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Silver Nanoparticles Synthesized by Orange Peel Extract

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Abstract
The current work is presenting the biosynthesis of silver nanoparticles, using $AgNO_3$ as a precursor and orange peel extract as reducer and stabilizer agent. The research structure is based on the synthesis process, from extract preparation, precursor, to final colloidal solutions. The samples were prepared in a ratio of 9:1, precursor to plant extract. The first signs of successful synthesis appeared in about 30 minutes, when the formation of nanoparticles was assigned to a change in colour, from pale yellow to brown. After the synthesis steps, the obtained samples were characterized by UV-Vis spectrophotometry. This analysis has indicated an absorbance peak with highest intensity around 420 nm wavelength. This is matching with surface plasmon resonance of silver nanoparticles, being the first step in proving that silver nanoparticles were formed in the colloidal solution. The removal of toxic elements from the synthesis stages opens new opportunities for the use of particles, there these are intended to be used in medicine and water treatment, afterwards testing antimicrobial and photocatalysis potential. Moreover, this method of obtaining nano-scale particles is an efficient and economical one.

Keywords
silver nanoparticles, orange peel extract, green synthesis

1. Introduction

Many fields have developed in recent years due to the increased interest in nanotechnology research. This has led to the design of new materials, at the nanometric scale, using different methods, from physical, chemical to biological. The last category caused a greater demand for the use of nanomaterials, in the fields of medicine, catalysis, bioengineering and pharmaceuticals [1]. Green synthesis makes nanoparticles suitable for biomedical applications and other fields where special attention to environmental and health impact is required [1, 2].

Plant extracts have been targeted a lot recently for the green synthesis of nanoparticles because it is an economical, non-invasive, and environmentally friendly method [2]. These approaches offer a sustainable alternative to traditional nanoparticle synthesis methods, which can often involve toxic chemicals or energy-consuming processes [3]. The biological elements are used as reducing and capping agents, due to their compounds, such as, proteins, carbohydrates, alkaloids, tannins, phenolics, oils and saponins [4]. Plant extracts have helped in the synthesis processes for different types of metal nanoparticles, from noble metal (palladium, silver, platinum, gold) nanoparticles to those based on iron [1, 5]. It has been reported that some of the nanomaterials of particular importance in human life are silver nanoparticles, especially since they are obtained by green methods, having the potential to be biocompatible and less toxic compared to those synthesized by traditional chemical methods [6].

There is a large amount of research reported on the synthesis of silver nanoparticles using plant extracts. An even larger number refers to the plants used. Among the most common studies are those that use *Aloe vera*, *Ficus*, *Cactus* extracts and so on [7-10]. Silver nanoparticles are acknowledged for their antimicrobial properties and have been used in a variety of applications in this regard. Silver has antibacterial and antifungal properties, and when it is reduced to nanoparticle sizes, these properties become even more noticeable. On the strength of the great antimicrobial potential, silver nanoparticles are used from antimicrobial bandages to implantable devices [7-11]. In addition to green synthesis using plant extracts, researchers also tend to use microorganisms to reduce metal ions to nanoparticles. In a previously work paper, the obtaining of silver nanoparticles, using microorganisms from the *Bacillus* species was achieved. The obtained particles were later used in antimicrobial assay, against a considerable number of microorganisms [5].

This work aimed to present a green method for the synthesis of silver nanoparticles by using orange peel extract as is shown in the schematic representation from Figure 1. The samples have been characterized by UV-visible spectroscopy and will be further assayed both structurally and morphologically using analysis methods such as X-ray diffraction and electron microscopy.

