GREEN AGENTS FOR SYNTHESIS OF SILVER NANOPARTICLES THROUGH MULTI- ROUND RECYCLING OF WASTE AS AN ALTERNATIVE TO CHEMICAL METHODS: SYNTHESIS AND CHARACTERIZATIONS

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Abstract
Green nanoparticle (NP) synthesis is a novel area of nanotechnology that succeeds in terms of biocompatibility, scalability, cost-effectiveness, and environmental friendliness. Due to the widespread of metal nanoparticles in industrial scale applications, green and efficient process that are required free toxic solvent is being emphasized. Plants have lately been used to produce metal nanoparticles as an alternative approach that apply extracts made from as reducing and capping agent. Due to their excellent properties, silver nanoparticles have been widely used for several applications, including as antibacterial agents, in industrial, household, and healthcare-related products, in consumer products, medical device coatings, optical sensors, and cosmetics. Regarding this, the purpose of our research firstly was to find out whether the green martials Turkish coffee (TC) and Virginia Creeper (VC) extracted and used for synthesis of silver nanoparticles (Ag NPs) could be recycled for further NP synthesis. Another objective was to compare Ag NPs morphology synthesized by biological reagent to chemical reagents as sodium borohydride ($NaBH_4$) as reductant, and sodium citrate and Polyvinyl-Pyrrolidone (PVP) 55k as the stabilizing agents by conventional method. The characteristics of the Ag NPs was confirmed by transmission electron microscopy (TEM), U.V spectroscopy and dynamic light scattering (DLS) measurements.

Introduction
Nowadays, nanotechnology plays a crucial role in various industries, including electronics, chemicals, biotechnology, bioanalytics, and others. (1). Scientists formed a novel area known as "green nanotechnology" via linking the concept of sustainability with nanotechnology. Green improvement took birth out of the repeated thought method and act plans of researchers. Plants and its counterparts are comprehensively used in synthesis of nanoparticles (2). Additional when technology advanced the green route of synthesis was selected for replacing non-ecofriendly by yields with eco-friendly ones. This greener route employs biotic entities of the environment as its incredible ingredient by altering the traditional ingredients in physical and chemical methods of synthesis (3). Metal nanoparticles have been used extensively in current research, between the diverse metal nanoparticles, Ag NPs further have been paid attention throughout the past few years because of their prospective. The modern studies for the preparation of silver nanoparticles with a controlled size will be valuable in numerous approaches such as: chemical reduction of silver ions commonly in the presence of stabilizing agents (4). It is noteworthy that this method and the most of the chemical methods have possible hazards to health and environment. Nonetheless by reduction potential of plant extract, we could be able to reduce the metal ions. Therefore, the potential of plants as biological materials for the synthesis of nanoparticles still should be explored like the mechanism of reduction which is not well described in the articles, their process conditions and concentration of both reducing agent and main precursors. Green synthesis of NPs by means of plants extract has numerous rewards above chemical synthesis, such as easiness, cost effectiveness as well as compatibility

for biomedical and pharmaceutical applications (5). Thus, the present study focused on the green materials (TC and VC) extracted and used for the synthesis of nanoparticles, the major key was through the multi-round recycling for further NP synthesis. This study aims to compare the chemical properties of green Ag NPs with those synthesized using chemical reagents, providing a explore a clean, sustainable, direct alternative to chemical approach for Ag NPs synthesis.

