Research Article

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Green approach in gold, silver and selenium nanoparticles using coffee bean extract

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Abstract: Green fabrication of metal nanoparticles (NPs), using natural reducing and stabilizing agents existed in plants and their derivatives, due to their unique properties, has gained more attention. The present study focuses on the synthesis of gold (Au), silver (Ag) and selenium (Se) NPs using coffee bean extract under hydrothermal conditions (1.5 atm and 121°C, for 15 min). Coffee bean extract obtained in 2 h processing using Clevenger apparatus and Fourier transform-infrared (FT-IR) spectroscopy indicated five highlighted peaks, namely, hydroxyl, amide, aromatic, alkane and ring groups. Dynamic light scattering analysis revealed that among three different NPs formed, fabricated Ag NPs had small particle size (153 nm) and high zeta potential value (16.8 mV). However, synthesized Au NPs had minimum polydispersity index (0.312). Results also indicated that fabricated Au, Se and Ag NPs had low antioxidant activity with values of 9.1, 8.9 and 8.7%, respectively. Morphological and antibacterial activity assessments, demonstrated that synthesized Ag, Au and Se NPs had spherical shape and high bactericidal activity against *E. coli* and *S. aureus*. Obtained results indicated that the synthesized NPs, can be utilized in various areas.

Keywords: antioxidant activity, coffee bean extract, green synthesis, metal nanoparticles, physicochemical properties

1 Introduction

According to the National Institute of Health of America, nanotechnology is defined as fabrication of organic and inorganic materials, devices and systems using various

techniques in the scale of nanometer (Nadagouda and Varma 2008). Metal nanoparticles (NPs) have unique characteristics compared to their bulk form. In fact, metal and metal oxide NPs have obtained more interests from the scientists because of their use in numerous areas and fields such as medicine, electronic, food and agriculture, biotechnology and wastewater treatment (Mohammadlou et al. 2017; Keshavarzi et al. 2018). Among metal NPs, gold (Au), silver (Ag) and selenium (Se) NPs draw great attention due to their wide applications and benefits. Au NPs are utilized in chemical catalysts, gene expression, drug delivery, sensors and fuel cells (Yola et al. 2015; Elahi et al. 2018). Ag NPs have been used in various areas including food packaging, biolabeling, waste water treatment, electoral devices, texture, paint and ceramics due to their high antimicrobial activities against several microorganisms (Zhang et al. 2016). Due to its anticarcinogenic activity and muscle functioning, Se NPs are utilized in medicines and pharmaceuticals (Khurana et al. 2019).

Generally, three types of synthesis methods are involved in forming inorganic NPs, namely, physical, chemical and green techniques. As compared to the numerous conventional methods of synthesis of NPs which are based on utilizing chemical components as reducing and stabilizing agents, green procedures use natural and biodegradable reducing and capping agents presented in biological systems, including microorganisms, enzymes and plants and their derivatives (Wu and Chen 2010; Eskandari-Nojehdehi et al. 2018). Because the green synthesis methods use less energy, without using toxic components and generating hazardous by-products, these fabrication techniques have gained more attention these days; therefore, this method could be used as an alternative of the common physicochemical NPs synthesis methods (Gour and Jain 2019; Salem and Fouda 2020).

Coffee is dark colored, bitter and slightly acidic from the genus *Coffea* which is native to tropical Africa (Páscoa et al. 2013; Rein et al. 2013). Several studies demonstrated that coffee plays protective role against colorectal cancer and Alzheimer's disease and possesses high antioxidant activity (Carman et al. 2014; Vignoli et al. 2014). Furthermore, coffee contains important minerals such as calcium,

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potassium, iron, phosphorous, nickel and magnesium. Furthermore, coffee beans contain polyphenols, carbohydrates, caffeine, caffeic acid, chlorogenic acid, diterpenes and trigonelline, which can be utilized as reducing and capping biomolecules in inorganic NPs (Beer 1988; Buldak et al. 2018). Our present study focuses on (i) the potential application of coffee extract to form three different metal NPs, namely, Ag, Au and Se NPs; (ii) the assessment of physicochemical attributes of the formed three NPs and also highlight the suitability of the coffee extract in metal ion reduction and (iii) measure the antioxidant and bactericidal properties of the resultant different NPs.

2 Materials and method

2.1 Materials

Coffee beans were provided from a local shop in Tabriz, East Azerbaijan province of Iran. Sodium selenite and silver nitrate were bought from Merck Company (Darmstadt, Germany), as Se and Ag salts, respectively. Gold(III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was bought from Sigma-Aldrich Company (St. Louis, MO, USA). From Sigma Company (St. Louis, MO, USA), 2,2-Diphenyl-2-picrylhydrazyl (DPPH) was obtained. Bacteria strains of *Escherichia coli* (Persian Type Culture Collection [PTCC] 1270) and *Staphylococcus aureus* (PTCC 1112) were provided from microbial PTTC (Tehran, Iran).

