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Orginal Research Article

Eco-friendly biosynthesis of silver nanoparticles using aqueous solution of *Spartium junceum* flower extract

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ABSTRACT

Green synthesis of nanoparticles has received great attention from scientists due to their undeniable applications in all field of science. In this study, an eco-friendly and fast approach is reported for the preparation of silver nanoparticle (Ag NPs) using *Spartium junceum* flower extract, as a reductant and stabilizer agent, from aqueous solution of silver nitrate. The biosynthesis of silver nanoparticles was optimized by investigating the reaction parameters including: pH, temperature, concentration of plant extract and interaction time. The silver nanoparticles were characterized by UV-vis, fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), dynamic light scattering (DLS) and transmission electron microscopy (TEM) analyses. Moreover, the biosynthesis of Ag NPs was confirmed by UV-vis spectroscopy through the presence of a characteristic surface plasmon resonance (SPR) band for Ag NPs at λ_{max}=420 nm. The synthesized nanoparticles were crystalline in nature, nearly spherical in shape with 15-25 nm range of sizes.

Graphical Abstract

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Introduction

Silver nanoparticles (Ag NPs) which are one of the noble NPs that have unbeatable properties like electrical, conductivity, chemical stability, sensing ability, catalytic, and biological activity [1–3] making them as a versatile tool to various kinds of applications in medicine (Diagnostic, orthopedic, drug delivery, ...) [4–7], dentistry, clothing, respirators, electronics, mirrors, optics, cosmetic, detergent, photography, and food industry [8, 9].

Different approaches, whether chemical or physical, have been developed for the synthesis of Ag NPs [10–15], but reasons such as being expensive, unavailable, harsh reaction conditions, tedious process and non-environmentally friendly, limit their application for the preparation of these nanoparticles. Thus, given that environmental and economic concerns, nowadays, using plant extract has become a suitable alternative to the previously reported chemical and physical methods for the preparation of NPs. In this sense, plant extract as a reducing and stabilizer agent helps the efficient formation of nanoparticles [16]. The For plant mediated biosynthesis of Ag NPs in literature can be point to the following plants: *Ficus benghalensis* [17], *Aloe vera* [18], *Talinum triangulare* [19], *Cressa Cretica* [20], *Azadirachta indica* [21], *onion* [22], *basil* [1], *banana peel* [23], *Tamarind fruit* [24], and *Ipomoea asarifolia* [25].

The *Spartium junceum* (Spanish broom) is a *perennial* shrub native of the Mediterranean area and belongs to the *Leguminosae* family [26] that grows on hill slope (They have strong root system), coastlines, arid, calcareous and rocky areas [27]. This plant can be used in bioengineering stabilization techniques [27], soil retainer in erosion control [26], and for composite additive applications [28]. Moreover, they have various biological activities such as: sedative and diuretic activities [26], antimicrobial, antioxidant, cytotoxic [29], antiulcer [30, 31], anti-inflammatory, analgesic [32], antifertility [33] and antitumor [34] activities. In this work, Ag NPs were biosynthesized with the help of *S. junceum* flower extract in an aqueous silver nitrate medium. Furthermore, the effect of the reaction parameters, i.e., temperature, pH, interaction time and the extract concentration (Ratio of plant sample to extraction solvent) have been investigated in this study.

Experimental

Plants and chemicals

Silver nitrate ($AgNO_3$) was purchased from Merck chemicals and fresh *S. junceum* flowers were collected from the area around of Birjand, Iran. All solutions were prepared using triply distilled deionized water.

