Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 121 (2014) 596–604

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Surface plasmon resonance optical sensor and antibacterial activities of biosynthesized silver nanoparticles

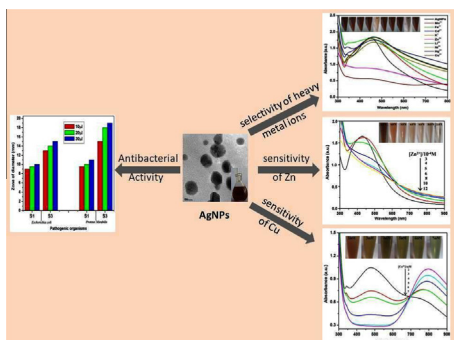
M.R. Bindhu, M. Umadevi *

Department of Physics, Mother Teresa Women's University, Kodaikanal 624101, Tamil Nadu, India

HIGHLIGHTS

- Green synthesis of Ag nanoparticles using *Ananas comosus* fruit extract as reducing agent.
- Stable and spherical Ag nanoparticles were prepared.
- Shows size dependent antimicrobial activity.
- Act as very good copper and zinc sensors.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 September 2013
Received in revised form 3 November 2013
Accepted 5 November 2013
Available online 13 November 2013

Keywords:
Silver nanoparticles
Ananas comosus
Surface plasmon resonance
Antibacterial activity
Zinc sensor
Copper sensor

ABSTRACT

Silver nanoparticles were prepared using aqueous fruit extract of *Ananas comosus* as reducing agent. These silver nanoparticles showed surface plasmon peak at 439 nm. They were monodispersed and spherical in shape with an average particle size of 10 nm. The crystallinity of these nanoparticles was evident from clear lattice fringes in the HRTEM images and bright circular spots in the SAED pattern. The antibacterial activities of prepared nanoparticles were found to be size-dependent, the smaller nanoparticles showing more bactericidal effect. Aqueous Zn^{2+} and Cu^{4+} selectivity and sensitivity study of this green synthesized nanoparticle was performed by optical sensor based surface plasmon resonance (SPR) at room temperature.

Introduction

Noble metal nanoparticles are used for the purification of water which is one of the essential enablers of life on earth [1]. Water is one of the purest symbols of wealth, health, tranquility, beauty and originality. Pure water, which is free of toxic chemicals and pathogenic bacteria, is necessary for human health. Water and environment get contaminated by the heavy metals due to industrial and agricultural pollution. Heavy metals such as cadmium (Cd), Zinc (Zn), mercury (Hg), arsenic (As), silver (Ag), chromium (Cr), copper (Cu), iron (Fe), and the platinum group elements [2] in water causes dangerous toxic effects on human beings. In particular the detection of Cu^{4+} and Zn^{2+} in water, air and soil has been of great research interest due to the important role of Zn and Cu plays in the biological processes within the human body [3–5]. Zinc and copper are essential at trace concentrations as heavy metal ions or nutrients to maintain the metabolism of human body [5,6]. Drinking water can be a source of Zn and Cu to humans as the result of water treatment, usage of galvanized pipes, copper pipes and tanks in distribution systems. The beverages stored in metal

* Corresponding author. Tel.: +91 04542241685; fax: +91 04542 241122.
E-mail address: ums10@yahoo.com (M. Umadevi).

1386-1425/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.saa.2013.11.019

containers, which are coated with zinc in order to resist rust, contain high levels of Zn. So, detection and control of Cu and Zn ions in various media such as water, biological, environmental, medical and industrial samples is very important. Keeping this in mind, detection of Zn and Cu concentration in water is explained in the present study.

A number of techniques have been developed for heavy metal ions analysis, including Atomic absorption spectroscopy (AAS), Inductively coupled plasma mass spectrometry (ICPMS), Anodic stripping voltammetry, X-ray fluorescence spectrometry and microprobes. However, these techniques generally require expensive equipment, sample pretreatment, and/or a long measuring period. Thus, a simple, rapid, inexpensive, sensitive and selective method is strongly needed. Optical sensor based on surface plasmon resonance for detection of heavy metals in water is one of the most sensitive methods which will be advantageous over other earlier techniques as it will be a simple, inexpensive and fast. In the past years a number of nanoparticles based sensor have been reported [7–10]. Recently green synthesized silver nanoparticles used in an optical sensor based on localized SPR for ammonia and mercury detection was studied [11,12]. In this study, we have designed a silver nanoparticles based optical sensor for detection of concentration of Cu^{4+} and Zn^{2+} ions in water.

Waterborne pathogens including helminthes, protozoa, fungi, bacteria, rickettsiae, viruses and prions, can cause many diseases [13]. In India 80% of the diseases are due to bacterial contamination of drinking water. To protect the water purity, the removal or deactivation of pathogenic bacteria in water is very important. Silver is being used as a bactericide for water purification and also to prevent the buildup of bacteria and algae in water filters since more than a decade. Antibacterial activities of silver nanoparticles against various pathogens have also been established [14–16]. In the present study, the antibacterial assay was done on various pathogenic bacteria like *Escherichia coli* and *Proteus Mirabilis,* which are commonly found in water.