Plate count agar (PCA) was obtained from Oxoid (Oxoid Ltd, Hampshire, England).

2.2 Coffee bean extract preparation

Coffee beans were powdered by a miller (MX-GX1521; Panasonic, Tokyo, Japan) and 100 g of that was subjected into a Clevenger device for 2 h. Coffee bean extract with a pleasant odor was collected in a dark vial and kept at 4°C.

2.3 Synthesis of Metal NPs

According to the literatures, 1 mM solutions of Na_2SeO_3 , $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and AgNO_3 were prepared (Eskandari-Nojehdehi et al. 2016; Mohammadlou et al. 2017; Sheikhlou et al. 2020). After that, 10 mL of prepared coffee extract was added into 10 mL of the salt solutions and the provided colloidal solutions were placed into an autoclave for 15 min (at 121°C and 1.5 atm).

2.4 Physicochemical analysis

FT-IR spectroscopy (FT-IR 8400S; Shimadzu Co., Kyoto, Japan) was utilized to determine the main existed functional groups in the provided extract (Theingi et al. 2019).

Figure 1: FTIR spectra of the coffee bean extract.

Figure 2: UV-Vis spectra of the solutions containing Se NPs (a), Ag NPs (b) and Au NPs (c).

UV-Vis spectrophotometry (Jenway UV-Vis spectrophotometer 6705; Jenway, Stone, UK) was utilized to verify the fabrication of Au, Ag and Se NPs according to surface plasmon resonance (SPR) of the NPs (Fardsadeh and Jafarizadeh-Malmiri 2019). In fact, the presence of SPR signal of the fabricated NPs in the mixture solutions causes maximum absorbance ($\lambda_{\max}$) in the wavelength ranging 270–350 nm, 510–570 nm and 380–450 nm for Se NPs, Au NPs and Ag NPs, respectively (Eskandari-Nojehdehi et al. 2018; Ghanbari et al. 2018).

Dynamic light scattering technique (Zetasizer Nano ZS; Malvern Instruments, Worcestershire, UK) was utilized to measure particle size and its distribution (PSD), zeta potential and its distribution and polydispersity index (PDI) of the produced NPs.

Antioxidant activity of the formed three different NPs was assessed with method described by Anzabi (2018) and equation (1):

$$I\% = \frac{(A_{\text{control}} - A_{\text{sample}})}{A_{\text{control}}} \times 100 \quad (1)$$

In the mentioned equation, $I\%$, A_{control} and A_{sample} are percentage of inhibition and absorbance of control and samples, respectively, at wavelength of 517 nm.

2.5 Bactericidal activity

Bactericidal effect of the synthesized NPs was measured using the technique described by Bakht Dalir et al. (2020), based on well diffusion method and the diameter of the formed transparent zone around the holes.

2.6 Microstructure analysis

Shape and size of the produced Au, Ag and Se NPs, as their morphological attributes, were studied by transmission electron microscopy ([TEM]; CM120; Philips, Amsterdam, the Netherlands) with an acceleration voltage of 120 kV.

2.7 Statistical analysis

Characteristics of the fabricated three studied NPs were measured three times and the mean values of data were compared together utilizing Tukey's comparison test with p value < 0.05 , using Minitab v.16 statistical package (Minitab Inc., PA, USA).

3 Results and discussions

3.1 Specifications of coffee bean extract

FT-IR spectra of the provided coffee extract are presented in Figure 1. As can be observed in this figure, five predominated peaks were detected with wavenumbers 3454.16,

Table 1: Physicochemical properties of the synthesized three different metal NPs using coffee bean extract

Properties	Mean particle size (nm)	PDI	Zeta potential (mV)
Se NPs	595	0.748	6.8
Ag NPs	153	0.681	16.8
Au NPs	1,258	0.312	15.2

Figure 3: Particle size distribution of the synthesized Se NPs (a), Ag NPs (b) and Au NPs (c) using coffee bean extract.

1639.18, 1406.14, 1358.95 and 710.43 cm^{-1} , which were interconnected to stretching vibration of the –OH (water), RCO (amide), C–C (aromatic), COH (alkane) and ring and skeleton modes of the main components, respectively.

3.2 Formation of fabricated NPs

UV-Vis spectra for the synthesized Se, Ag and Au NPs are shown in Figure 2(a–c). As these figures indicate, centered λ_{max} at 277 nm (Figure 2a), 407 nm (Figure 2b) and 561 nm (Figure 2c) revealed the formation of Se, Ag and Au NPs in the colloidal solutions, respectively. The

results were in agreement with the achievements of other research. Sheikhlou et al. (2020) prepared Se NPs by walnut leaf extract with λ_{max} of 375 nm. Mohammadlou et al. (2017) also fabricated Ag NPs using *Pelargonium* leaf extract with λ_{max} of 405 nm. Eskandari-Nojehdehi et al. (2018) synthesized Au NPs using gum Arabic with λ_{max} ranging 525–546 nm.

