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Ecofriendly Route for Waste Upcycling and Silver Nanoparticles Synthesis from *Citrus reticulata* Peel

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ABSTRACT

In this work, green biosynthesis and upcycling waste were combined for silver nanoparticles (AgNP's) production from citrus reticulata peels as a new natural factories by bottom-up approaches, it was accomplished using a hot aqueous extract of citrus reticulata peels as a rapid, one-step, safe, economically and ecofriendly route. This work proved the capability of plant mediated s'AgNP *production firstly by color change of the extract after two hours, then the well dispersed spherical* s'AgNP *production with size 27 nm was proved by using techniques;ultra violet-visiable spectroscopy (UV-vis), X-ray diffraction (XRD) and scanning electronic microscope (SEM) coupled with energy dispersion x-ray (EDX).*

Keywords: Silver Nanoparticles, *Citrus Reticulata*, Green Biosynthesis, Upcycling Waste.

1. INTRODUCTION

With increasing the need to recycle and reuse biomaterials, the efforts was rising to recycle material waste and push ahead with the green revolution [1]. Recently, the application of the nanomaterials has created the new research area of nanobiotechnology, which plays a fundamental role in disease diagnosis, agriculture, drug delivery, biosensing and bioimaging devices [2,3]. The manufacturing of metallic nanoparticles via a varied biological methods have been recently practiced as an alternate bottom up method to form a nanometre scale particles [4]. The production of s'AgNP have presently been established although usage of silver is as old as human being development. They have been specially used in health care, agronomy, biotechnology and as antioxidants and antimicrobial agent irrespective of the method of their synthesis [5]. Among all the metallic nanoparticles, s'AgNP are attractive in the nanotechnology field because of their distinctive properties like: catalytic, chemical constancy, antimicrobial in addition to to anti-inflammatory actions which be able to linked into composite fibers, cosmetic products and food industry [6]. The preparation of s'AgNP is uncomplicated, also their size is controlable, and they can be merged into different materials effortlessly [7]. The physical and chemical techniques for s'AgNP synthesis are often discouraged as they include the use of dangerous and toxic solvents [8]. Thus, in last few decades, the biosynthesis of nanoparticles through biological routes such as plant extracts or microorganisms acquired much attentiveness in nanotechnology[9]. Hence, medicinal plants taking a traditional therapeutic importance that commonly used for synthesis of nano silvers with particular shape and size [10]. Now, it is capable to manufacture the materials through green chemistry based techniques by incorporates nanotechnology and biology to create a novel area of nanobiotechnology by using a plants in a many of biophysical and biochemical methods [11].

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Recently, there is a need to search for new methods for the development nanoparticles, so, in this study, mandarine (*Citrus reticulata*) peel waste was utilized for the first time as a source of an extract for AgNP's synthesis which appear low cost, one step, enviroment-friendly and alternate procedure for common methods, then the AgNP's synthesis were approved by various chemical and physical methods such as color changing, UV-visible spectroscopy, energy dispersion x-ray diffraction (EDX), x-ray diffraction (XRD) and scanning electronic microscope (SEM). This work suggests the possibility to convert useless low-priced fruit waste into innovative nanomaterial with high product value.

2. MATERIAL AND METHODS

2.1 The Extract Preparation

In this experiment, clean and free of disease mandarine peels was collected from a local juice center, Baghdad, Iraq, then brought to the laboratory in polythene covers and cleaned thoroughly using distilled water and running water for one hour to remove any particles may be adhering of peel. Each ten gram of peel was cut into smaller pieces macerated in 100 ml of boiled distilled water with stirring vigorously for thirty minutes to get aqueous peel extract. This aqueous solution was then filtrated through Whatman's filter paper 0.45µM for further purification, 100 ml of silver nitrate ($AgNO_3$, Sigma–Aldrich) was prepared and H_2O was the solvent [12].

