Crystallography, morphology and optical properties of silver nanoparticles synthesized by extract of black pepper as a green method

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Abstract: An important aspect of nanotechnology is the development of reliable methods for the synthesis of nanomaterials in vitro that in view of the size, composition and shape can be controlled. In recent years, with increasing environmental problems, many due to green chemistry and attempts for the synthesis of nanomaterials through the environmental clean methods increased. The use of biological organisms for the clean synthesis of nanomaterials is important. In this article we report the synthesis of silver nanoparticles from silver nitrate solution by extract of black pepper from silver nitrate aqueous solution in various environment pH, 9, 10, 12 and 13. Then crystalline structure, morphology and optical properties of these nanoparticles is presented. Prepared samples have been characterized by X-ray diffraction (XRD), UV-Visible Spectrometer (UV-vis) and Scattering Electron Microscope (SEM).

Keywords: Silver, Nanoparticles, Biological Synthesis

1. Introduction

Nanoparticles (NPs) are defined as having one dimension 100nm or less in size and due to their large surface area they tend to react differently than larger particles of the same composition, allowing them to be utilized in novel applications [1]. Among all nanomaterials, silver nanoparticles (AgNPs) are unique as they are used in vast arrays of applications including medicine, food and consumer products [2]. Synthesis of such variety of AgNPs is possible by thermal decomposition [3], laser ablation [4], ultrasound [5] and aqueous chemical reduction method [6]. In order to minimise the risk of environmental hazards and to ensure economic sustainability by reducing production costs, there is a growing need to develop eco-friendly protocols for the nanoparticles synthesis employing green chemistry approaches using cheaply available, renewable natural resources [2]. One of them is synthesis of nanoparticles by biological process which implemented to develop safe, cost-effective and environmentally friendly technologies [7]. Very recently green silver nanoparticles have been synthesized using various natural products like green tea (Camellia sinensis) [8], neem (Azadirachta indica) leaf broth [9], natural rubber [10], starch [11], aloe vera plant extract [12], lemongrass leaves extract [13,14] leguminous shrub (Sesbania drummondi) [15], etc. Black pepper broth is known to contain several biomolecules such as alkaloids, proteins, polysaccharides, amino acids and vitamins. These biomolecules could be used as bioreductants to react with metal ions and they could also be used as scaffolds/template to direct the formation of nanoparticles in solution. The mechanism responsible for the reduction may postulate as follow: the silver ions were trapped on the surface of proteins/or predominated alkaloid piperine in the extract via electrostatic interactions. This stage was the recognition process. The silver ions were then reduced by the proteins leading to changes in their secondary structure and the formation of silver nuclei. The silver nuclei subsequently grew by the further reduction of silver ions and their accumulation of the nucle.

2. Experimental

2.1. Extraction of Black Pepper

For extraction, 20 g black pepper seeds washed thoroughly with distilled water and air-dried. After that powdered the
seeds and boiled in 200 ml distilled water for 10 min. The cooled filtrate was adjusted at pH 14 by adding NaOH.

2.2. Synthesis of Silver Nanoparticles

The chemicals and reagents were used with high quality and purity (Merck, Germany).

Took 100 ml of AgNO₃ aqueous solution in a conical flask and adjusted at pH 9, 10, 12 and 13 by adding extract drop by drop. Put the above solution on magnetic stirrer for 2 h and centrifuged at 3000 rpm for 10 min, supernatant decanted off and residue collected. Residue was washed three times with double distilled water followed by ethanol. Finally, residue kept in oven at 80 °C for 10 h.

3. Results and Discussion

Fig. 1 shows XRD patterns of the dried samples using CuKα radiation (0.154 nm) for 2θ ranging from 20° to 80°. The XRD patterns confirms the face-centered-cubic (fcc) lattice (JCPDS file no. 087-0718) with strong diffraction peaks at 38, 44, 64 and 77 degrees of 2θ which corresponds to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystal planes.

Fig. 2 shows XRD pattern of the dried sample that synthesis in dark environment. Pattern of this sample and D sample after heating shown in Fig. 3. There was no significant change in the peak position of silver nanoparticles in this patterns compared with Fig. 1.

Fig. 4 shows the Scattering Electron Microscope (SEM) images of the AgNPs. The nanoparticles formed had spherical shape of varied size. There was no marked difference in the shape. The biosynthesized AgNPs ranged in size between 20 and 60 nm, this size range can be applied in areas of non-linear optics and solar cells, where very small nano-silver is required.
Silver nanoparticles absorb radiation in the visible region of the electromagnetic spectrum due to the surface plasmon resonance (SPR) transition. Measurements were carried out on UV-visible spectrophotometer T80. The UV–vis absorption spectrum of the silver nanoparticles is shown in Fig. 5. In all these spectra, there are no peaks located around 335 and 560 nm, indicating the complete absence of nanoparticle aggregation [16, 17]. UV–vis confirmed the existence of Ag particles because it is known from the reports in literature that spherical AgNPs display an UV–vis absorption peak in the region 400–450 nm. Although all preparations lead to the formation of silver nanoparticle but (according to Mie theory [18]) the different spectra suggest differences in particles sizes.

In Fig. 6 spectrum (E) shows the black pepper broth with NaOH treated (maintained at pH 14), suggesting many peaks at UV wavelengths suggesting the basic amino acids or alkaloids, they might play role for AgNPs formation. Whereas, spectrum (F) shows the black pepper broth without NaOH treated, no peak appeared. However, work is in progress for deciphering the exact biomolecules of black pepper for playing crucial role to establish systematic AgNPs formation mechanism.
4. Conclusions

A rapid, eco-friendly and novel synthesis route for preparing silver nanoparticles was carried out using black pepper extract as a reducing agent. The alkaloid piperine (or few basic amino acids or both) of the black pepper seed extract plays a leading role for the formation and stabilization of AgNPs, respectively.

The morphology of the NPs was determined from scanning electron microscopy (SEM). The formed nanoparticles were ranging in dimension 20 to 60 nm which was almost spherical in shape. The NPs was analyzed using UV–Vis spectroscopy and it points out to the formation of silver nanostructures with different sizes. Green synthesis method involved using black pepper extract in environmentally friendly universal solvent namely water, which would open new ventures in the application of formed silver nanoparticle. Our findings could be targeted for the promising potential applications including water purification, recording media, biosensing devices, nanoelectronic, and catalysis. Future research based on synthesis of size specific nanoparticle based on the optimization of reaction condition and study on the other properties of prepared silver nanoparticles such as antimicrobial, catalysis and etc would be an interesting area.

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