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Green synthesis, characterization and biochemical properties of waste walnut (*Juglans regia* L.) inner shell-based silver nanoparticles

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Abstract: Sustainability is important for future ecology and the increase of waste in recent years negatively affects sustainability. The management of waste and using them in the technology field could be a solution for sustainability. Nanotechnology is a developing technology aiming to improve the physical, chemical and biological properties of matter with the size of 1–100 nm. Nanoparticles could be synthesized by different methods such as physical, biological, and chemical. The green synthesis (biological synthesis) method is the most preferred when compared to chemical and physical methods because it is eco-friendly, energy-saving, cheaper, less waste-producing, easy to scale, sustainable and biologically compatible. Walnut is a versatile fruit with its leaves, dry and green fruit, timber, inner/outer shell and outer peel. Its inner shell and outer peel are not used as food and are waste. In this study, a waste walnut inner shell was used to synthesize silver nanoparticles (WS-AgNPs). WS-AgNPs were synthesized by green technique, characterized and biochemical properties were determined. WS-AgNPs exhibited the maximum absorbance at 460nm with 46–51 nm size and they inhibited urease enzyme by 82.16±1.30 %. It was clear that herbal-based wastes could be used in nanotechnology and have the potential to be used in medicine.

Keywords: waste management; green synthesis; silver nanoparticles; *H. pylori*; antioxidant.

INTRODUCTION

Sustainability is defined as the ability to continue the functions, processes, and productivity of ecology and ecological systems in the future.[1] It has been emphasized in recent studies that the world's resources and the environment are moving toward the limit of depletion as a result of human activities.[1] With the

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increasing population and developing technology, the amount of waste is also increasing due to the variety of materials produced. According to the report published by the Turkish Statistical Institute (TUIK) on December 23, 2021, a total of 104.8 million tons of waste was generated in thermal power plants, manufacturing industry areas, organized industrial zones, mining enterprises, health centres and households throughout. 30 Million tons of this waste was generated in 2020. The total amount of waste was reported nearly 94.9 million tons in 2018 and increased by 10.5 % in 2021 compared to 2018.[2] The amount of waste per capita for Turkey was 1.16 kg per day in 2018. The total amount of processed waste increased by 22 % compared to 2018.[2] Considered from this perspective, sustainability can only be achieved by using the resources provided by nature at a pace that allows them to renew themselves.[1] For this purpose, it is important to develop production processes that use inputs with low environmental impacts, have high efficiency, contain little or zero waste, and do not create pollution. Waste prevention, also known as zero waste, is an approach that includes the most efficient use of resources, reducing the amount of waste generated and recycling waste.[3] It is clearly seen that preventing the increase in the amount of waste or recycling waste is extremely important. Studies should be carried out within the scope of the principles of sustainable cities and communities and responsible production and consumption, which are among the sustainable development goals. One of the important studies carried out within the scope of sustainability is the production of waste-based nanoparticles by green synthesis technique and their introduction into the field of technology.

Nanotechnology is a new technology that allows the processing of particles in sizes between 1–100 nm.[4,5] Nanotechnology is widely used in medicine, dentistry, drug delivery systems, many biomedical applications, the environment and engineering. Silver nanoparticles (AgNP) are important with their properties such as chemical stability, conductivity and catalytic and antibacterial activities. Compared to other elements, silver has a more antimicrobial effect and it is the least toxic element. AgNPs can be synthesized by many different methods such as chemical, biological and physical. The most common is the biological synthesis method, and it is also known as green synthesis. The green synthesis is the most preferred because it is ecologically friendly, energy-saving, cheaper, less waste-producing, easy to scale, sustainable, using no toxic chemicals and has biological compatibility.[5] In addition to the use of bacteria, mould, yeast, algae and plants as a reducing and stabilizing agent, it is not toxic due to the absence of chemicals. Nanoparticles could be synthesized faster than other applications by green synthesis. It is the most preferred method due to its biocompatibility. Silver nanoparticles could be synthesised by the green synthesis technique.[6] The silver nanoparticles are used in antimicrobial application areas, separation of toxic compounds, biosensors, environment and various treatment systems.[7–9] In addition to these, silver nanoparticles have an applications in areas like the prevention of diseases in agriculture, the rapid elimination of existing diseases, increasing the ability of plants to absorb nutrients from the soil in agriculture, antibacterial and odour-repellent textile products, anti-scratch car paints, dirt-repellent coatings, transparent protective sunscreens and self-cleaning glass silver.[4–9]

Walnut is a versatile fruit with its leaves, dry and green fruits, inner membrane and outer shell. Walnut is a widely consumed nut because it contains valuable nutrients and oils. Its fruit could be used as food but its inner membrane and outer shell are waste not used in any application (Fig. 1).