The physicochemical and optoelectronic properties of metal nanoparticles are based on specific characteristics such as size, distribution and morphology [17]. Among the known nanoparticles, silver has been widely studied for its optical, spectroscopic, catalytic, antimicrobial and SERS properties. Due to these properties, silver nanoparticles have been broadly applied in consumer products and industrial fields. In recent years, green synthesis approaches of metal nanoparticles, using microorganisms and plants have received great attention to chemical and physical methods. Generally the reduction of silver nitrate using plant extract was slow, but it had some advantage of producing stable and uniform size nanoparticles without using any additional chemical stabilizers [18]. Recently, green synthesis of silver nanoparticles using *Hibiscus cannabinus*, *Solanum lycopersicums*, *Moringa oleifera*, *Murraya koenigii* leaf, *Citrus* limon and *Daucus carota* have been reported [19–24]. *Ananas comosus* is a readily available fruit and it is a good source of water, carbohydrates, sugars, vitamins A, C and carotene, beta [25]. It is one of the fruits with highest in the flavonoid antioxidant Vitamin C. This antioxidant reduces the oxidative damage such as that caused by free radicals and chelating metals [26]. It contains low amount of protein, fat, ash and fiber. There are three types of amino acids in *A. comosus* that promote exceptional health benefits through essential, semi-essential, and non-essential amino acids. Along with this, *A. comosus* also contain bromelain, a protein-digesting enzyme that reduces inflammation. Modified pineapple peel fiber was used to remove heavy metal ions in water through the reaction with succinic acid anhydride [27,28]. Bhosale et al. has reported the synthesis of silver and gold nanoparticles using *A. comosus* extract with kanamycin A, and neomycin as stabilizing agents [29]. They prepared larger nanoparticles with agglomeration. In the present study, the synthesis and characterization of monodispersed smaller silver nanoparticles using fruit extract of *A. comosus* has been described. Here the size and aggregation of the nanoparticles were controlled without additional stabilizing agents. In the present study, the synthesis and characterization of biosynthesized silver nanoparticles for sensor and antibacterial activities have been described.

Experimental details

Material and methods

A. comosus fruit was collected from the local supermarket in Kodaikanal, Tamilnadu, India. Silver nitrate, copper sulphate, ferric chloride, nickel nitrate, potassium chloride, cadmium acetate, manganous acetate, mercuric iodide, lithium hydroxide and zinc acetate were obtained from Sigma Aldrich Chemicals. All glasswares were properly washed with distilled water and dried in hot air oven before use.

Preparation of A. comosus extract

Fully riped *A. comosus* fruit, weighing 50 g was taken and cut into fine pieces and were crushed into 100 ml distilled water in a mixer grinder for extraction. The extract was then separated by centrifugation at 1000 rpm for 10 min to remove insoluble fractions and macromolecules. The extract thus obtained was filtered and finally a light yellow extract was collected for further experiments.

Synthesis of silver nanoparticles

5 ml of *A. comosus* extract was added to aqueous solution of $AgNO_3$ (3 mM) and stirred continuously for 5 min. The reaction completed slowly and it showed stable reddish brown color of the silver colloid (S1). Similarly by adding 10 and 15 ml of fruit extract two more set of samples, henceforth called (S2) and (S3) respectively, were prepared. UV–vis spectra of these solutions were recorded. Here the formation of silver nanoparticles started within 20 min, and increased up to for 2 h. After 2 h, no color variation was observed up to 1 month, showing that the silver nanoparticles prepared by this green synthesis method were very stable. Then the solutions were dried. The dried powders were characterized by X-ray diffraction (XRD), Fourier Transform Infrared Radiation (FTIR), Transmission Electron Microscope (TEM) and Energy Dispersive X-ray Spectroscopy (EDX).

Characterization methods and instruments

The absorption spectra of the prepared nanoparticles were measured using a Shimadzu spectrophotometer (UV 1700) in 300–800 nm range. X-Ray Diffraction analysis of the prepared nanoparticles was done using PANalytical X'pert – PRO diffractometer with Cu Kα radiation operated at 40 kV/30 mA. FTIR measurements were obtained on a Nexus 670 FTIR instrument with the sample as KBr pellets. Transmission Electron Microscopic (TEM) analysis was done using a JEOL JEM 2100 High Resolution Transmission Electron Microscope equipped with an EDX attachment, operating at 200 kV. For the detection of concentration of zinc in water using optical characteristics of silver nanoparticles, different concentration of aqueous solution of zinc acetate dehydrate salt were prepared. This analyte solution was added to the prepared silver nanoparticle solution from 3×10^{-4} M to 12×10^{-4} M and stirred continuously for 1 min at room temperature. For the detection of concentration of copper in water, different concentration of aqueous solution copper sulphate (2 mM to 7 mM) and of the same conditions were added into the silver nanoparticles. The antibacterial