are responsible for the bioreduction of silver ions. These groups are also responsible for the capping as well as stabilization of silver nanoparticles [27].

Scanning electron microcopy

The SEM images of AgNPs synthesized using shoot (Fig. 3A) and seed extracts (Fig. 3B) depict the morphology and distribution of nanoparticles. The slight aggregation of AgNPs of shoot extract was noticed while more singularly dispersed seed extract mediated AgNPs were observed. The scanning electron microscopy of shoot and seed extract mediated nanoparticles was explained by using ImageJ software. The particle size distribution (Fig. 3C) of shoot extract mediated AgNPs shows that the size of particles lies between 20–100 nm with average size of 58.2 nm, where 55% particles were observed below 60 nm and 44% particle size was from 70–100 nm. The average size of seed extract mediated AgNPs was found to be 51.6 nm, where 60% particles were found to be below 60 nm and 40% NPs were found to be above 60 nm. Both shoot and seed extract mediated AgNPs were found to have 98% cycloid. These outcomes can be explained by the fact that the biomolecules including polyphenols, alcohols, amines and aromatics play an important role towards the reduction of Ag^{+} to Ag^{0} and later stabilizing the AgNPs by capping them *in situ* [18, 19].

Table 1 FTIR data comparison of shoot and seed extracts and their AgNPs.

SHOOT		SEED	
Extract	AgNP	Extract	AgNP
3350(b,s); OH stretch, H-bonded alcohols/phenols	3350(b,s); OH stretch, H-bonded alcohols/phenols	3312(b,s); OH stretch, H-bonded alcohols/phenols	3297 (b,s); OH stretch, H-bonded alcohols/phenols
2932 (m) C—H stretch, alkanes	2932 (m) C—H stretch, alkanes	2932 (m) C—H stretch, alkanes	2928 (m) C—H stretch, alkanes
2858 (m) O—H stretch, Carboxylic acid	2874 (m) O—H stretch, Carboxylic acid	2858 (m) O—H stretch Carboxylic acid	2557 (m) O—H stretch Carboxylic acid
2150(w) C ≡ C stretch alkyne		2150(w) C ≡ C stretch alkyne	
1652 (m), C=C stretch, alkenes	1623 (m) C=C stretch, Metal coordination effect	1715 (s) C=O carbonyls	1740 (s) C=O carbonyls
1430 (m) C—C stretch, aromatic	1370 (m) C—H rock alkanes	1653 (m), C=C stretch, Alkenes	1652 (m), C=C stretch, Metal coordination
1284 (s) C—O stretch	1040 (s) C—O stretch	1422 (m), C—C stretch, aromatic	1568 (s) Metal coordination effect
1067 (s) C—O stretch	838 (s) =C—H bend, alkenes	1283 (s) C—O stretch	1371 (m) C—H rock, alkanes
		1155 (s) C—O stretch	1153 (s) C—O stretch
		1080 (s) C—O stretch	1050 (s) C—O stretch
		1000 (s) =C—H bend, alkenes	999 (s) C—O stretch Metal coordination effect
		941 (s) =C—H bend, alkenes	841 (s) =C—H bend, alkenes

Effect of metallic salt solution on synthesized AgNPs

Heavy metals are considered highly toxic to living organisms and can cause various fatal diseases such as cancer of various types, brain tissue damage, etc. They also cause serious damage to the environment by degrading soil, air and water quality. Development of simple, easy and robust procedure is of prime importance to tackle problems associated with heavy metals. To study the effect of different heavy metals, selected metal salt solutions: Cobalt (Co^{2+}), Zinc (Zn^{2+}), Copper (Cu^{2+}) and Nickel (Ni^{2+}) were added in different volumes i.e. (50–200 µl) to the AgNPs. The mixture was kept for 30 min, and their surface plasmon resonance (SPR) was recorded. The shoot extract mediated AgNPs (Fig. 4A) were found to be affected by copper and zinc salts at 250 µl. The decrease in the concentration of AgNPs was clearly noticed when 250 µl of 1 mM Cu and Zn salt solution was treated with 1 ml of AgNPs while the seed extract mediated AgNPs (Fig. 4B) were affected by 1 mM Cu and Ni salts at 250 µl/ml of AgNPs. It is to mention here that the concentration of Cu, Ni, Co and Zn solution below 200 µl/ml of AgNPs did not affect the absorbance SPR of AgNPs. Due to strong electron donating ability which is responsible for the complex formation of Cu, Cd, and other metals with silver, the instability in silver nanoparticles was profoundly noted as compared to Zn and Ni [28–30].