Fig. 1. Inner shell of walnut.

In this study, the waste inner shell of walnut was used as an electron precursor and the potential of employing waste walnut was examined *via* nanotechnology. For this purpose, waste inner shell-based silver nanoparticles were synthesized, characterized and biochemical properties were determined. Thus, the walnut inner shell was used in nanotechnology within the scope of sustainability and evaluated for use in different applications.

EXPERIMENTAL

WS-AgNPs were synthesized according to Keskin (2022) with minor modifications.[10] For this purpose, walnut inner shell extract and 0.05 M silver nitrate ($AgNO_3$) solution were mixed in a dark flask at a 1:1 volume ratio. The mixture was stirred for ~2 h at room temperature. The changes of color to dark brown were noted and confirmation of nanoparticle synthesis was done by UV absorption spectroscopy (Hach, DR/4000U) between 250 and 750 nm. The UV scanning was performed for each 30 min and the maximum absorbance at maximum wavelength of each scan was graphed. At the end of the synthesis, centrifugation was performed for 15 min at 9000 rpm with a high-speed centrifuge device to precipitate AgNPs from the aqueous medium. The resulting AgNPs were washed with distilled water to wash off impurities and dried at 75 °C. Obtained nanoparticles were characterized by scanning electron microscopy (SEM, ZEISS/Supra 40 VP), Fourier transform infrared spectroscopy (FTIR) (Thermo Fisher) and energy dispersive X-ray (EDX).

*Total phenolic content of walnut (*Juglans regia *L.) inner shell extract and WS-AgNPs*

The total phenolic content of natural products could be determined according to the Folin method.[11,12] The phenolic compounds and Folin–Ciocâlteu reagent become a colored complex and give a maximum absorbance at 765 nm. Gallic acid (GA) is usually used as a standard to produce a calibration curve.[11,12] The results are represented in mg of GA equivalent (GAE) per g. The analyses were performed in triplicate.

Antioxidant activity of WS-AgNPs

2,2-Diphenyl-1-picrylhydrazyl (DPPH) radical scavenging activity. DPPH radical is a commercially available radical and a 100 µM methanol solution of this radical was used in the experiments.[13] WS-AgNPs sample solutions were prepared at different concentrations (0.25, 0.5, 1, 1.25 and 1.5 mg mL^{-1}). Equal volumes (750 µL) of DPPH solution and WS-AgNPs sample solutions (different concentrations) were mixed and kept at room temperature for 50 min. At the end of the time, absorbance was recorded at 517 nm where DPPH gives maximum absorbance. These absorbance values were plotted against the corresponding concentrations and SC_{50} values were calculated and expressed against the Trolox standard.[13] The analysis was performed for walnut inner shell extract and all analyses were performed in triplicate.

Iron reduction capacity (FRAP). FRAP method is the most commonly used method for the determination of the antioxidant capacity of natural products and is based on the principle that antioxidant substances in natural products reduce iron (III) ions in Fe(III)–TPTZ complex.[14] Fe(III) reduced by antioxidant substances present in solution gives absorbance at 593 nm. The results were expressed in µM $FeSO_4 \cdot 7H_2O$.

Urease inhibition. Urease (E. C 3.5.1.5) is an enzyme that converts urea to ammonia and carbon dioxide. The formation of urea was determined using the indophenol method.[15] 200 µL Jack Bean urease, 500 µL buffer (100 mM urea, 0.01 M K_2HPO_4, 1 mM EDTA and 0.01 M LiCl, pH 8.2), and 100 µL inner shell extract were incubated for 20 min at room temperature. After incubation, phenol solution (550 µL, 1 % phenol, and 0.005 % sodium nitroprusside) and alkaline mixture (650 µL, 0.5 % sodium hydroxide and 0.1 % NaOCl) were added to the tubes and absorbance were recorded at 625 nm after 50 min. IC_{50} values were determined using standards at different concentrations. The same procedure was performed for WS-AgNPs at different concentrations (0.25, 0.5, 1, 1.25 and 1.5 mg mL^{-1}). All analyses were performed in triplicate.

