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Biogenic Silver Nanoparticles as Sensors of some of Heavy Metal in Aqueous Solutions

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Abstract

Silver nanoparticles (Ag-NPs) were prepared by green synthesis using *Camellia sinensis* extracted from green tea. The formation of the nanoparticles was confirmed by UV-Vis spectrophotometry across the detection of the surface plasmon resonance (SPR). These biosynthesized Ag-NPs were found to exhibit good sensing properties towards heavy metal ions in aqueous solutions. The metal ions-sensing ability of the biogenic Ag-NPs was monitored by UV-Vis spectrophotometry (SPR analyses).

Keywords: Biogenic-silver Nanoparticles, Camellia Sinensis, Nanoparticles Ion-sensing, Surface Plasmon Resonance Fluorescence, Green Synthesis.

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1. Introduction

Nanostructured materials exhibit a host of interesting new phenomena directly related to their reduced dimensionality. Not only the electronic, magnetic and optical properties but also chemical, electrochemical and catalytic properties of nanostructured materials are very different from those of the bulk form and depend sensitively on size, shape, and composition. There are, mainly, two ways of synthesis: chemical and physical methods [1-6]. These methods have many problems such as the use of toxic solvents, generation of hazardous products and/or are not suitable to scale-up, among others. In order to avoid the bad genocidal effects during synthesis and applications of nanoparticles; preparation using the biological approach can be used [7, 8] because it is economical and friendly to the environment. As an example of the green synthesis method is the use of Camellia sinesis extract, which is rich in polyphenolic compounds and thus can be used for the synthesis of metal nanoparticles, due to the dual nature of the biomass as a reducing as well as a stabilizing agent [9-14].

At recent days the detection and quantification of heavy metal ions are important for our life. In the past, chromo ionophores can be used in optical sensing schemes for selective naked-eye detection of metal ions in aqueous media that do not require specific instrumentation, especially for field-test [15]. Noble metals as silver are characterized by the presence of surface Plasmon resonance with wavelength depends on the chemical environment surrounding the Ag nanoparticles [16-18]. Thus, we can use the plasmon shift of Ag-nanoparticles to detect different metal ions.

In this work, silver nanoparticles have been prepared through a green method by using reducing agent Camellia sinensis (green tea). The colloidal solution of the prepared Ag-nanoparticles is used as a selective colorimetric method to detect some of the heavy transition metal ions.

2. Materials and Methods

2.1. Materials

Green tea was obtained from a local store. Silver nitrate ($AgNO_3$) (98 %) was purchased from Windsor laboratories limited (slough-Berkshire-united kingdom), Cupric sulfate ($CuSO_4$), (99%) and Manganese acetate ($Mn(CH_3CO_2)_2.4H_2O$), (98%) were purchased from LOBA CHEMIE PVT.LTD, Chromium nitrate ($Cr(NO_3)_3.9H_2O$), (99%) from Spectrum C1251-2.5KG, Technical Grade, Lead nitrate Pb (NO_3) from Merck (Germany) and Ammonia solution (NH_3 aq.) (33%) from Nasr Company (Egypt). All chemicals were used as received without further purification.

2.2 Preparation of Camellia Sinensis Extract

The green tea was grounded in a coffee grinder for 1 min. The ground tea powder was mixed with water (1:10) and boiled for 10 min. The supernatant was filtrated by vacuum filtration.

2.3. Biosynthesis of Ag-NPs

The green synthesis of silver nanoparticles was done by adding 2.5 mL of an ammonia solution to 5mL of a 10^{-3} M silver nitrate solution, followed by heating at 60°C for 24 h and then adding 3 mL of *Camellia sinensis* aqueous extract. The main biomolecules existing in Camellia sinensis that act as reducing and passivating agents which once added to silver solution color change to brownish.

This color change means that the biomolecules present in the extract reduce the Ag metal ions to generate nanoparticles [19-25]. Protocatechuic, caffeic acid, vanillic acid, syringic acid, catechin, epicatechin, and benzoic acid are existing in extract solution which has the hydroxyl moieties, which are responsible for the reduction of metal nanoparticles, and the OH groups are oxidized to the corresponding quinone [26].

2.4. Characterization of Ag-NPs

The UV–vis absorption spectra of the samples were taken at room temperature using a Cary 5G equipment, at wavelengths ranging from 300 to 750 nm.