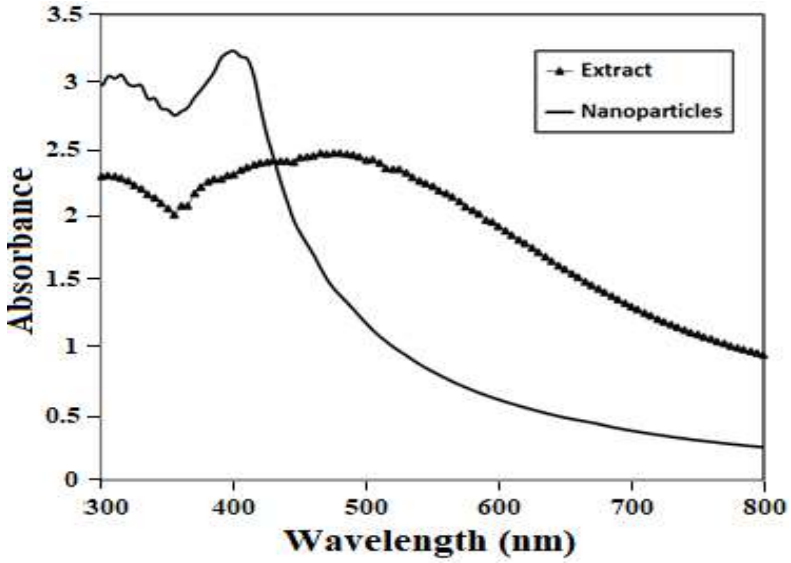


Figure 1. UV-vis spectra of silver nanoparticles and *S. junceum* flower extract

Instruments

The UV-vis analyses of the samples were conducted by UV spectrolab BEL photonics over the 200–900 nm wavelength range. FT-IR measurements were done using AVATAR 370 (Thermo Nicolet, USA) spectrophotometer in a range of 400-4000 cm^{-1}. The morphology as well as the size of silver nanoparticles were investigated using transmission electron microscopy (TEM) CM 120 instrument. The X-ray diffraction (XRD) pattern of the synthesized Ag NPs was studied by XRD BRUKER D2 PHASER instrument operated at 30 kV with CuKα radiation at a scanning rate of 8°/min.

Preparation of S. junceum flower extract

Briefly, freshly collected *S. junceum* flowers from the area around of Birjand, Iran, were rinsed with deionized water, shade-dried and finely meshed and grinded with mortar and pestle. Then, 5 g of the flower powder was added to 100 mL of deionized water. The mixture was boiled for 15 min along with mechanical stirring. The resultant mixture was filtered (Whatman No.1 filter paper) and freshly prepared flower extract was stored at room temperature in air atmosphere.

Synthesis of silver nanoparticles

25 mL of aqueous solution of $AgNO_3$ (0.025 M) was added dropwise into 25 mL of *S. junceum* flower extract. The resultant mixture was mechanically stirred at 80 °C for 20 min. The silver nanoparticles were obtained by centrifugation of the mixture (5500 rpm) for 20 min followed by re-dispersion in deionized water in order to eliminate of any uncoordinated biological molecules [17].

Results and discussion

The initial diagnosis of the silver nanoparticles was made by changing the color of the reaction solution from yellow to brown within 30 min after addition of silver nitrate solution into the flask containing the flower extract [27]. This change demonstrated the excitation of surface plasmon resonance (SPR) within the synthetization of Ag NPs [35]. The properties of the prepared NPs, including shape, morphology, dielectric environment and size, affect the SPR band [36]. This phenomenon is responsible for the unique and tunable optical properties mediating the shape and distribution size of the NPs. Figure 1 shows the UV-vis spectra of aqueous component of silver nanoparticles and *S. junceum* flower extract. The absorption band of metallic silver nanoparticles appeared at λ_{max}= 420 nm and resulted in surface plasmon resonance which is compatible with the reported spherical Ag NPs absorption band [37]. *S. junceum* extract exhibited a broad absorption band at 476 nm (Figure 1).