Stability of the synthesized silver nanoparticles

Effect of pH

The AgNPs of both seeds and shoots having initial (starting) pH 6.4 and 5, respectively, were subjected to various acidic and basic pH using aqueous 0.1 M

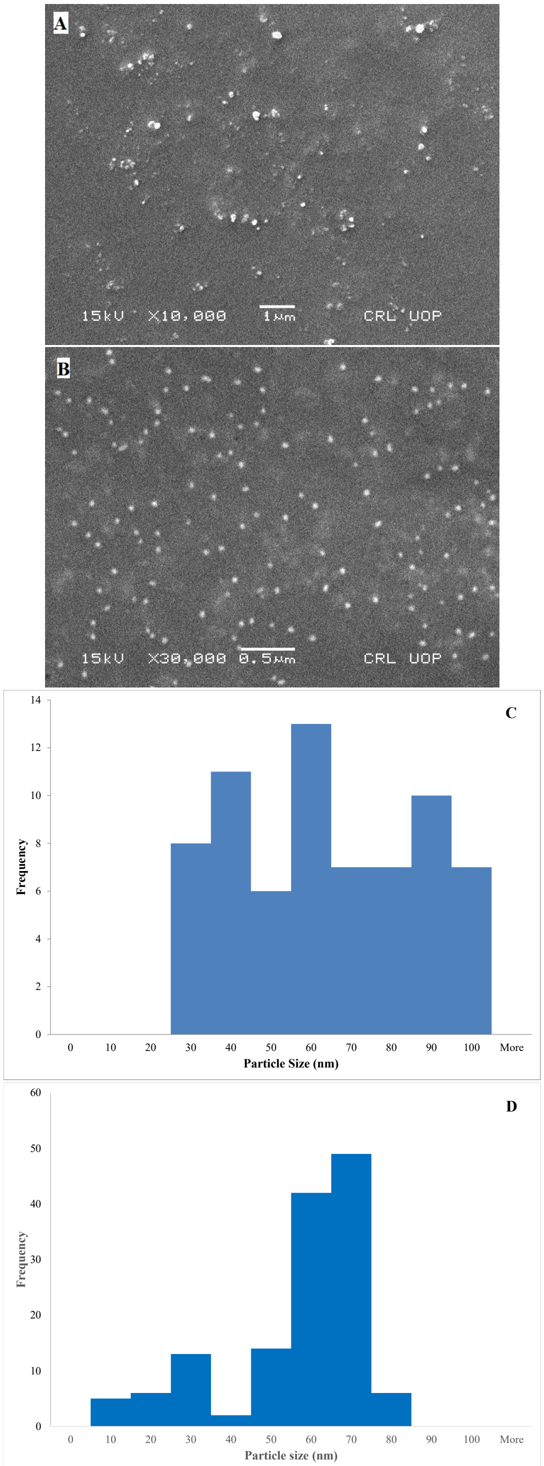

Fig. 3 SEM images of (A) shoot extract mediated AgNPs, (B) seed extract mediated AgNPs, (C) size distribution histogram of shoot extract mediated AgNPs and (D) size distribution histogram of seed extract mediated AgNPs.