RESULTS AND DISCUSSION

The population growth and the difficulties in disposing of the increasing amount of waste are catastrophic to the environment and climate conditions. For a sustainable environment, it is important to recycle waste and bring it into the field of technology. Organic solid waste management and ecological worries have been escalating in recent days.[16] Hence, fruit wastes, such as fruit peels, and other organic fractions of domestic solid wastes may be used effectively in nanotechnology-based applications.[17–19] In this study, silver nanoparticles were obtained by green synthesis technique using walnut inner membrane, which is produced in significant amounts in our country and its use is quite limited. Different parts of walnut contain linolelaidic acid, 1-heptatriacotanol, oleamide, ethyl isoalcoholate, hexadecanoic acid, cinnamic acid, brassica sterol acetate and β-sitosterol.[20–23] It was stated that specially walnut inner shell is rich in polysaccharides and polyphenols and contains also fat, protein, amino acids, flavonoids, saponins and alkaloids.[24] The fact that the walnut inner membrane is rich in bioactive components indicates that it may be an important agent in silver nanoparticle synthesis (Fig. 2).

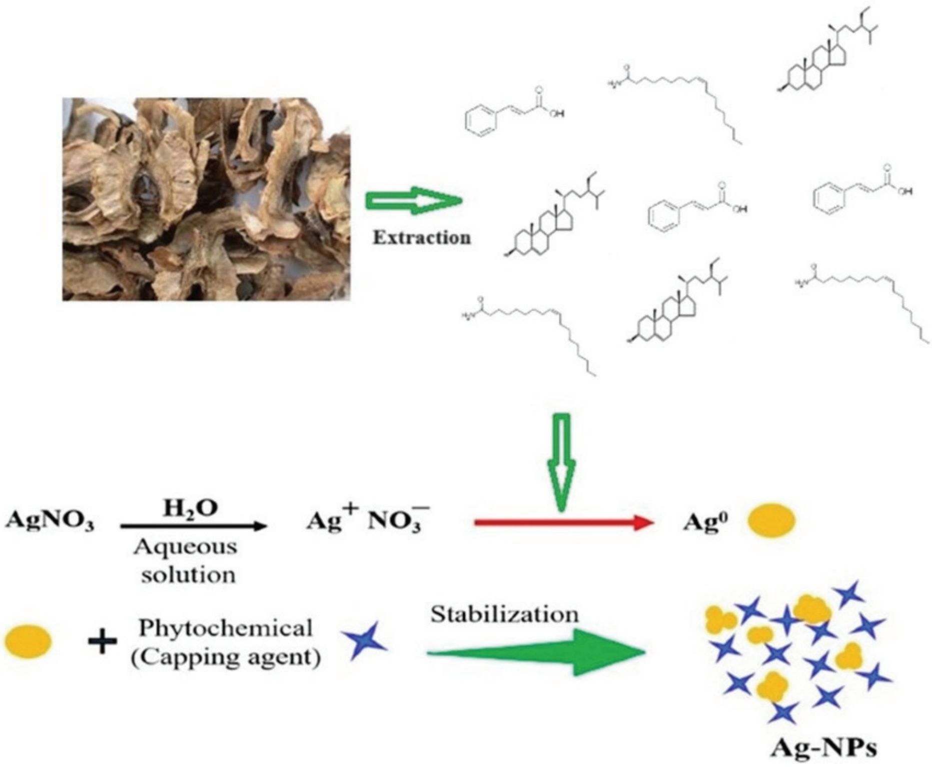

Fig. 2. Potential mechanism of synthesis of WS-AgNPs.[25]