Optimization of different parameters for nanoparticles synthesis

Influence of the pH of the extract solution, temperature of the process, time of the interaction and concentration of the flower extract on the preparation of silver nanoparticles were investigated. Initially, the influence of pH of the *S. junceum* as an important factor was investigated by measuring UV–vis spectra at different pH values, i.e., 5, 7, 8, 9 and 11 using 0.1 N HNO_3 and 0.1 N NaOH solutions (Figure 2**a**). As shown in the Figure 2**a**, increasing of pH from 5 to 11, increases the intense absorption at the corresponding wavelength (λ_{max}=435 nm). This behavior could be attributed to the increase of colloidal silver nanoparticles and reduction rate [35]. It is well-known that the particle size is expected to be larger in acidic medium than in basic [38]. Hydroxide ions charging the surface of NPs and thus maximum electrostatic interactions occurs [39]. It could be concluded that alkaline pHs were ideal for the formation of Ag NPs by *S. junceum* flower extract. Deviation from spherical shape, could be responsible for the appeared shoulder in high pH values due to the fact that this deviation leads to the beginning of transverse plasmon [40].

The influence of temperature on the silver nanoparticles was also investigated in the range from 25 °C to 80 °C at the constant pH=9 (Figure 2**b**). The results in Figure 2**b** show that the rate of Ag NPs synthesis enhances with increasing temperature from 25 °C to 80 °C.

The effect of interaction time was also studied by measuring the absorption spectra of the solution at the time interval of 5, 10, 15 and 20 min while temperature and pH are kept constant at 80 °C and 9, respectively. As shown in Figure 2**c** it was observed that there is an increase in the absorbance with the passage of time from 5 to 20 min, indicating an enhancement in the formation of the Ag NPs. This observation may be due to increasing the particle size and departure from spherical shape of Ag NPs moderates the SPR bond [41].

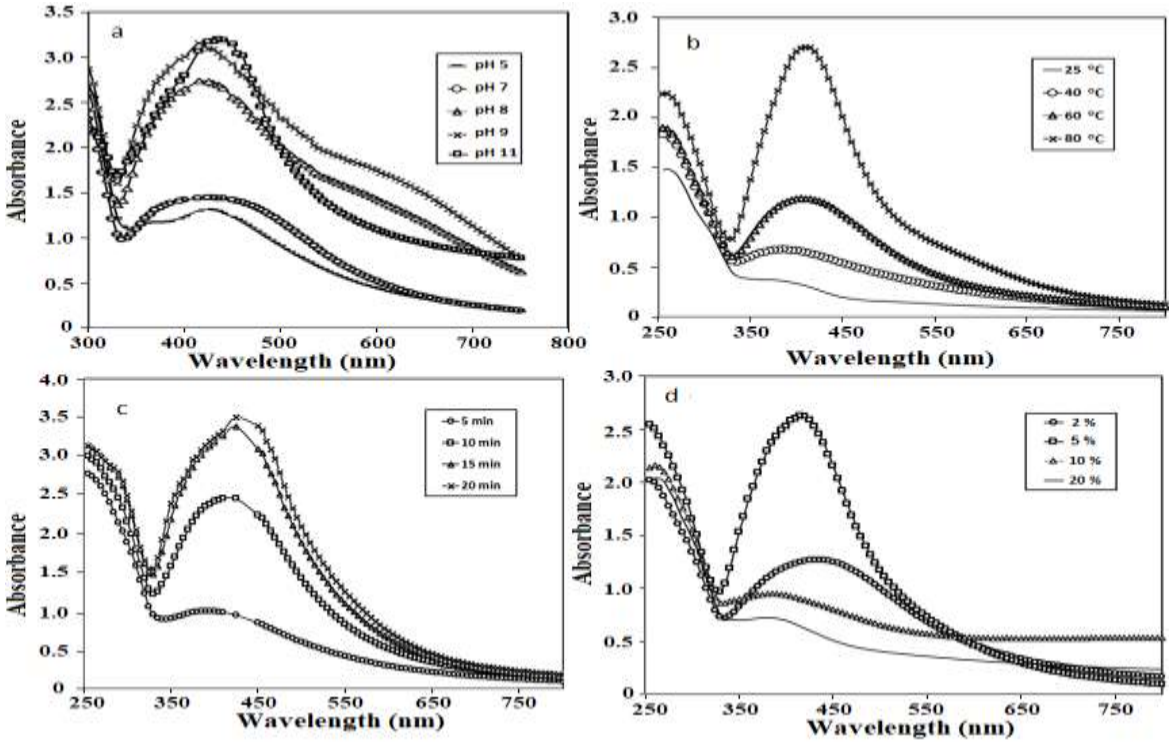
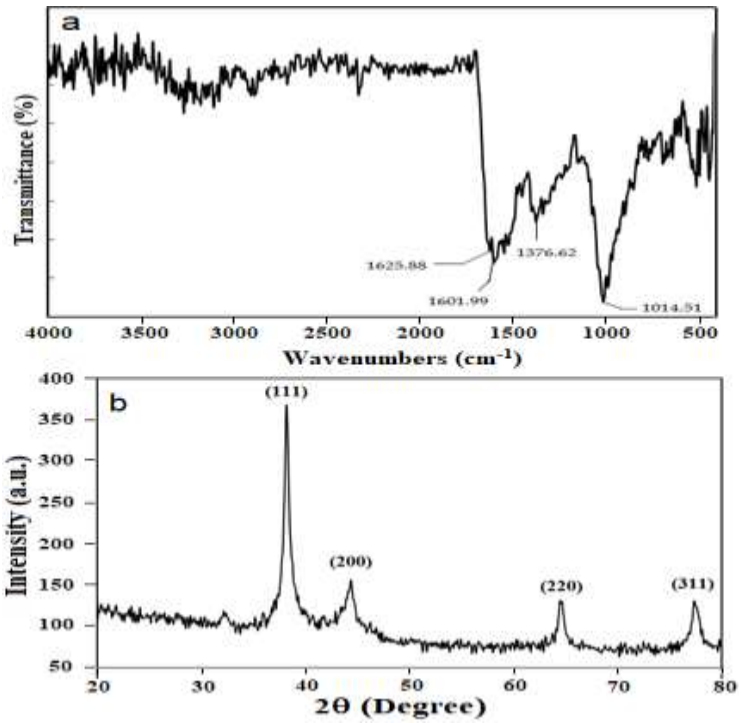