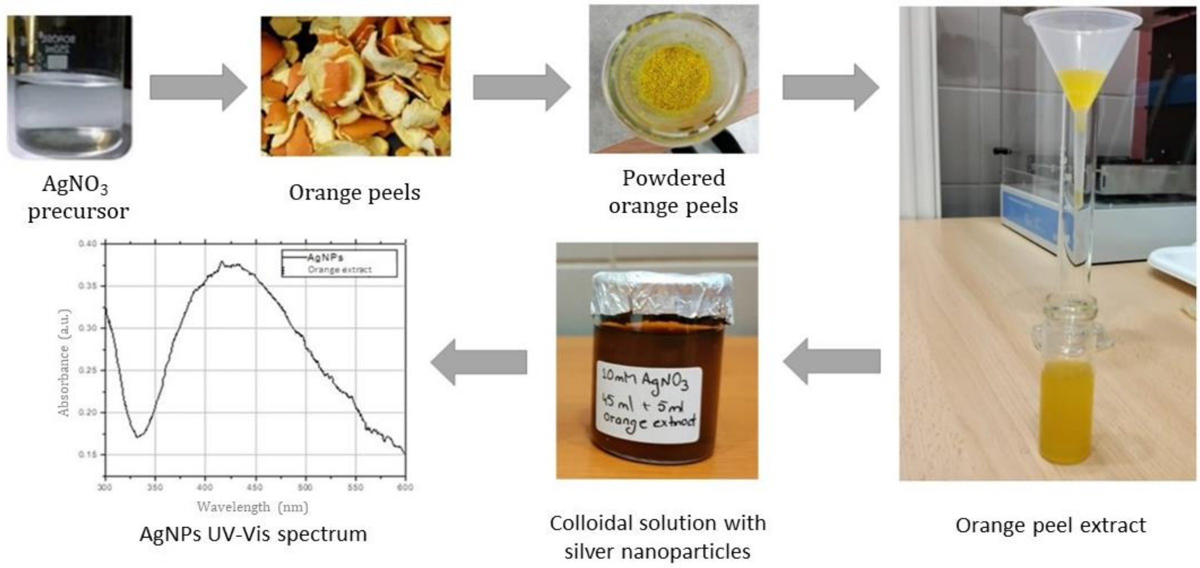

Fig. 1. Schematic presentation of research design

2. Materials and Methods

2.1. Preparation of orange peels extract

Freshly harvested oranges fruits, from season October 2023, were provided from a local hypermarket. The removal of solid particles from the surface of the orange fruits was achieved using distilled water. The oranges were peeled, and the peels were left in oven to dry at 60 °C. After they dried, the peels were shredded in a blender. The dried orange peels were weighed, and 20 grams were used, over which 300 ml of distilled water were added. The solution was kept at 90 °C in the oven until it reached a volume of 100 ml. After the mixture cooled down, it was filtered to separate the extract from the orange peels. The extract was filtered twice, the first time with the help of a filter paper with a grain size of 100 µm and the second time the filtration was done with the help of a Whatman paper of 47 mm in diameter and with a pore size of 1.6 µm.

2.2. Precursor solution

In the case of this research, the precursor used to obtain silver nanoparticles was silver nitrate. The aqueous precursor was prepared in a concentration of 10 mM, using $AgNO_3$, purchased from Scharlau, 99% purity and distilled- sterile water.

2.3. Synthesis process of nanoparticles

The orange peel extract, which contains active compounds, was added to a solution containing silver nitrate. The sample preparation ratio extract to precursor was 1:9. The compounds in the extract act as reducing agents, causing the silver ions to be reduced to the silver nanoparticle stage. The prepared samples were kept for 30 minutes, in an incubator with orbital shaking, at 100 rpm, at ambient temperature, to ensure a faster reduction of metal ions. All experiments were carried out in triplicates and representative data is presented here.

2.4. UV-Vis spectroscopy characterization

Ultraviolet-visible absorption spectra were recorded using a Halo XB-10 absorption spectrophotometer in the 300-600 nm range (using quartz cuvettes as sample supports) at 2 nm intervals. The material samples were taken after obtaining the final product. Double-distilled water and orange peel extract were used as a control sample.