2.2. Synthesis Techniques of AgNP's

The bottom-up approach was used to synthesize the AgNP's, 10 ml of mandarine peel extract added dropwise to 30 ml of one millimolar solution of $AgNO_3$ and stirrer the solution well under dark condition, quickly the solution color has changed which suggests the reduction was complete in two hours at room temperature [13] with the development of yellowish brown which approves of AgNP's synthesis, figure (1). The resulted AgNP's were additional analyzed by using UV-Vis, XRD, SEM as well as EDX.

2.2 Characterization Techniques

2.3.1 Preliminary Color Observation

The color change in the mixture was noted by visual examination. The yellowish solution was turned to yellowish brown indicated that the AgNP's were produced.

2.3.2 UV Spectroscopy

The absorption spectra of the AgNP's were studied using UV-vis 1700 (Shimadzu, Japan) at room temperature. The range for the samples analysis was 300–800 nanometer at a scan speed of 300 nm/min with a resolution of 1 nm, all samples were dilute previously with distilled water.

2.3.3 XRD Analysis

X-ray diffraction is a general method which has been used for the molecular and crystal nature analysis, a thin film of sample was smeared on the glass slide by droped 100 µL of the sample with dry for half an hour. The intensity data for the powdered sample were assembled over a 2θ range of 10°–80°.

2.3.4 Transmission Electron Microscope (SEM) Analysis

To get knowledge about topography and sub-structure of the AgNP's, a newly made sample was dropped on thin metal surfaces with air dehydrated and clean environment and the resultant flat surfaces of AgNP's powder were further analysised by SEM coupled with EDX.

3. RESULTS AND DISCUSSION

The aqueous extract of *C. reticulata* peels was prepared for AgNP's biosynthesis by silver ions reduction that firstly diagnosed by the color change from yellow to yellowish brown when *C. reticulata* extract was added into $AgNO_3$ solution The color formation occurred within 20 minutes, Figure (1,2).

Figure 1. Preparation of hot extract of *citrus reticulata* from peels wastes.

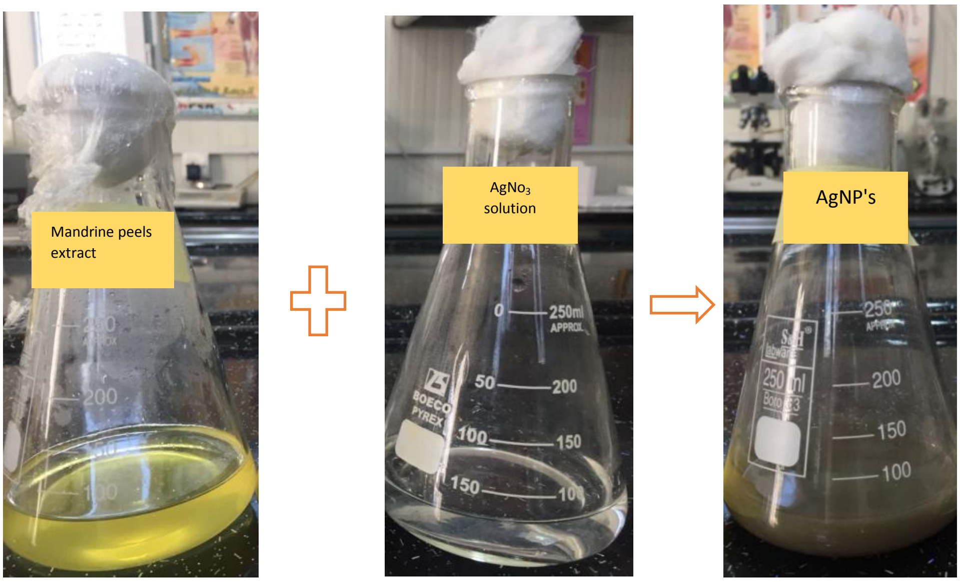

Figure 2. Color change as indication of AgNP's production of *C. reticulata* when add AgNO3 solution.

This color change was because of the free electrons excitation in nanosilver particles [14] which produces absorption band of the surface plasmon resonance (SPR) by the merged electrons vibration of AgNPs in resonance in light wave [15]. The transformation of the solutions color also may be as a result of some chemical compound like: flavonoids, alkaloids, steroids that acts as a reducing agent that reduced Ag^{+} to Ag^{0}. Metallic nanoparticles shows different colors in solution due to their optical properties [16].