The optical properties of synthesized nanoparticles were determined using a UV–Vis spectrophotometer. It was determined that the obtained nanoparticles gave maximum absorbance at 460 nm (Fig. 3). The reduction of Ag^+ to Ag was defined by intermittently measuring the absorption spectra of the reaction solution using a UV–Vis spectrophotometer. Usually, due to the excitation of free electrons, AgNPs would display a surface plasmon resonance (SPR) band at 450––550 nm,[16] 400–500nm[26] and 430 nm.[27] In the current study, the SPR value of WS-AgNPs was detected at 460 nm. The obtained data in this study is similar to the previously reported AgNPs synthesis result.[16,28–30]

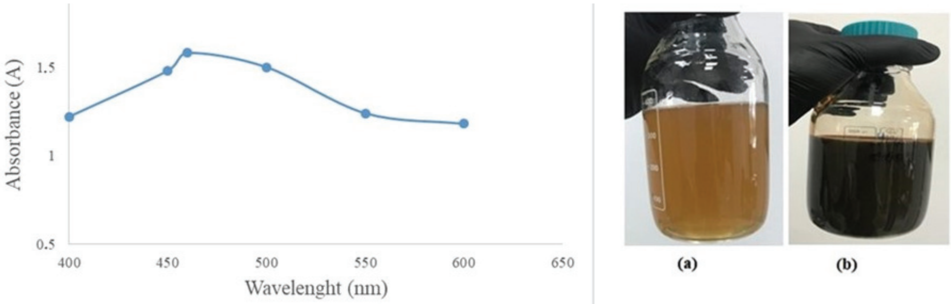

Fig. 3. UV spectrum of WS-AgNPs; a) Walnut inner shell extract; b) WS- AgNPs solution.

Functional groups of walnut inner shell extract and WS-AgNPs supernatant were determined using FT-IR and the results were shown in Figs. 4 and 5, respectively. FTIR data allow us to compare walnut inner shell extract and WS-AgNPs supernatant functional groups to determine possible reactions. As seen in Figs. 4 and 5, there were changes at 2122.54 cm^{-1} band and there was a new band at 1065.98 cm^{-1}. The band at 3200 to 3400 cm^{-1} represents O–H stretching groups.[31] In the study, silver nanoparticles were synthesized from maize (*Zea mays* L.) extract. According to this study, AgNPs had differences at functional groups of 3336.64–3334.57 cm^{-1} O–H bands and there are no differences at 1636.82–1636.48 cm^{-1} C–C bands.[31] It was clear that the functional groups and maximum absorbance of AgNPs vary over a wide range and the results obtained in this study were compatible with the literature.[16,28–31]

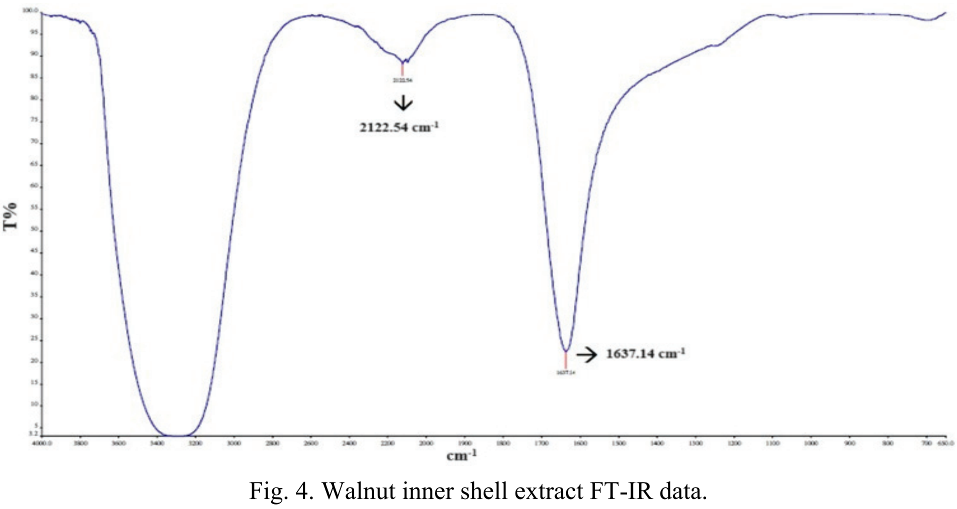

Fig. 4. Walnut inner shell extract FT-IR data.