3. Results and Discussions

3.1. The orange peel extract

Orange peel extract was prepared similar in certain points to method presented by Leela Joshi [11]. Fruits provided from local hypermarket, were thoroughly washed with distilled water, eliminating any pesticide residues or other impurities. The peels were dried at 60 °C (Figure 2a,) and then shredded in a blender until it was obtained a powder (Figure 2b). The powder was immersed in 300 ml distilled water (Figure 2c) and kept in the oven at 90 °C until the final volume of the solution was reached 100 ml. After cooling the solution was filtered and the supernatant was saved for further use.

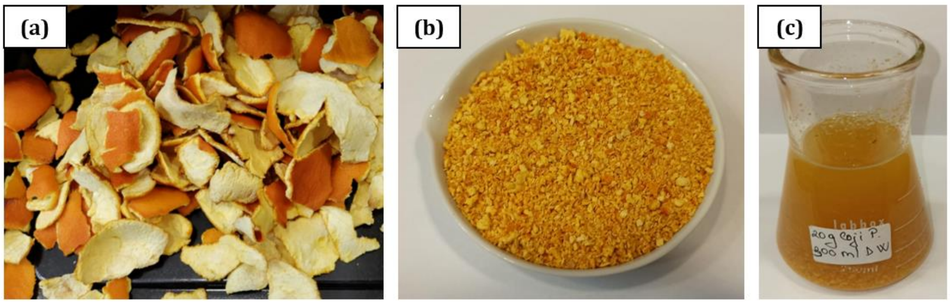

Fig. 2. Preparation of orange peels extract

The speciality literature presents research on obtaining silver nanoparticles using even banana peel extracts. This synthesis may be due to reducing agents which may be polysaccharides, phenolic compounds, alkaloids, triterpenoids. Some parameters of this synthesis technique must be controlled in terms of uniformity in size and dispersion to avoid agglomeration and sedimentation in solutions. As it is presented, the samples have presented some agglomeration, after 15 days [12]. Among the most important parameters that can influence the results, are given by the concentration of the reagents, of the plant extract, respectively of the metal salts. Besides these, the quantitative ratio between the plant extract and the metal salts, the pH of the solution, the reaction temperature and time are also influential.

3.2. Silver nitrate as precursor

$AgNO_3$ was used to prepare the precursor. The required mass of silver nitrate was calculated to obtain 10 mM in a volume of 400 ml of distilled water, after which the exact amount was measured using an analytical balance. The solution was quickly homogenized using a magnetic stirrer. This was subsequently used for green synthesis.

Even if $AgNO_3$ is one of the precursors most often used in the green synthesis of silver nanoparticles, other precursors were also used, chosen according to the specific purpose and the requirements of the final application of nanoparticles.

Besides, silver nanoparticles biosynthesis was reported by using the precursor AgCl for different equimolar concentrations (0.1–0.5 mol/L), with the reducing agent vitamin C [13]. Likewise, in a remarkable study, the manufacture of silver nanoparticles was investigated using (bis)amine-silver carboxylate complex as precursor. It was indicated the significance of amine ligands during the nucleation and stabilization of the final silver nanocrystals [7].

3.3. Colloidal samples

AgNPs were successfully synthesized by mixing the orange peel extract and $AgNO_3$ in 1:9 ratio, under constant and moderate stirring, at 100 rpm, by using the orbital shaker. The initial colour of the sample mixture was pale yellow, towards colourless, the proportion of silver precursor predominating, after which approximately 30 minutes the colour of the samples changed (Figure 3). The colloidal solutions acquired a brownish hue, this being a first indication of the formation of silver nanoparticles.

Hemlata and his co-authors have used aqueous leaf extract of *Cucumis prophetarum*, from *Cucurbitaceae* family, to mediate the synthesis of silver nanoparticles. From the phytochemical screening of the extract, it can be observed that there have been identified several constituents that can be responsible for this reduction of silver ions, such as, tannis, alkaloids, triterpenoids, phenol, saponins.

