Research Article

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

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 pharmaceutics (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 Coffee 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,
potassium, iron, phosphorous, nickel and magnesium. Furthermore, coffee beans contain polyphenols, carbohydrates, caffeine, caffeic acid, chlorogenic acid, diterpenes and trigenilline, 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 (HAuCl₄·3H₂O) 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 Na₂SeO₃, HAuCl₄·3H₂O and AgNO₃ 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.](image-url)
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 (Fardsadegh and Jafarizadeh-Malmiri 2019). In fact, the presence of SPR signal of the fabricated NPs in the mixture solutions causes maximum absorbance ($\lambda_{\text{max}}$) 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 and 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):

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

In the mentioned equation, $I\%$, $A_{\text{control}}$ and $A_{\text{sample}}$ 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 predominate peaks were detected with wavenumbers 3454.16, 3300.15, 1716.15, 1620.15 and 1435.15.

### 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                |
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 \(\lambda_{\text{max}}\) 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 \(\lambda_{\text{max}}\) of 375 nm. Mohammadlou et al. (2017) also fabricated Ag NPs using Pelargonium leaf extract with \(\lambda_{\text{max}}\) of 405 nm. Eskandari-Nojehdehi et al. (2018) synthesized Au NPs using gum Arabic with \(\lambda_{\text{max}}\) 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 3: Particle size distribution of the synthesized Se NPs (a), Ag NPs (b) and Au NPs (c) using coffee bean extract.](image-url)
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 polydispersed 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 $13 \pm 1$, $10 \pm 1$ and $8 \pm 1$ 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 $11 \pm 1$, $8 \pm 1$ and $7 \pm 1$ 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).
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.

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 ranging 10–50 nm (Fardsadegh and Jafarizadeh-Malmiri 2019). Eskandari-Nojehdehi et al. (2016) also green synthesized

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.

References

[1] Ahmadi O, Jafarizadeh-Malmiri H, Jodeiri N. Optimization of processing parameters for hydrothermal silver nanoparticles synthesis using Aloe vera leaf extract and estimation of their physico-chemical and antifungal properties. Z Phys Chem. 2019;233(5):651–67.
[2] Anzabi Y. Biosynthesis of ZnO nanoparticles using barberry (Berberis vulgaris) extract and assessment of their physico-chemical properties and antibacterial activities. Green Process Synth. 2018;7(2):114–21.
[3] Bakht Dalir SJ, Djahaniani H, Nabati F, Hekmati M. Characterization and the evaluation of antimicrobial activities of silver nanoparticles biosynthesized from Carya illinoinsensis leaf extract. Heliyon. 2020;6(3):e03624, doi: 10.1016/j.heliyon.2020.e03624.
[4] Beer J. Litter production and nutrient cycling in coffee (Coffea arabica) or cacao (Theobroma cacao) plantations with shade trees. Agrofor Syst. 1988;7(2):103–14.
[5] Buldak BJ, Hejmo T, Osowski M, Buldak Ł, Kukla M, Polaniak R, Birkner E. The impact of coffee and its selected bioactive compounds on the development and progression of colorectal cancer in vivo and in vitro. Molecules. 2018;23(12):3309–16.

[6] Carman AJ, Dacks PA, Lane RF, Shineman DW, Fillit HM. Current evidence for the use of coffee and caffeine to prevent age-related cognitive decline and Alzheimer’s disease. J Nutr Health Aging. 2014;18(4):383–92.

[7] Dong Y, Zhu H, Shen Y, Zhang W, Zhang L. Antibacterial activity of silver nanoparticles of different particle size against Vibrio natriegens. PLoS One. 2019;14(9):e0222322. doi: 10.1371/journal.pone.0222322.

[8] Elahi N, Kamali M, Baghersad MH. Recent biomedical applications of gold nanoparticles: a review. Talanta. 2018;184:537–56.

[9] Eskandari-Nojehdehi M, Jafarizadeh-Malmiri H, Rahbar-Shahrouzi J. Optimization of processing parameters in green synthesis of gold nanoparticles using microwave and edible mushroom Agaricus bisporus extract and evaluation of their antibacterial activity. Nanotechnol Rev. 2016;5(6):537–48.

[10] Eskandari-Nojehdehi M, Jafarizadeh-Malmiri H, Jafarizad A. Microwave accelerated green synthesis of gold nanoparticles using gum Arabic and their physico-chemical properties assessments. Z Phys Chem. 2018;232(3):325–43.