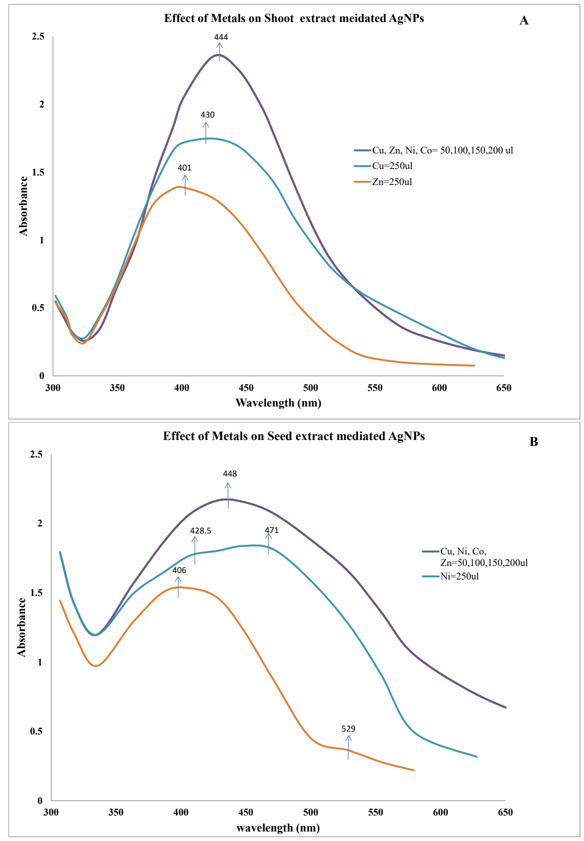

Fig. 4 Effect of different metal salts on (A) shoot extract mediated AgNPs and (B) seed extract mediated AgNPs.

solutions of acid (HCl) and base (NaOH), respectively. The shoot extract mediated AgNPs were found to be stable from pH 4.5 to 11. Decreasing pH below 4.5 caused decomposition, and at pH 3.5, the shoot AgNPs were completely lost (Fig. 5A) even after 10 min. At high pH values, although the shoot extract mediated AgNPs were fairly stable, their concentration started to decrease with the appearance of surface plasmon resonance peak above 463 nm. At highly basic pH (14), the concentration of shoot extract AgNPs reduced appreciably (Fig. 5B). This is due the presence of different bioactive molecules in both seeds and shoots. These molecules took part in capping and stabilization of AgNPs, resulting in different kinetic interactions towards pH conditions. Both low and high pH has effects on the stability and dissolution of silver nanoparticles. At low pH, dissolution of silver increases which in turn decreases the stability of silver nanoparticles while in case of high pH, the dissolution of silver decreases which provides stability to the silver nanoparticles [31, 32]. The seed extract mediated AgNPs started degrading

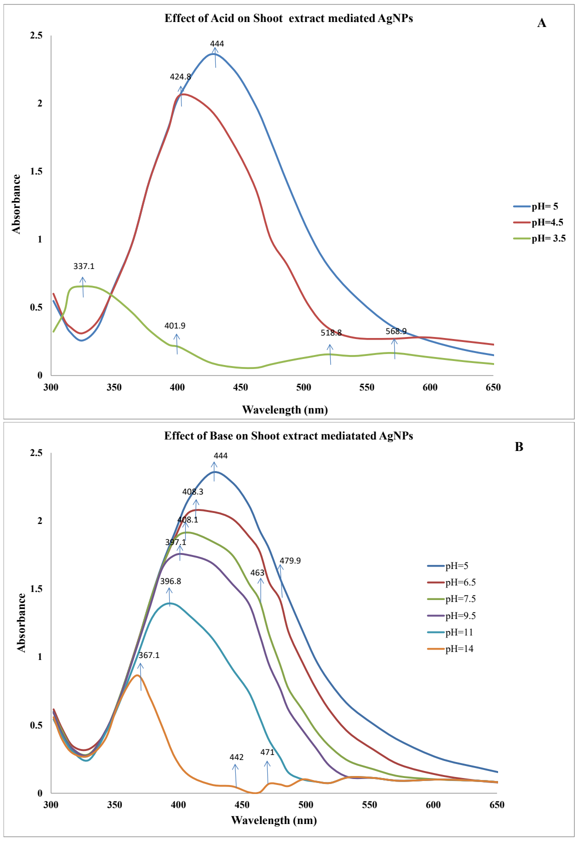

Fig. 5 Effect of (A) acidic pH on shoot extract mediated AgNPs and (B) basic pH on shoot extract mediated AgNPs.