Experimental

Preparation of plant extracts in multiple rounds. The selected plant extracts were prepared according to earlier described procedures (6,7) with some modifications. Virginia Creeper (VC) leaves were collected locally (Szeged, Hungary) in September 2023. The leaves washed by deionized water to remove any surface dust and dried at room temperature until achieving constant weight. Afterward, the VC leaves were cut to small pieces. For the duration of first-round extraction, the extracts were prepared by using 5 g of VC small pieces leaves in 100 mL of deionized water set up temperature to 70 °C for 30 min, and then the extracts were paper- and vacuum-filtered to remove residual plant particles. The extracts were stored at fridge for somedays before used for NPs synthesis. A similar procedure was working for coffee (TC) extracts, except that purchased powder coffee (Hazer Babe, Turkish coffee) were boiled directly without any pretreatment. After the first-round extractions remaining plant materials (used upon the first extraction, left behind as "waste") were air-dried and recycled two further times to gain individual extracts each time (second- and third-round extractions). In these multiple rounds, the extraction technique was undistinguishable as described above for first-round extractions. The extracts formed were labeled according to the name of the plant extract and the order number of the extraction round, namely TC1, TC2, and TC3 for coffee and VC1, VC2, and VC3 of Virginia Creeper extractions, respectively. These extracts were all stored in fridge, then applied separately for Silver nanoparticle (Ag NPs) synthesis as reducing and capping agents. Synthesis of AgNPs, TC-Ag- and VC-Ag – labeled green Ag nanoparticles were synthesized by adding the corresponding extracts (of the first-, second-, and third-round extractions: TC1, TC2, TC3 and VC1, VC2, VC3, respectively) added to 0.002 mole/L aqueous of $AgNO_3$ solution 1:1 volume ratio at 75 °C , PH 7 by continuous stirring for 1h . Then the prepared Ag nanoparticles cooled down and kept in fridge for later use. Whereas chemical reagents citrate and PVP Ag NPs where synthesized by the seed-mediated growth conventional approach (8,9). The method is based on chemical reduction using silver nitrate ($AgNO_3$) as a silver source, sodium borohydride ($NaBH_4$) as reductant, and sodium citrate and polyvinyl-pyrrolidone (PVP) 55k as the stabilizing agents.

Results and discussion

Consideration of the suitability of the plant extracts obtained in several recycling rounds to form Silver nanoparticles (Ag NPs). Following the procedure described earlier (6,7) we achieved Ag NPs synthesis with the benefit of each extract obtained in the multiple round of extraction. Our primary objective was to assess the appropriateness and recyclability of green household waste materials for the generation of Ag NPs and to determine which green material provides sufficient quantities and quality of key components after successive extraction steps to produce AgNPs. During the reaction when certain aqueous green extracts were added to the reaction mixture, while the continuous of reduction of silver ion and constant of growth of Ag nanoparticles, we observed a color change. UV–Vis Spectroscopy was used to measure the localized surface plasmon resonance, The UV spectrum is shown specific peaks in (400 to 450 nm) region for synthesized Ag NPs by various reagents that confirmed the present of silver nanoparticles (Figure 1). Dynamic light scattering (DLS) was used to determine the size

distribution (d.nm) (Figure 2). The hydrodynamic size was around 6nm for PVP and 18 nm for citrate whereas for green reagents 19nm for TC and 30 nm for VC.

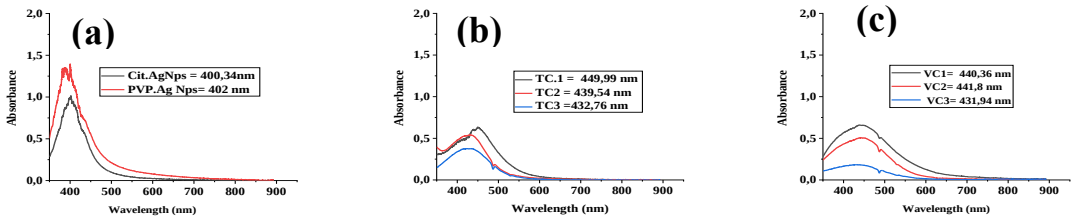

Figure 1. UV-vis absorption spectra of chemical approaches PVP and Citrate AgNPs (a), and green synthesized AgNPs prepared by coffee (TC1,2 and 3) (b) and (c) for VC (1,2 and 3).