2.5. Sensing Studies

Sensing studies were performed by preparing two concentrations of heavy elements 10, and 50 ppm. To detect the sensitivity effect of the biogenic silver nanoparticles toward detection of metal ions, one ml of biogenic Ag-NPs is added to one ml of different concentrations of the heavy element ions then analyzed by UV-V spectrophotometer.

3. Results and Discussion

3.1UV-Vis Analysis of Ag-NPs sensor.

The Ag-Nps solution was analyzed by UV–vis spectroscopy to confirm the presence of Ag-Nps. All samples showed a peak for surface plasmon resonance (SPR) at 425 nm characteristic for the Ag-Nps, Fig. 1. The broadness of the spectrum indicates the polydispersity of the nanoparticles obtained [27, 28]. To check the stability of the prepared Ag-Nps solutions, the SPR absorption spectrum was examined as a function of the time for 10 days. The results obtained (shown in Fig. 1) refer to the high stability of the silver nanoparticles in solution during the testing period.

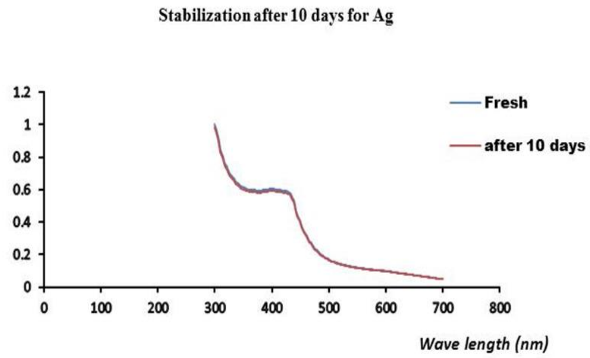

Fig. 1: UV-Vis spectra of biogenic Ag-NPs prepared by Camellia sinensis.

3.2. Metal Ions Sensing Studies

The sensitivity of Ag-Nps solution was tested for various metal ions: Ni^{2+}, Cu^{2+}, Pb^{2+}, Mn^{2+} and Cr^{3+} using a fixed value of the concentration (10 ppm). The SPR band in each of the absence and the presence of the test metal ions were recorded and represented in Fig. 2. A bathochromic shift in the SPR band is observed for all tested ions. The shift in absorption increases in the order:
Ni^{2+} > Pb^{2+}> Cu^{2+} > Mn^{2+} > Cr^{3+} and decrease in the intensity in the order: Ni^{2+} > Pb^{2+} > Cu^{2+} > Cr^{3+} > Mn^{2+}.

For higher concentrations of the toxic metal ions investigated (100 ppm), a reduction in the intensity of the SRB is observed. This can be attributed to the decrease in the apparent number of Ag-Nps owing to aggregation induced by the examining metal ions.

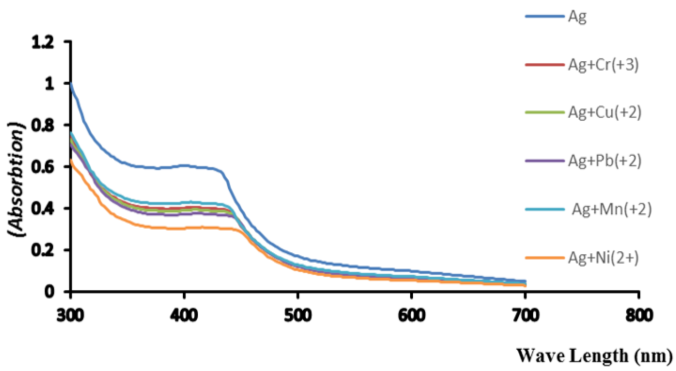

Fig. 2: Optical Absorption spectra for metal ions: Ni^{2+}, Cu^{2+}, Pb^{2+}, Mn^{2+} and Cr^{3+}.

4. Conclusions:

In the present work, the silver nanoparticles have been successfully synthesized by green method using Camellia sinensis extracted from green tea. The UV-Vis spectrum of the suspended solution Ag-NPs shows a surface plasmon resonance band (SPR) at 425 nm. The addition of transition metal ions of Cu^{2+}, Pb^{2+} Mn^{2+}, Ni^{2+} or Cr^{3+} causes a bathochromic shift in SPR band in the order Ni^{2+} > Pb^{2+}> Cu^{2+} > Mn^{2+} > Cr^{3+}, and a decrease in its intensity with increasing the concentration of the toxic metal ions according to Ni^{2+} > Pb^{2+} > Cu^{2+} > Cr^{3+} > Mn^{2+}. The results obtained show a simple and economic method to detect toxic metal ions using a green method.

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