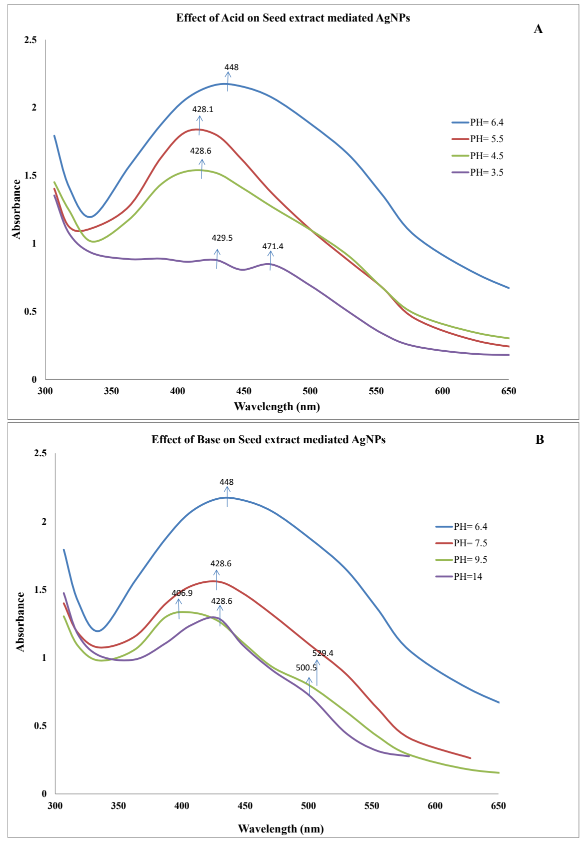

Fig. 6 Effect of (A) acidic pH on seed extract mediated AgNPs and (B) basic pH on seed extract mediated AgNPs.

with a decrease in pH below 4.5, and at pH 3.5, complete degradation was observed (Fig. 6A). At high pH (basic conditions), the seed extract mediated AgNPs were more stable as compared to shoot AgNPs although the decrease in the concentration of NPs was visible from UV-Vis spectrum (Fig. 6B).

Effect of Temperature

Both shoot and seed extract mediated AgNPs were subjected to various temperatures for 30 min, and with the increase in temperature above 30 °C, the AgNPs started losing their stability. When the temperature was raised to 60 °C, both shoot and seed extract mediated AgNPs completely decomposed. The effect of various temperatures on AgNPs was determined through SPR of shoot AgNPs (Fig. 7A) and seed AgNPs (Fig. 7B), and their stability was maintained at 30 °C. It could be due to the loss of interaction between the silver and the capping biomolecules (alkaloids, phenols, tannins, saponins, etc.) present in the extract of *Asphodelus tenuifolius*. Temperature affects the aggregation mechanism and kinetics of the chemical reaction according to LaMer mechanism. Both type and concentration of the reducing agent as well as availability of excess silver ions affect the temperature factor. According to literature, an increase in temperature shifts the SPR of AgNPs to shorter wavelength (blue shift) by speeding the reaction kinetics. This causes a decrease in size of the silver nanoparticles while at low temperature due to low activation energy or Brownian motion of reactants, an increase in the wavelength (red shift) is recorded. Same pattern was observed in this study [33–35].