Citrus aqueous extract is composed of a variety of compounds such as: flavonoids, triterpenoids, phenolic acid and thiamine, also it was rich in ascorbic acid and citric acid may responsible for metal ions reduction that efficient for biosynthesized AgNP's [17]. The unique optical features of nanoparticles may related to the surface plasmon resonance depending on the size, shape and refrective index for the nanoparticles. When *C. reticulata* aqueous extract added to $AgNO_3$ solution caused the solution color change due to surface plasmon excitation of the $AgNO_3$ which indicating the nanoparticles formation in the solution and produced a peak placed about at 340 nm after examination by UV-Vis, figure (3).

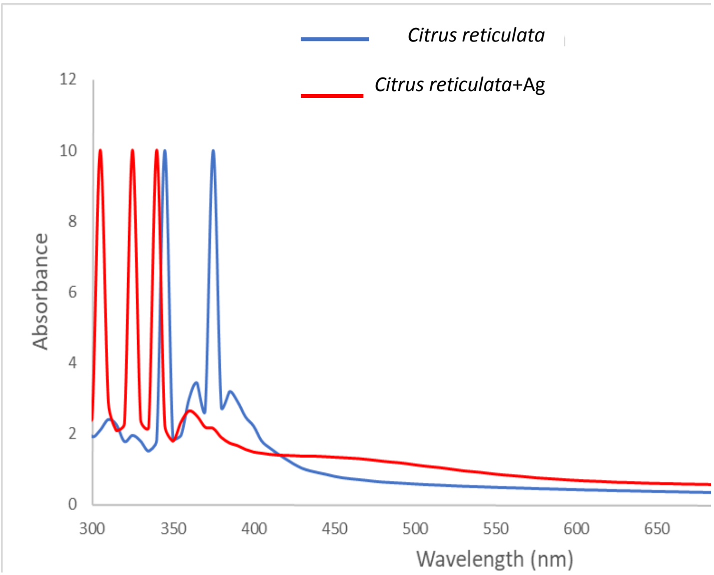

Figure 3. UV-vis spectra of Gaps formation.

Furthermore, it was noted that the silver ions were reduced into silver atom rapidly. In general, many of studies were stated the wavelength range of AgNPs absorption peak is in (300-360) nanometer [18]. In this study, AgNP's solution showed absorbance peak near at 340 nm as illustrated in figure (3), as a rule, increasing the nanoparticle size will produce a sensible broadening of the plasmonic band towards larger wavelengths.

The XRD investigation of biosynthesized AgNP's by *C. reticulata* peel aqueous extract was achieved to observe the structure and crystalline character of Ag nanoparticles, . Figure (4) showed the diffraction peaks at 2 theta value of 30.0°, 38.13° and 38.6°, which correspond to crystal facets of (121), (202), (223).

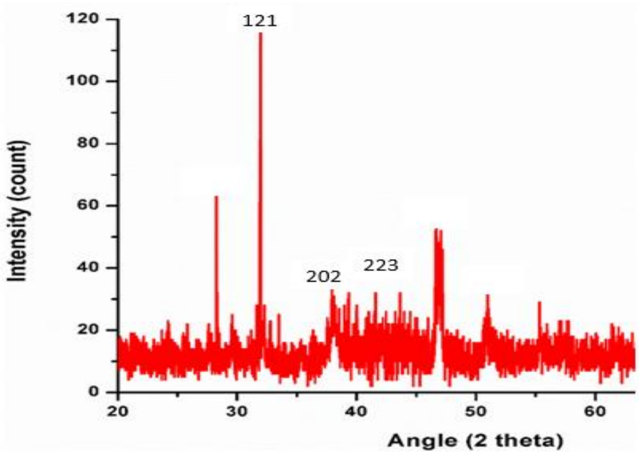

Figure 4. XRD Spectra of biosynthesized AgNP's.