Figure 2. UV-vis spectra obtained from *S. junceum*-mediated preparation of Ag NPs at different: a) pH values of the reaction mixture; b) temperature; c) interaction time intervals. d) Reaction of 0.025 M silver nitrate solution with different concentration of the flower extract. Various concentrations (2, 5, 10, 20%) of aqueous extract of *S. junceum* were prepared by boiling different amounts of the plant in deionized water (100 mL) for 15 min

Figure 3. a) FT-IR spectrum and b) XRD pattern of silver nanoparticles synthesized by *S. junceum* flowers extract



In following, in order to complete the reduction of silver ions to silver nanoparticles, we screened the effect of changing the concentration of the flower extract from 2 to 20% in 0.025 M silver nitrate solution. Figure 2**d** shows the obtained absorption spectra of Ag NPs with changing the concentration of flower extract at the optimized conditions, i.e., 80 °C, pH=9 and an interaction time of 20 min. As depicted at the Figure 2**d**, 5% extract concentration provides the highest possible absorption. With an enhancement in concentration of the flower extract, the peak intensity decreases. Also, due to the direct relationship of ratio of silver ions as reducing and stabilizing agents to the size of Ag NPs, different mixing ratios of flower extract and silver salt were examined [36]. It was found that when the concentration of extract to silver nitrate is in the mixing ratio 1:1 (Not shown in the Figure), a strong absorption band is observed.

Characterization of the silver nanoparticles

FT-IR spectra of the biosynthesized Ag NPs showed characteristic bands at 1625.88 and 1014.51 cm^{-1} corresponding to stretching vibration of C=C and C-O, respectively (Figure 3**a**). Also a peak which appeared at 1601.99 was assigned to bending vibrations of N-H groups (Figure 3**a**). These functional groups corroborate the presence of biomolecule reducing agents of the Ag^{+} ions in the solution. Moreover, these biomolecules which play a vital role in capping and stabilizing NPs prevent the aggregation of the nanoparticles and lead to stabilizing them [42].