The size of nanoparticles varied between 46 and 51 nm (Fig. 6). The histogram was obtained by using Fig. 6. In another study, *Tribulus terrestris* based silver nanoparticles were synthesized and particle size was determined in a range between 15 and 65 nm.[32] In the literature, AgNPs were obtained in different sizes such as 14.3–14.7,[29] 16.7,[30] 12.63,[31] 46.26[32] and 65.92.[33] It was seen that particle sizes of silver nanoparticles could be changed in a wide range.[26–33]

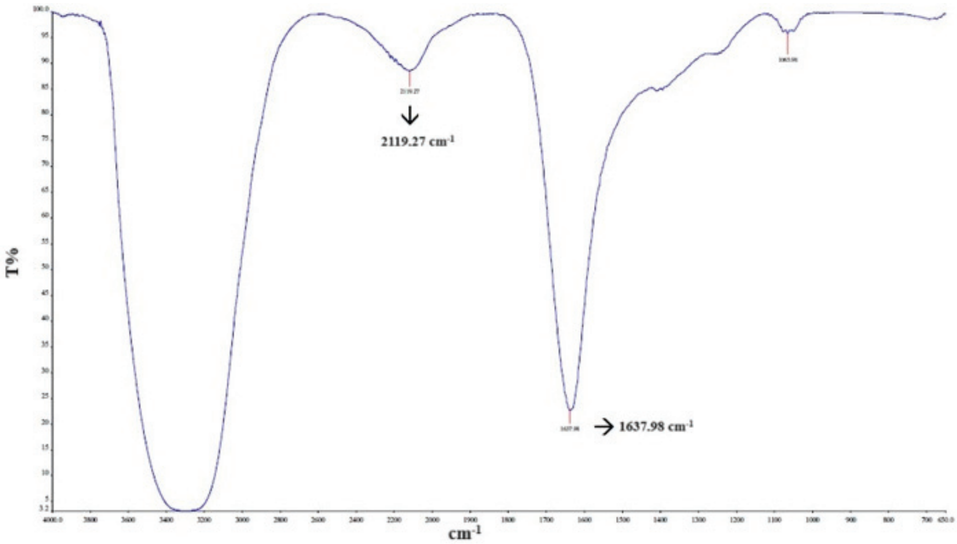

Fig. 5. WS-AgNPs supernatant FT-IR data.

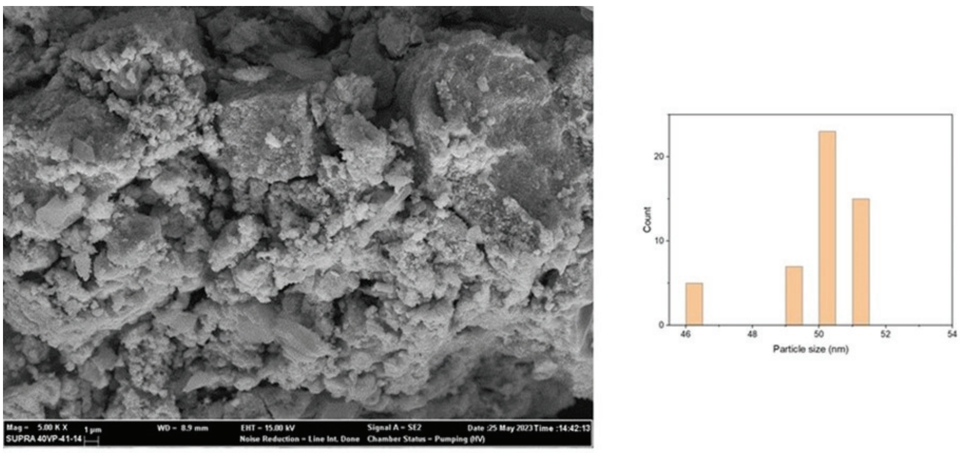

Fig. 6. SEM image and histogram of WS-AgNPs.

The WS-AgNPs had a peak at 3 keV in EDX analyses (Fig. 7). EDX analysis for silver nanoparticles usually shows characteristic peaks in EDX spectra around 3 keV due to surface plasmon resonances with weak carbon, oxygen and nitrogen peaks.[34] In this study, silver nanoparticles showed a strong well-defined signal at 3 keV.