Effect of NaCl salt solution

Sodium chloride concentration affects the surface plasmon resonance peak of the silver nanoparticles. With the increase in concentration of NaCl, the SPR peaks start shifting towards longer wavelength i.e. red shift, thus causing the aggregation and instability of silver nanoparticles while the reverse

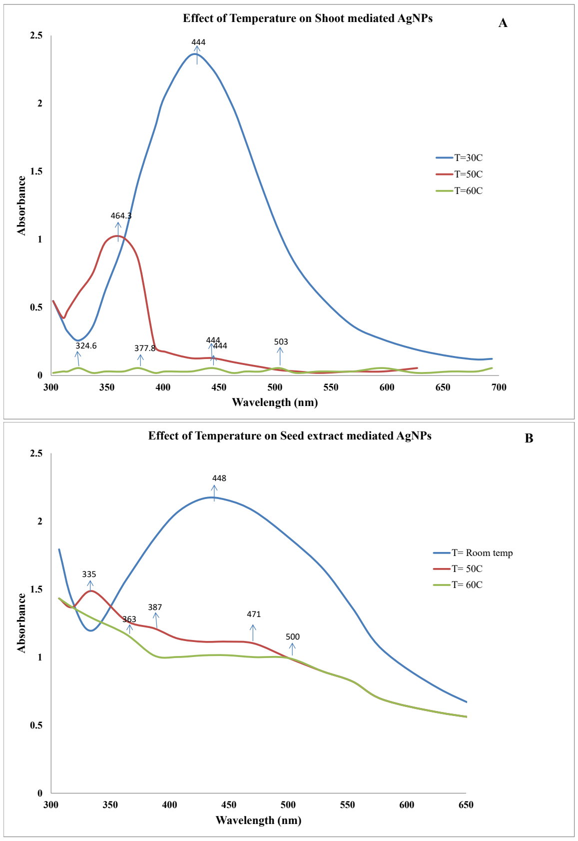

Fig. 7 Effect of (A) temperature on shoot extract mediated AgNPs and (B) temperature on seed extract mediated AgNPs.

is observed in decreased concentration of NaCl [36]. To investigate the stability effect of AgNPs towards NaCl solution, 50–250 µl/ml of 1 mM NaCl of AgNP solution was added and kept for one week with periodical measurement of resonance plasmon through UV-Vis spectrometer. The SPR data was recorded from day 1–day 7, but no significant effect was observed. This clearly indicates the stability of AgNPs towards a NaCl aqueous solution.

CONCLUSION

The environmental friendly synthesis of silver nanoparticles was achieved successfully using seed and shoot aqueous extract of *Asphodelus tenuifolius*. These particles were stable at room temperature. The AgNPs were fairly stable at basic pH but decomposed quickly at acidic pH below 4. Both shoot and seed extract mediated AgNPs were successfully employed for the sensing of various heavy metal ions where Cu, Zn and Ni could be easily estimated by the use of these NPs in aqueous medium. It was concluded that silver NPs prepared from both shoots and seeds gave characteristic absorption. Thus, it could be concluded that phyto-synthesis of AgNPs using aqueous extract of *A. tenuifolius* is cost effective and environmental friendly, which excludes the use of harmful and toxic chemicals as reducing and stabilizing agents. Moreover, this process could easily be scaled up for industrial production of heavy metal detection kits at micro level detection.

Acknowledgements: The authors wish to thank the University of Agriculture, Peshawar and University of Peshawar for providing facilities to undertake this research.