[11] Fardsadegh B, Jafarizadeh-Malmiri H. Aloe vera leaf extract mediated green synthesis of selenium nanoparticles and assessment of their in vitro antimicrobial activity against spoilage fungi and pathogenic bacteria strains. Green Process Synth. 2019;8(1):399–407.

[12] Ghanbari S, Vaghari H, Sayyar Z, Adilpour M, Jafarizadeh-Malmiri H. Autoclave-assisted green synthesis of silver nanoparticles using A. fumigatus mycelia extract and the evaluation of their physico-chemical properties and antibacterial activity. Green Process Synth. 2018;7(3):217–24.

[13] Gour A, Jain NK. Advances in green synthesis of nanoparticles. Artif Cell Nanomed Biotechnol. 2019;47(1):844–51.

[14] Keshavarzi M, Davoodi D, Pourseyedi S, Taghizadeh S. The effects of three types of alfalfa plants (Medicago sativa) on the biosynthesis of gold nanoparticles: an insight into phyto-mining. Gold Bull. 2018;51(3):99–110.

[15] Khurana A, Tekula S, Saiﬁ MA, Venkatesh P, Godugu C. Therapeutic applications of selenium nanoparticles. Biomed Pharmacother. 2019;111:802–12.

[16] Manosalva N, Tortella G, Diez MC, Schalchli H, Seabra AB, Durán N, Rubilar O. Green synthesis of silver nanoparticles: effect of synthesis parameters on antimicrobial activity. World J Microbiol Biotechnol. 2019;35(6):88. doi: 10.1007/s11274-019-2664-3.

[17] Mohammadlou M, Jafarizadeh-Malmiri H, Maghsoudi H. Hydrothermal green synthesis of silver nanoparticles using Pelargonium/Geranium leaf extract and evaluation of their antifungal activity. Green Process Synth. 2017;6(1):31–42.

[18] Nadagouda MN, Varma RS. Green synthesis of silver and palladium nanoparticles at room temperature using coffee and tea extract. Green Chem. 2008;10(8):859–62.

[19] Nakakal JR, Bhagat E, Suchiand K, Sadras SR. Comparative study of antioxidant and catalytic activity of silver and gold nanoparticles synthesized from Costus pictus leaf extract. J Mater Sci. 2015;31(10):986–94.

[20] Páscoa RN, Magalhães LM, Lopes JA. FT-NIR spectroscopy as a tool for valorization of spent coffee grounds: application to assessment of antioxidant properties. Food Res Int. 2013;51(2):579–86.

[21] Rein MI, Renouf M, Cruz-Hernandez C, Actis-Gorellta L, Thakkar SK, da Silva Pinto M. Bioavailability of bioactive food compounds: a challenging journey to bioefficacy. Br J Clin Pharmacol. 2013;75(3):588–602.

[22] Salem SS, Fouda A. Green synthesis of metallic nanoparticles and their prospective biotechnological applications: an overview. Biol Trace Elem Res. 2020. doi: 10.1007/s12011-020-02138-3.

[23] Sheikhiho K, Allahyari S, Sabouri S, Najian Y, Jafarizadeh-Malmiri H. Walnut leaf extract-based green synthesis of selenium nanoparticles via microwave irradiation and their characteristics assessment. Open Agric. 2020;5:1–9.

[24] Tang S, Zheng J. Antibacterial activity of silver nanoparticles: structural effects. Adv Healthc Mater. 2018;7(13):1701503. doi: 10.1002/adhm.201701503.

[25] Theingi M, Tun KT, Aung NN. Preparation, characterization and optical property of LaFeO3 nanoparticles via sol–gel combustion method. Sci Med J. 2019;1(3):151–7.

[26] Vignoli JA, Viegas MC, Bassoli DG, de Toledo Benassi M. Roasting process affects differently the bioactive compounds and the antioxidant activity of arabica and robusta coffees. Food Res Int. 2014;61:279–85.

[27] Wu CC, Chen DH. Facile green synthesis of gold nanoparticles with gum Arabic as a stabilizing agent and reducing agent. Gold Bull. 2010;43(4):234–40.

[28] Yola ML, Eren T, Atar NA. A sensitive molecular imprinted electrochemical sensor based on gold nanoparticles decorated graphene oxide: application to selective determination of tyrosine in milk. Sens Actuators B. 2015;210:149–57.

[29] Zhang XF, Liu ZZ, Shen W, Gurunathan S. Silver nanoparticles: synthesis, characterization, properties, applications, and therapeutic approaches. Int J Mol Sci. 2016;17(9):1534. doi: 10.3390/ijms17091534.