Crystalline nature and structure of the as synthesized silver nanoparticles were studied by XRD analysis (Figure 3**b**). The XRD spectrum showed four diffraction peaks at 38.1°, 44.3°, 64.5° and 77.3° corresponding to the indices of (111), (200), (220) and (311) planes respectively. Moreover, it confirmed the formation of face centered cubic crystalline Ag nanoparticles [42]. The XRD pattern results are completely in agreement with the reference of JCPDS file No. 89-3722 and the reported biosynthesized Ag NPs [20, 22, 23, 25, 42]. Also, sharpness of the peaks is the evidence of the crystalline structure of the nanoparticles. Furthermore, size of the silver nanoparticles was calculated using Debye scherer equation ($d=0.9\ \lambda/\beta\ \mathrm{Cos}\ \theta$) [17] and the results showed that the size of silver nanoparticles is about 23 nm.

Figure 4**a** represents the TEM image of the synthesized Sg NPs. The TEM image revealed that the biosynthesized silver nanoparticles were predominantly spherical in shape with the average size of 21.99 nm. The hydrodynamic diameter of the silver nanoparticles is determined by the DLS technique (Figure 4**b**). According to DLS analysis, the size distribution of silver nanoparticles is centered at 21.99 nm.

Conclusion

In summary, we have reported the *S. junceum* mediated green biosynthesis of silver nanoparticles with average diameter of 22 nm and spherical in shape from aqueous solution of silver nitrate in short reaction time. Ag NPs were suitably characterized by UV-vis, FT-IR, XRD, DLS and HRTEM instruments. Alkaline medium with 1:1 mixing ratio of *S. junceum* extract: $AgNO_3$ at 80 °C for 20 min were found to be the premium conditions for the preparation of Ag NPs. Cost-effective, biocompatibility, non-toxic, and mild reaction conditions are advantageous of the present method that making the it as an ecofriendly and economic-efficiency alternative to the previously reported physical and chemical methods.

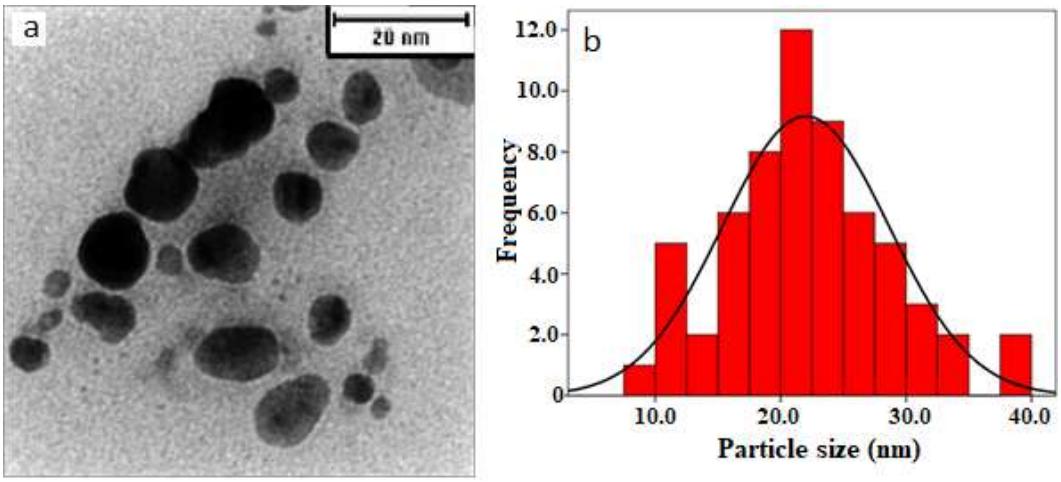


Figure 4. a) HRTEM image and b) DLS analysis of the synthesized silver nanoparticles

Disclosure statement

No potential conflict of interest was reported by the authors.

Orcid

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