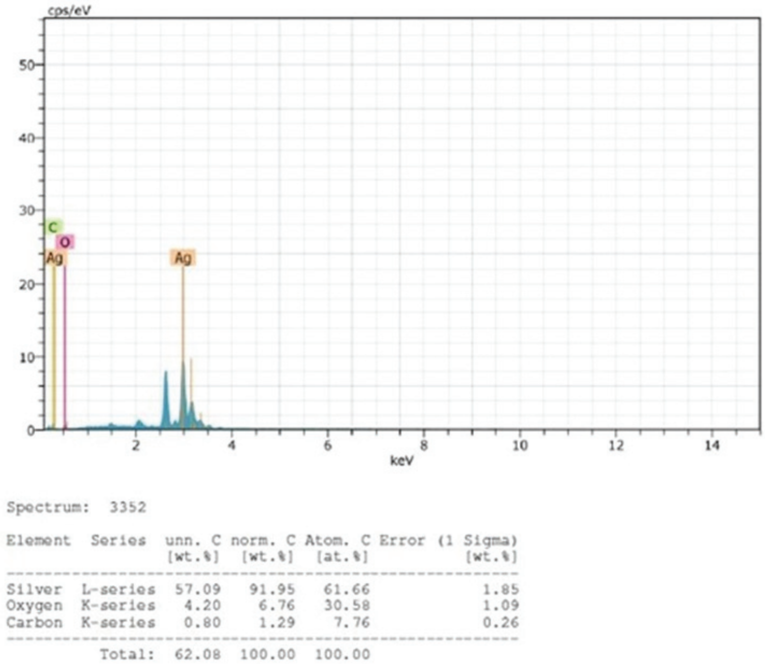

Fig. 7. EDX results of WS-AgNPs.

The total phenolic content of walnut inner shell extract and WS-AgNPs were determined as 21.33±0.18 and 27.63±0.22 mg GAE/g DW and the inhibition effect of urease enzyme was calculated as 52.83±1.19% and 82.16±1.30 %, respectively (Table I). In a study, *Asphodelus aestivus* Brot. aerial part extract-based silver nanoparticles were synthesized and antioxidant activity was determined. It was reported that the AgNPs (67.54 %) had a good inhibition effect according to plant extract (31.82 %) for DPPH.[35] In another study, *Primula vulgaris* based silver nanoparticles were synthesized and the total phenolic content and antioxidant activity of NPs were determined. The antioxidant activity of AgNPs, biosynthesized using *P. vulgaris* flower extract, was found 90.6 %.[36] It was clear that the antioxidant activity and total phenolic content could be changed in a wide range and our results were compatible with the literature.[35–42]

Helicobacter pylori is the most common infectious bacteria affecting almost half of the world's population with diseases such as gastritis, peptic ulcers and gastric cancer. While proton pump inhibitors, antibiotic combinations, and bismuth compounds are used in the first-line treatment of patients infected with *H. pylori* and symptomatic patients, treatment is usually unnecessary in symptom-

-free patients due to the risk of reinfection in a short time.[43] Despite all these treatment options, H. *pylori* infection is still an important health problem due to antibiotic resistance.

TABLE I. Biochemical properties of Walnut inner shell extract and WS-AgNPs

Sample	Total phenolic content mg GAE g^{-1} DW sample	FRAP μM TE g^{-1}	DPPH %	Urease inhibition %
Walnut inner shell extract	21.33±0.18	107.44±2.04	72.71±0.98	52.83±1.19
WS-AgNPs	27.63±0.22	181.12±1.89	85.23±1.02	82.16±1.30

H. *pylori* in order to survive, in the stomach strong acid pH, needs to reach the mucus layer. The flagella and the urease enzyme secreted by the bacterium enable it to reach the mucus layer. The urease enzyme breaks down urea secreted by gastric epithelial cells into ammonia and the ammonia released causes an increase in the pH of the stomach and provides a suitable environment for the bacteria to survive. Therefore, inhibition of the urease enzyme is very important. In this study, the synthesized nanoparticles inhibited the urease enzyme by 82.16±1.30 %. Borase *et al.* synthesized silver nanoparticles based on *Ficus carica* in their study and stated that the extract and silver nanoparticles inhibited ammonium formation by 4.73 % and nearly 80 %, respectively.[44] Amin *et al.* synthesized silver nanoparticles based on *Solanum xanthocarpum* L. and found that the nanoparticles inhibited the urease enzyme by 64 %.[45] Gul *et al.* synthesized silver nanoparticles based on *Ricinus communis* and reported that the nanoparticles inhibited the urease enzyme by 94.2 %.[25] Many studies are showing that silver nanoparticles obtained by using different herbal sources have many effects such as antimicrobial, antioxidant, etc. (Table II). In this study, it was determined that the particles obtained had antioxidant activity and inhibited the urease enzyme.

