One-pot greener synthesis of silver nanoparticles using tangerine peel extract: large-scale production

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In this reported work, superfine silver nanoparticles were synthesised from silver nitrate through a simple, rapid and eco-friendly route applying tangerine extract, which acts as a solvent, reducing agent and stabilising agent simultaneously. The appearance of a darkish brown colour solution is indicative of silver nanoparticles that were confirmed by a UV–vis spectrophotometer. The as-prepared sample was further characterised using X-ray diffraction and energy dispersive X-ray analysis analyses. The morphology and size of the nanoparticles were characterised by scanning electron microscopy and transmission electron microscopy. The silver salt exposing the tangerine extract is reduced and stabilised over long periods of time that results in the green synthesis of silver nanoparticles. The produced nanoparticles were stable over a long period of time and appropriate for applications in biotechnology.

1. Introduction: During the last decade, research on inorganic nanomaterials has been developing increasingly because of their exceptional optical, catalytic, electronic, magnetic and other chemical and physical properties, which are entirely different from the bulk state [1].

Usually, toxic reducing agents and organic solvents are used in the chemical synthesis of nanomaterials. These methods also suffer from disadvantages such as high-energy consumption, low yield and a demand for wasteful purifications [2, 3]. The chemicals used for these syntheses are often toxic and non-environmentally friendly. Nowadays, a great deal of effort has been made to apply bioreduction methods based on microorganisms, fungi and plant extracts because of the easily synthesised, environmentally benign nature and greater stability of nanoparticles [4–6].

Silver nanoparticles (AgNPs), among noble metal nanoparticles, have attracted great interest because of the large number of applications, such as in biolabelling, as intercalation materials for electrical batteries as optical receptors, in nonlinear optics, as a catalyst in chemical reactions and as antibacterial capacities. The application of AgNPs as biosensors and in other molecular techniques necessitates the application of biocompatible materials for their synthesis. Thus, it is essential to develop an efficient green environmentally-friendly synthetic method [7].

Recently, some of the green methods for the synthesis of AgNPs have been reported by using various natural products like green tea (Camellia sinensis) [8], neem (Azadirachta indica) leaf broth [9], starch [10], aloe vera plant extract [11], lemongrass leaves extract [12], leguminous shrub (Sesbania drummondii) [13], Arbutus unedo leaf extract [14], Macrotlyoma uniflorum [15], seed extract of Jatropha carcas [16], Zingiber officinale extract [17], Malva parvi- flora extract [18] and Terminalia chebula fruit extract [19] and so on.

In the investigation reported in this Letter, we developed an environment-friendly, cost-efficient, ultra-fast green method for the synthesis of AgNPs using readily available aqueous extract of tangerine peel. Also, during the synthesis, no toxic chemicals are used as reducing and stabilising agents. To the best of our knowledge this is the first report of using tangerine extract for the synthesis and large-scale production of AgNPs.

2. Materials and methods

2.1. Preparation of tangerine extract: Silver nitrate was purchased from Sigma-Aldrich Chemicals and fruit tangerine from a local market. The fresh fruit tangerine was washed several times with tap water followed by doubly distilled water to completely remove the dust. Then, the tangerine peel was pared and cut into small pieces. About 25 g of tangerine peel was mixed with 200 ml of distilled water and boiled. The extracts were filtered with Whatman filter paper. Then, the filtrates were collected and refrigerated for further experiments.

2.2. Synthesis of Ag nanoparticles: One gram of AgNO3 was added to 50 ml aqueous solution of extract and the mixture was stirred at a temperature of 30°C. The synthesis of AgNPs was continuously observed via colour change with the naked eye. After 15 min, the solution turned light brown and then the colour of the solution changed to dark brown.

3. Results and discussion: X-ray diffraction (XRD) analysis was performed by using a Bruker D&A advance X-ray powder diffractometer with graphite monochromatised CuKα radiation (k = 1.5406 Å). Energy dispersive X-ray analysis (EDAX) analysis was conducted by a NEW XL30 144-2.5. UV–vis spectra were recorded on a UV–Vis Spectrophotometer Cary-Varian. Also, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were taken on a Hitachi S-4160 Scanning Electron Microscope and JEOL JEM-1210 transmission electron microscope a using copper grid as the sample holder.

Fig. 1 shows the XRD pattern of as-prepared AgNPs. A number of Bragg reflections with values of 2θ = 38.03°, 46.18°, 63.43° and 77.18° are corresponding to the (111), (200), (220) and (311) sets of planes, which may be indexed as the face-centred cubic structures of silver. To confirm the synthesis of AgNPs and investigate the purity or impurity of the product, EDAX analysis was performed. Fig. 2 shows the EDAX analysis of produced AgNPs. As can be seen, EDAX analysis reveals a strong signal in the silver region and confirms the formation of AgNPs. Owing to surface plasmon resonance [20], metallic silver shows a typical optical absorption peak approximately at 3 keV. Also, other elemental signals have been recorded which are probably because of elements from tangerine peel or other biomolecules.

Fig. 3 shows the UV–vis spectra of AgNPs (Fig. 3a) and tangerine extract (Fig. 3b). The sharp band of silver colloids was observed at 412 nm which is indicative of AgNPs. The tangerine extract solution has absorption in the range of 550–220 nm. The whole procedure of AgNPs production is shown in Fig. 4.
By measuring the absorbance intensities of the solutions, the stability of produced AgNPs was investigated. Fig. 5 indicates the UV–vis spectra of as-synthesised nanoparticles and three-month-old nanoparticles at room temperature. As is obvious, no significant change in the wavelength and absorption intensity of the AgNPs were observed after this period. This shows that synthesised AgNPs are stable even over a long period of time.

To determine the morphology and the size of nanoparticles, SEM and TEM images were recorded (Fig. 6). The SEM image shows that the synthesised nanoparticles are spherical and uniformly distributed in size. TEM image shows that the size of the nanoparticles is in the range of 1–10 nm, which is in a good agreement with the XRD results. As is clear, nanoparticles with a range of 1–3 nm have...
been pointed in the image. Hence, the nanoparticles are superfine nanoparticles.

This method showed that tangerine peel extract acts as a good reducing agent and stabiliser to synthesise AgNPs.

4. Conclusions: We report a green chemistry approach for the synthesis of AgNPs by using tangerine peel extract. This method is efficient, simple and clean for synthesising AgNPs. Also, a rapid biological synthesis of AgNPs applying tangerine extract has provided an environmentally-friendly, simple route for the synthesis of benign nanoparticles. The size of the AgNPs was in the range of 5 and 20 nm. From a technological point of view, the synthesised AgNPs have potential applications in the biomedical field. Here, tangerine peel extract, which is environmentally benign, acts as both a reducing and a stabilising agent.

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6 References