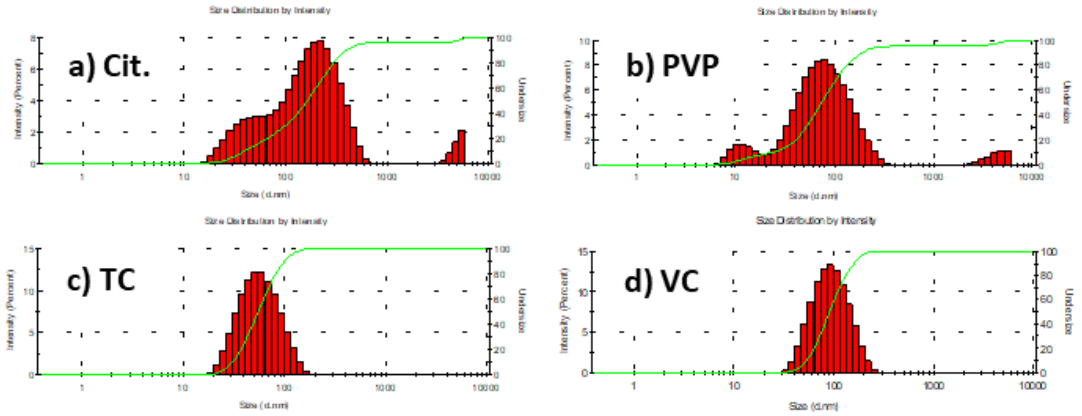

Figure 2. Size distribution (d.nm) Citrate-SB Ag Nps (a) PVP -SB Ag Nps (b) and (c) is TC- Ag Nps and (d) is VC-Ag Nps .

TEM measurements were employed to ascertain the size and morphological characteristics of the obtained Ag NP samples. According to these images (Figure 3) Ag NPs synthesis was successful with chemical reagent as well as green reagents applied. The shape (spherical) of Ag NPs produced by green synthesis was similar to chemical ones. The size of AgNPs by green synthesis appeared larger compared to (SB) Ag NPs as around 5 nm.

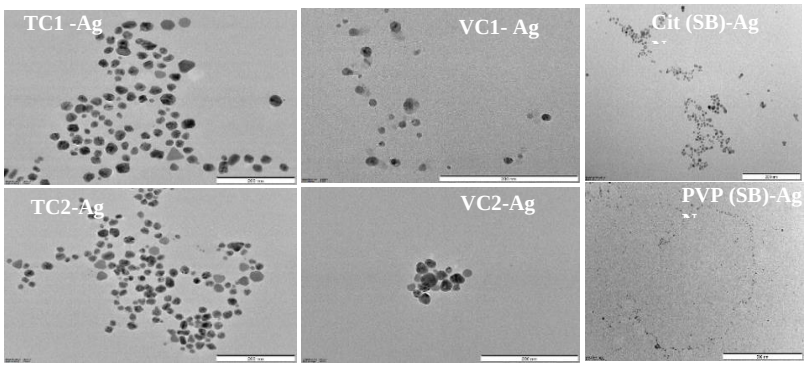

Figure 3. TEM images of silver nanoparticles produced by using various green waste extracts obtained in round extraction of Turkish Coffee (TC1-Ag, TC2-Ag), Virginia Creeper (VC1-Ag, VC2-Ag) compared to chemical reagent sodium borohydride (SB-Ag).

Conclusion

In the last decade, the green production of nanoparticles had been a major ground of research. Nowadays, one of the most basic needs to the field of nano is its compatibility with environment. In this regard, this work focused on investigation of the multiple applicability such as recyclability of (coffee and Virginia Creeper) waste extraction for green Ag NP synthesis and compare the synthesized particles to the conventional produced Ag NPs (SB-Citrate and PVP). All green extracts obtained from first to third round extraction samples of TC, VC were found to be adequate for Ag NPs synthesis, although TC extracts appeared to be better compare to VC extracts. These outcomes show that the well-selected green waste materials can be reprocessed in multiple rounds for nanoparticles synthesis.

Acknowledgements

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