TABLE II. Synthesis of AgNPs by using different sources

Biological source	UV absorbance, nm	Av. size, nm	Biomedical application	Reference
Honey	443/456	14.3/14.7	Antibacterial activity	29
Aristolochia bracteolata Lam	430	16.7	Antioxidant and antibacterial activities	30
Zea mays L.	461.25	12.63	Antimicrobial activity	31
Tagetes erecta L.	422	46.26	Antioxidant activity	32
Glycosmis mauritiana	435	65.92	Antioxidant activity, antimicrobial activity and enzyme inhibition properties	33
Solanum xanthocarpum L.	406	4 to 18	Antioxidant activity and enzyme inhibition properties	45
Mikania cordata	451	26.8–46.0	Antioxidant and antibacterial activities	46

TABLE II. Continued

Biological source	UV absorb-ance, nm	Av. size, nm	Biomedical application	Reference
Tribulus terrestris	400–450	21–73	Antioxidant activity and enzyme inhibition properties	47
Humulus lupulus L.	450	30.60 to 36.72	Antioxidant activity and enzyme inhibition properties	48
Parsley stem	460	31	Antioxidant activity	49
Citrullus colocynthis	450	10–45	Antioxidant and anti-gout activities	50
This study	460	46–51	Antioxidant activity and enzyme inhibition properties	–

CONCLUSION

Walnut is a widely consumed nut because it contains valuable nutrients and oils. Due to the consumption of walnuts as food, the inner shell of the walnut remains a significant amount of waste along with its phytochemicals. In this study walnut inner shell-based silver nanoparticles were synthesized, characterized and biochemical properties determined. It was shown by this study that herbal-based wastes could be used in nanotechnology for different purposes. The walnut inner shell extract was used as an electron processor to synthesize WS-AgNPs. After detailed characterization, it was determined that WS-AgNPs are a good antioxidant and urease inhibitor. It could be concluded that WS-AgNPs had potential as an antimicrobial agent and could be used in many applications for health benefits.

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ИЗВОД

ЗЕЛЕНА СИНТЕЗА, КАРАКТЕРИЗАЦИЈА И БИОХЕМИЈСКА СВОЈСТВА НАНОЧЕСТИЦА СРЕБРА НА БАЗИ ОТПАДНЕ УНУТРАШЊЕ ЉУСКЕ ОРАХА (*Juglans regia* L.)

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Одрживост је важна за будућу екологију, а пораст отпада последњих година негативно утиче на одрживост. Управљање отпадом и његово коришћење у области технологије могло би да буде решење за одрживост. Нанотехнологија је технологија у развоју, која се примењује за побољшање физичких, хемијских и биолошких својстава материје величине 1–100 nm. Наночестице се могу синтетизовати различитим методама као што су физичке, биолошке и хемијске. Метода зелене синтезе (биолошке синтезе) је најповољнија у поређењу са хемијским и физичким јер је еколошки прихватљива, штедљива, јефтинија, мање ствара отпад, лака за скалирање, одржива и биолошки компатибилна. Орах је воће које има разноврсну употребу, од листова, сувог и зеленог воћа, дрвета, унутрашње/спољне љуске и коре. Његова унутрашња и спољашња љуска се не користе као храна и представљају отпад. У овој студији, отпадна унутрашња љуска ораха коришћена је за синтезу сребрних наночестица (WS-AgNP). WS-AgNP су синтетизоване зеленом техником, окарактерисане и одређена су им биохемијска својства. Честице WS-AgNP величине 46–51 nm су показале максимум апсорпције на 460 nm, и инхибирале су ензим уреазу за 82,16±1,30 %. Очигледно је да се отпад на бази биљака може користити у нанотехнологији и да такође има потенцијал да се користи у медицини.

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