REFERENCES

1. Pérez J, Bax L, Escolano C (2005) *Roadmap Report on Nanoparticles*. Willems & van dar Wildenberg Espana sl, Barcelona, Spain.
2. Luo X, Morrin A, Killard AJ, Smyth MR (2006) Application of nanoparticles in electrochemical sensors and biosensors. *Electroanalysis* **18**, 319–326.
3. Saha S, Pal A, Kundu S, Basu S, Pal T (2009) Photochemical green synthesis of calcium-alginate-stabilized Ag and Au nanoparticles and their catalytic application to 4-nitrophenol reduction. *Langmuir* **26**, 2885–2893.
4. Murphy CJ, Sau TK, Gole AM, Orendorff CJ, Gao J, Gou L, Hunyadi SE, Li T (2005) Anisotropic metal nanoparticles: synthesis, assembly, and optical applications. *J Phys Chem B*, **109**, 13857–13870.
5. Lee Y, Choi J-r, Lee KJ, Stott NE, Kim D (2008) Large-scale synthesis of copper nanoparticles by chemically controlled reduction for applications of inkjet-printed electronics. *Nanotechnology* **19**, ID 415604.
6. Tiwari DK, Behari J, Sen P (2008) Application of nanoparticles in waste water treatment, *World Appl Sci J* **3**, 417–433.
7. Abirami B, Siva D, Abinaya S, Praveenkumar D, Vinothkumar A, Saravanan G, Achiraman S (2017) Biosynthesis of silver nanoparticles derived *Acorns calamus* rhizome extract and their biomedical application. *J Adv Appl Sci Res* **1**, ID 124.
8. Laurent S, Forge D, Port M, Roch A, Robic C, Vander Elst L, Muller RN (2008) Magnetic iron oxide nanoparticles: synthesis, stabilization, vectorization, physicochemical characterizations, and biological applications. *Chem Rev* **108**, 2064–110.
9. Abalaka ME, Akpor OB, Osemwegie OO (2017) Green synthesis and antibacterial activities of silver nanoparticles against *Escherichia coli*, *Salmonella typhi*, *Pseudomonas aeruginosa* and *Staphylococcus aureus*. *Adv Life Sci* **4**, 60–65.
10. Abbas Q, Saleem M, Phull AR, Rafiq M, Hassan M, Lee KH, Seo SY (2017) Green synthesis of silver nanoparticles using *Bidens frondosa* extract and their tyrosinase activity. *Iran J Pharmac Res* **16**, 760–767.

