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Original Article

Green synthesis of silver nanoparticles using onion extract and their application for the preparation of a modified electrode for determination of ascorbic acid

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ABSTRACT

A high-quality method for one-pot biosynthesis of silver nanoparticles (AgNPs) using onion extracts as reductant and stabilizer is reported. The synthesized AgNPs were characterized by ultraviolet-visible spectroscopy (UV-Vis), X-ray powder diffraction (XRD), and transmission electron microscopy (TEM). UV-Vis spectroscopy results showed that the AgNP absorption band was located at a peak of 397 nm in aqueous solution. Both XRD and TEM results confirmed that the AgNPs were mainly spherical with average diameters of 6.0 nm by TEM and about 5.3–10.2 nm calculated using XRD data. The ability of AgNPs to reduce charge transfer resistance was also investigated using electrochemical impedance spectroscopy. Finally, the effect of synthesized NPs on ascorbic acid signal was investigated by square wave voltammetry. The peak current of square wave voltammograms of ascorbic acid increased linearly with its concentration in the range of 0.4–450.0μM. The detection limit for ascorbic acid was 0.1μM.

1. Introduction

Nanotechnology deals with biotic and abiotic materials that vary in size from 1 nm to 100 nm [1–5]. Nanoparticles (NPs) have novel properties, which depend on specific characteristics such as size, morphology, and distribution [6–12]. Nowadays, inorganic NPs and their nanocomposites are extensively used in various industries, biomedicines, and catalysis reactions [13–15]. In particular, silver NPs (AgNPs) have various important applications. Historically, silver has been known to have disinfecting effects and is used in a broad range of applications from traditional medicines to culinary items. It has been reported that AgNPs are nontoxic to humans and most effective against bacteria, viruses, and other eukaryotic microorganisms at low concentrations without any side effects [16].

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AgNPs play a significant role in the field of diagnostic medicine [17], antimicrobial synthesis, and therapeutics [18,19]. Ag^+ contributes to the antimicrobial ability of AgNPs under various hypothesis including Ag^+ adherence, breakdown, permeabilization of cell membrane, and interaction with proteins and DNA; however, reactive oxygen species are reported to interfere with its physiological functions [20,21].

Stable AgNPs can be synthesized by chemical methods such as chemical reduction, electrochemical techniques, and photochemical reduction [22–24]. Meanwhile, the use of biosynthetic methods has attracted much attention because of their safe conditions in synthesis procedures, good distribution of synthesized NPs, use of nontoxic solvents, etc. [25].

Many biotechnological applications such as remediation of toxic metals use microorganisms such as bacteria [26] and yeast [27] for the synthesis of NPs. Nair and Pradeep [28] have synthesized NPs of gold, silver, and their alloys by treating the corresponding metal ions within cells of lactic acid bacteria present in buttermilk.

In recent years, plant-mediated biological synthesis of NPs is gaining importance due to its simplicity and eco-friendliness [29]. Moreover, plant extracts could be advantageous over microorganism synthesis because there is no need to expand the process of culturing and maintaining cell lines, and they are of low cost, fast, efficient, and generally lead to the formation of crystalline NPs with a variety of shapes and sizes [30–36].

Allium cepa L. is one of the most widely cultivated and used plants, and its bulb (onion) is used as both food and medicine. Onions (*A. cepa* L.) possess strong, characteristic aromas and flavors, which have made them important ingredients of various food items. Onions and onion flavors (essential oil) are important seasonings widely used in food processing. It has been shown that onion possesses various biological properties, including antibiotic, antidiabetic, antioxidant, antiatherogenic, and anticancer effects [37].

In this study, we wish to report a green synthesis of AgNPs by reduction of silver ions using aqueous and alcoholic onion extracts for facile and fast phytosynthesis of AgNPs. The ability of AgNPs to reduce charge transfer resistance and the effect of these extracts on ascorbic acid signal using electrochemical impedance spectroscopy (EIS) and voltammetric methods is also investigated. To the best of our knowledge, only one report describing the synthesis of AgNPs using water extracts of onion can be found in the literature [38] and no further reports pertaining to the use of methanolic onion extract for green synthesis of AgNPs and its effect on ascorbic acid signal by square wave voltammetry (SWV) have been published.

2. Methods

2.1. Materials and procedure for the preparation of onion extracts

Pure silver nitrate ($AgNO_3$), ascorbic acid, and $K_4[Fe(CN)_6]$ were purchased from Merck (Tehran, Iran). NaOH was purchased from Sigma-Aldrich (Tehran, Iran). Onions (*A. cepa*) were purchased from a local store in Babol, and these onions were reportedly collected from Mazandaran Province (Qaemshahr, Iran). Double-distilled water was used in all experiments. A certain weight of onions (*A. cepa*; 10 g) was washed 10 times with double-distilled water and boiled with 100 mL water for 45 minutes and then filtered through a Whatman Number 1 filter paper. The filtrate was used as a reducing and stabilizer agent for the synthesis of AgNPs.

2.2. Synthesis of AgNPs

A certain volume of the onion extract (10 mL) was added to a 10 mL silver nitrate solution (1×10^{-2}M) and the volume was adjusted to 40 mL with deionized water. The flask was then incubated at room temperature. The measured pH was 5.42. Different conditions were used for the optimization of AgNPs synthesis in this work.

2.3. Ultraviolet-visible spectroscopy

The formation and stability of AgNPs were investigated by ultraviolet-visible (UV-Vis) spectrophotometry (Cary, UV-500, Japan). The absorption spectrum of reaction solutions as a function of reaction time, different biomaterials used, and $AgNO_3$ dosage were recorded at same time and at wavelengths ranging from 300 nm to 600 nm.

2.4. Microscopic investigations

Transmission electron microscopy (TEM) was applied for the morphological analysis of AgNPs; 3 μL of the sample was placed on a carbon-coated copper grid and allowed to dry at room temperature. The TEM images were obtained using a Philips cm10HT version of TEM, which was operated at 100 kV.

2.5. X-ray diffraction measurements

Crystalline metallic pattern of AgNPs powder was analyzed using X-ray diffraction (XRD). To obtain a pellet of pure NPs for XRD analysis, the reaction medium was centrifuged by five cycles at 18,000 rpm for 20 minutes followed by redispersion in deionized water. The XRD patterns were recorded on an X'Pert Pro MPD, which was operated at a voltage of 40 kV and current of 40 mA with Cu-K_α radiation. The scanning was done in the region of 2θ from 20° to 80°.

2.6. Electrochemical investigation

SWV was performed using a potentiostat/galvanostat connected to a three-electrode cell and Metrohm Model 663 VA stand linked with a computer (Pentium IV, 1200 MHz) running Autolab software. The system was run on a personal computer using GPES and FRA 4.9 software. For impedance measurements, a frequency range of 100 kHz to 0.1 Hz was used. A conventional three-electrode cell assembly consisting of a platinum wire as an auxiliary electrode and an Ag/AgCl (KCl_{sat}) electrode as a reference electrode was used.

AgNPs carbon paste electrode (AgNPs/CPE) was prepared by mixing of 0.1 g of AgNPs and 0.90 g of graphite powder in