The spectrum showed three distinct separate peaks at 2 theta that could be indexed to reflection planes of face centered cubic structure of silver respectively. The spectrum of XRD apparently displays that the AgNP's produced by a biological route using *C. reticulata* extract by reduction process are crystalline in character.

Average size of AgNP's from XRD data was 26.76 nm which estimated by Debye Scherrer's formula [16]:

$D= 0.9 \lambda / \beta Cos\theta$

Where 'D' represent silver nanoparticles crystal size, β represent the full width half maximum (FWHM) of diffraction peaks, θ represent the Bragg diffraction angle and λ represent the wavelength of CuKα and it was 0.15406 nm.
The occurrence of Ag atoms in the AgNP's was further approved by EDX technique, figure (5), EDX profile presented strong signal for silver next to carbon with faint oxygen peak which may have created from the biomolecules that are attached to the exterior of AgNP's, signifying the reduction of silver ions to elemental silver. The optical absorption peak was observed at energy between 0.3 and 3 keV, which is representative for silver nanocrystallite absorption as described in many researches due to surface plasmon resonance [19].

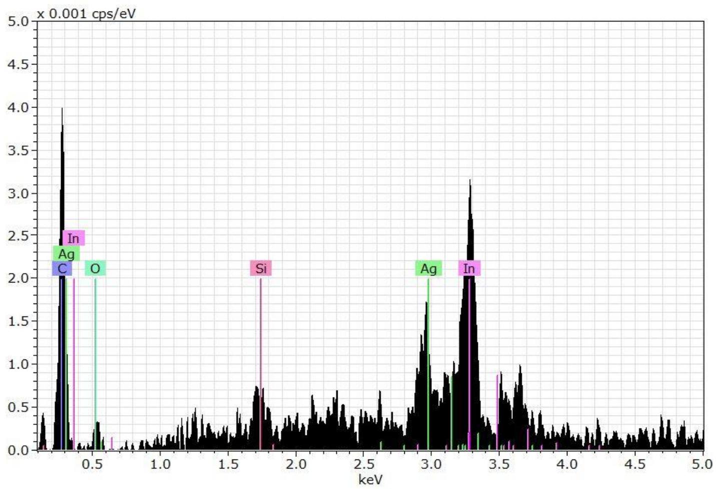

Figure 5. EDX spectroscopy of biosynthesized silver nanoparticles by *citrus reticulata* peel extract.

SEM image confirm that the biosynthesized AgNP's was spherical in shape with size of roughly 27 nm as proved by XRD analysis, figure (6).

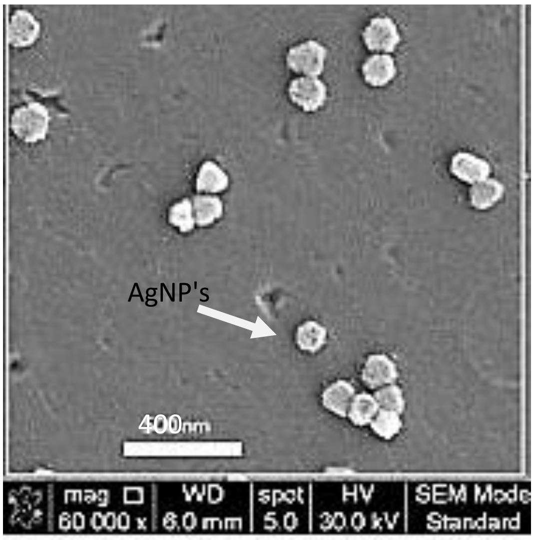

Figure 6. SEM image of silver nanoparticles synthesized using *Citrus reticulate.*

4. CONCLUSION

Green biosynthesis of nanoparticle is a broadly applicable technology for fast production of metallic nanomateriales using the most common tree in nature *C.reticulata* peels waste aqueous extract that offers an effortless, clean, safe and robust technique that does not require any special preparation that are usually required for microorganisms based techniques. This green chemistry method of using biological entities is in extreme difference with traditional chemical and physical procedures that often use toxic solvents and materiales that was hazardous and carcinogenic. Additionally, this method scaled up to progress an applied technology for the nano silver production and waste upcycling.

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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