The average hydrodynamic particle size distribution according to dynamic light scattering analysis was approximately 94 nm, while particles measured using electronic microscopy, fell into smaller size ranges, as expected. The applications proposed for the obtained particles fit very well in medicine, due to its antiproliferative potential on different human cancer cell lines [3]. Bunghez et al. stated the potential ability of *Hyacinthus orientalis L.* and *Dianthus caryophyllus L.* in reduction of metal ions. They have used as precursors silver salt, Ag^+ being reduced to Ag^0 during synthesis process. The nanoparticles obtained were found to have average sizes between 61.45 and 89.6 nm. Moreover, a comparison was reported regarding the antioxidant potential of the obtained nanoparticles and that of the plant extracts used. It was shown that the results were favourable for research involving nanoparticles [14].

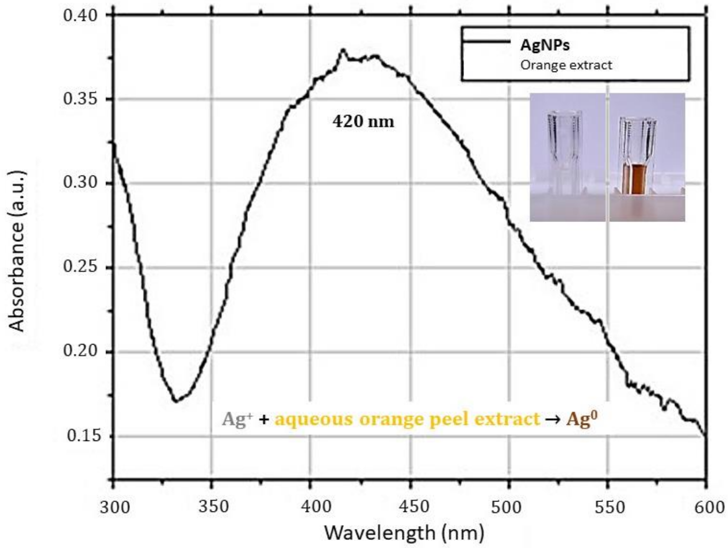

Fig. 3. UV- VIS absorption spectra for colloidal solution of silver nanoparticles

3.4. UV–Vis spectral analysis

Generally, silver nanoparticles exhibit strong absorption in the UV-Vis region due to the surface plasma resonance phenomenon. The most common wavelengths for silver nanoparticles are in the UV spectrum and the so-called "surface plasmon absorption band" can be observed. UV-VIS absorption spectroscopy allowed the identification of the presence of silver nanoparticles in colloidal solution. This mostly occurs in the 380 nm - 450 nm range for small spherical silver nanoparticles.

The Surface Plasmon Resonance peak for the synthesized AgNPs was observed around 420 nm (Figure 3). The results showed through spectrum highlighted the suitability of the plant in the production of nanomaterials, reducing silver ions in solution. Silver nanoparticles also synthesized using plant extracts, that time *Erythrina abyssinica* aerial parts, showed that the Surface Plasmonic Resonance peak was found at around 420 nm.

4. Conclusions

The synthesis method reported in this research is a sustainable, eco-friendly and economical one. Whereas orange peels are used for extracts that reduce silver ions to nanoparticles, the toxic elements present in the chemical synthesis are eliminated. Thus, these nanoparticles can be used with greater ease and recommendation in biomedical applications, including in diagnosis and treatment, due to their natural origin and possible bioactive properties.

As can be seen from this study, this approach is feasible to be applied, with a minimum required from an economic point of view. In addition, the results of the synthesis phase can be monitored by analytical methods, such as UV-Vis spectroscopy. The absorption signalled at 420 nm in the spectrum of silver nanoparticles suggests a great efficiency in the synthesis process. However, it is essential to continue research to better understand the characteristics and potential applications of these silver nanoparticles.

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