11. Mekseriwattana W, Srisuk S, Tantiapibalkun Y, Prapainop K (2019) Preparation of superparamagnetic iron oxide nanoparticles and investigation of their interaction with cells. *ScienceAsia* **45**, 60–64.
12. Benyettou F, Rezgui R, Ravaux F, Jaber T, Blumer K, Jouiad M, Motte L, Olsen JC, et al (2015) Synthesis of silver nanoparticles for the dual delivery of doxorubicin and alendronate to cancer cells. *J Mater Chem B* **3**, 7237–7245.
13. De Jong WH, Borm PJ (2008) Drug delivery and nanoparticles: applications and hazards. *Int J Nanomedicine* **3**, ID 133.
14. Iravani S (2011) Green synthesis of metal nanoparticles using plants. *Green Chem* **13**, 2638–2650.
15. Makarov V, Love A, Sinitsyna O, Makarova S, Yaminsky I, Taliansky M, Kalinina N (2014) Green nanotechnologies: synthesis of metal nanoparticles using plants. *Acta Naturae* **6**, 35–43.
16. Raveendran P, Fu J, Wallen SL (2003) Completely green synthesis and stabilization of metal nanoparticles. *J Am Chem Soc* **125**, 13940–13941.
17. Sharma VK, Yngard RA, Lin Y (2009) Silver nanoparticles: Green synthesis and their antimicrobial activities. *Adv Colloid Interface Sci* **145**, 83–96.
18. Noshad A, Iqbal M, Folkers L, Hetherington C, Khan A, Numan M, Ullah S (2019) Antibacterial effect of silver nanoparticles (AgNPs) synthesized from *Trichoderma harzianum* against *Clavibacter michiganensis*. *J Nano Res*, 10–19.
19. Noshad A, Hetherington C, Iqbal M (2019) Impact of AgNPs on seed germination and seedling growth: a focus study on its antibacterial potential against *Clavibacter michiganensis* subsp. michiganensis infection in *Solanum lycopersicum*. *J Nanomater* **2019**, ID 6316094.
20. Abalkhil TA, Alharbi SA, Salmen SH, Wainwright M (2017) Bactericidal activity of biosynthesized silver nanoparticles against human pathogenic bacteria. *Biotechnol Biotechnol Equip* **31**, 411–417.
21. Safder M, Imran M, Mehmood R, Malik A, Afza N, Iqbal L, Latif M (2009) Asphorodin, a potent lipoxygenase inhibitory triterpene diglycoside from *Asphodelus tenuifolius*. *J Asian Nat Prod Res* **11**, 945–950.
22. Safder M, Riaz N, Imran M, Nawaz H, Malik A, Jabbar A (2009) Phytochemical studies on *Asphodelus tenuifolius*. *J Chem Soc Pak* **31**, 122–145.
23. Abdel-Mogib M, Basaif SA (2002) Two new naphthalene and anthraquinone derivatives from *Asphodelus tenuifolius*. *Pharmazie* **57**, 286–287.
24. Philip D (2010) Green synthesis of gold and silver nanoparticles using *Hibiscus rosa sinensis*. *Physica E Low Dimens Syst Nanostruct* **42**, 1417–1424.
25. Bar H, Bhui DK, Sahoo GP, Sarkar P, Pyne S, Misra A (2009) Green synthesis of silver nanoparticles using seed extract of *Jatropha curcas*. *Colloid Surface A* **348**, 212–216.
26. Song JY, Kim BS (2008) Rapid biological synthesis of silver nanoparticles using plant leaf extracts. *Bioprocess Biosyst Eng* **32**, ID 79.
27. Jyoti K, Baunthiyal M, Singh A (2016) Characterization of silver nanoparticles synthesized using *Urtica dioica* Linn. leaves and their synergistic effects with antibiotics. *J Radiat Res Appl* **9**, 217–227.
28. Barman G, Samanta A, Maiti S, Laha JK (2014) Colorimetric assays for the detection of Hg(II) ions using functionalized gold and silver nanoparticles. *Adv Sci* **2**, 52–58.
29. Barman G, Samanta A, Maiti S, Konar LJ (2014) Detection of Cu^{+2} ion by the synthesis of bio-mass-silver nanoparticle nanocomposite. *Int J Eng Res* **5**, 1086–1097.
30. Frederix F, Friedt JM, Choi KH, Laureyn W, Campitelli A, Mondelaers D, Maes G, Borghs G (2003) Biosensing based on light absorption of nanoscaled gold and silver particles. *Analyt Chem* **75**, 6894–6900.
31. Peretyazhko TS, Zhang Q, Colvin VL (2014) Size-controlled dissolution of silver nanoparticles at neutral and acidic pH conditions: kinetics and size changes. *Environ Sci Technol* **48**, 11954–11961.
32. Liu J, Hurt RH (2010) Ion release kinetics and particle persistence in aqueous nano-silver colloids. *Environ Sci Technol* **44**, 2169–2175.
33. LaMer VK, Dinegar RH (1950) Theory, production and mechanism of formation of monodispersed hydrosols. *J Am Chem Soc* **72**, 4847–4854.
34. Pacioni NL, Borsarelli CD, Rey V, Veglia AV (2015) Synthetic routes for the preparation of silver nanoparticles. In: Alarcon E, Griffith M, Udekwu K (eds) *Silver Nanoparticle Applications*, Springer, New York, pp 13–46.
35. You H, Fang J (2016) Particle-mediated nucleation and growth of solution-synthesized metal nanocrystals: A new story beyond the LaMer curve. *Nano Today* **11**, 145–167.
36. Sharif M, Dorranian D (2015) Effect of NaCl concentration on silver nanoparticles produced by 1064 nm laser ablation in NaCl solution. *Mol Cryst Liq Cryst* **606**, 36–46.