3.3 Fabricated NPs characteristics

Characteristics of the formed Se, Ag and Au NPs using coffee bean extract are shown in Table 1. As can be seen

Figure 4: Bactericidal activity of the synthesized Se NPs, Ag NPs and Au NPs using coffee bean extract against *E. coli* (a) and *S. aureus* (b).

in Table 1, among all three NPs formed, fabricated Ag NPs had small particle size (153 nm) and high zeta potential value (16.8 mV). However, synthesized Au NPs had minimum PDI (0.312). Figure 3(a–c) indicates PSD of the resultant Se, Ag and Au NPs. The presence of the broad and sharp peaks for all the NPs formed revealed that poly-dispersed Se, Ag, and Au NPs were fabricated using coffee bean extract (Figure 3). Achieved results were validated by high values of the PDI for three different metal NPs formed (Table 1), where its small values show greater size homogeneity of the created NPs (Manosalva et al. 2019).

3.4 Antioxidant and antibacterial activities of the fabricated three different NPs

Results indicated that fabricated Au, Se and Ag NPs had low antioxidant activity with values of 9.1, 8.9 and 8.7%, respectively. Statistical analysis indicated that antioxidant activity of the synthesized Au NPs was significantly ($p < 0.05$) higher than that of the fabricated Ag NPs. Nakkala et al. (2015) revealed that Au NPs had higher antioxidant activity as compared to the Ag NPs. Low antioxidant activities of the synthesized three different NPs

could be related to the low concentrations of the metal salts and the fabricated NPs in the mixture solutions. Nakkala et al. (2015) also reported that by increasing the concentration of Au and Ag salts, antioxidant activities of their NPs enlarged.

Bactericidal activities of the resultant Au, Ag and Se NPs against gram-positive and gram-negative bacteria strains are shown in Figure 4(a and b). In the plate containing PCA amended with *S. aureus*, the diameter of formed clear zones around the holes having Ag, Au and Se NPs was 13 ± 1 , 10 ± 1 and 8 ± 1 mm, respectively (Figure 4a). However, in the plate containing PCA amended with *E. coli*, the diameter of the formed transparent zones for the holes having Ag, Au and Se NPs was 11 ± 1 , 8 ± 1 and 7 ± 1 mm, respectively. It can be explained by the fact that the antibiotics have less bactericidal effects on gram-negative bacteria as compared to the gram-positive bacteria strains. In fact, the presence of lipopolysaccharide and protein layers on the cell wall of gram-negative bacteria do not allow them to access and digest the bacterial cell wall (Dong et al. 2019). Furthermore, other studies indicated that among the novel metal NPs, Ag NPs have higher antibacterial activity and Se NPs have weak bactericidal properties (Tang and Zheng 2018; Fardsadegh and Jafarizadeh-Malmiri 2019).

Figure 5: Typical TEM images of the fabricated Au NPs (a), Ag NPs (b) and Se NPs (c) using coffee bean extract.

3.5 Microstructure of the formed three different metal NPs

TEM images for the resultant Au, Ag and Se NPs are shown in Figure 5(a–c). These figures indicated that approximately spherical and polydispersed NPs were created with particle size of 300, 700 and 100 nm for the fabricated Au, Ag and Se NPs, respectively. Other research have fabricated spherical Se, Au and Ag NPs in hydrothermal manner. Fardsadegh and Jafarizadeh-Malmiri fabricated spherical and monodispersed Se NPs using *Aloe vera* leaf extract with a mean particle size of 50 nm (Fardsadegh and Jafarizadeh-Malmiri 2019). Eskandari-Nojehdehi et al. (2016) also green synthesized

well-dispersed Au NPs with a mean particle size ranging 10–50 nm using mushroom extract. Ahmadi et al. (2019) also green synthesized spherical Ag NPs with a mean particle size ranging 10–25 nm, using *Aloe vera* leaf extract.

4 Conclusions

In the present study, green synthesis of three different metal NPs, namely, Au, Ag and Se NPs based on subcritical water and coffee bean extract, as a non-toxic solvent and natural reducing agent, was achieved. Simple, clean, and fast developed inorganic NP synthesis technique makes it feasible to commercially fabricate metal NPs in large scales. Furthermore, the resultant stable and spherical Au, Ag and Se NPs, with high antibacterial activity, using coffee bean extract indicated high-potential application of coffee bean extract in converting inorganic ions into their NPs. It seems that by optimizing the synthesis parameters, different metal NPs with more desirable attributes can be fabricated for applications in various areas, including drug delivery, food packaging and formulation and medicine.

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Conflict of interest: The authors declare that they have no conflict of interest.

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