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Utilization of hydroxypropyl carboxymethyl cellulose in synthesis of silver nanoparticles

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ABSTRACT

Hydroxypropyl carboxymethyl cellulose samples having varying degrees of substitution and varying degrees of polymerization were used to reduce silver nitrate to silver nanoparticles. UV spectral analysis of silver nanoparticles colloidal solution reveal that increasing the pH of the reduction solution leads to improvement in the intensity of the absorption band for silver nanoparticles, to be maximum at pH 11. The absorption peak intensity also enhanced upon prolonging the reaction duration up to 60 min. The conversion of silver ions to metallic silver nanoparticles was found to be temperature-dependent and maximum transformation occurs at 60 °C. The reduction efficiency of hydroxypropyl carboxymethyl cellulose was found to be affected by its degree of polymerization. Colloidal solutions of silver nanoparticles having concentration up to 1000 ppm can be prepared upon fixing the ratio between silver nitrate and hydroxypropyl carboxymethyl cellulose at 0.017–0.3 g per each 100 ml of the reduction solution.

1. Introduction

The research in the nanotechnology field is considered to be one of the most rapidly growing research areas in the branch of materials science.

Materials in the nano size scale exhibit completely new performance properties different from the performance properties of the same materials when in the normal size scale. This difference in the performance properties due to different size scale is attributed to specific characteristics gained due to the extremely small size such as the size distribution and the particles morphology. During the last few decades, there has been great progress in the nanotechnology research field, due to numerous advanced methodologies developed by researchers for synthesis of nanoparticles having definite size and shape to fulfil very specific requirements. New applications of nanoparticles and nanomaterials are increasing rapidly and thousands of research papers and patents which describe new techniques for synthesis of nanoparticles are produced annually.

The term nanotechnology refers to any issue related to the development in the synthesis processes, the advancement in the characterization techniques and any new exploration or application field of materials in the nano size scale [1–15]. This branch of science deals with the study of new materials in the nano size scale, that the structure of the materials in such case is expected to exhibit completely different chemical, biological and physical properties, in addition to totally different functionality and phenomena due to the presence of these materials in the nano size scale. Due to the extremely small size, the weight unit of a given material in the nano size scale has a very larger surface area, compared to the same weight unit for the same material in the macro scale size. The particle size, particle shape, crystallinity, morphology and composition are main factors that govern the intrinsic properties of a given metal nanoparticle.

Many research papers worldwide have been reported different synthetic routes for the preparation of metals in the nanoparticle scale [16]. Among these routes for synthesizing nanoparticles the reduction of salts of the desired metal to get it in the nano size scale [17–23], synthetic route without any reducing agent in the autoclave [24,25], synthetic route based on the reverse micelles technique [26,27], synthetic route based on electrochemical reactions [28,29] and finally synthetic route based on irradiation technique [30]. During the last decade, it is noticed that there is good awareness towards green chemistry processes as an ecofriendly method in synthesizing nanoparticles. This interest increased continuously and let to the development of new environmentally friendly approaches for synthesizing nanoparticles. These environmentally safe approaches used in nanoparticles synthesis were found to be characterized by many advantages like simplicity

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in achievement, compatibility for applications in biomedical and pharmaceutical fields, in addition to be very cost effective when compared to other hazardous routes of synthesis. Most of the routes described for preparation of silver nanoparticles are not environmentally safe because these synthesis approaches depend on the utilization of hazardous materials like the known toxic reducing agent hydrazine [31] or the utilization of other hazardous solvents like, for example, the solvent N,N-dimethylformamide [32]. In spite of being extremely powerful and effective in synthesis of some nanoparticles like silver nanoparticles, the utilization of such hazardous chemicals was found to result in severe and complicated environmental problems and many biological risks.

The aim of the present study is to utilize cellulose extracted from olive tree branches and functionalized through successive hydroxypropylation and carboxymethylation reactions in the preparation of silver nanoparticles through the reduction of silver nitrate. The experimental activities in this study involves oxidative degradation of the mixed cellulose ether, hydroxypropyl carboxymethyl cellulose to get different grades of molecular weight. Moreover, hydroxypropyl carboxymethyl cellulose of different degrees of substitution was tried in the synthesis of silver nanoparticles to show the effect of both molecular weight and degree of substitution on the reduction efficiency of the cellulose ether, during silver nanoparticles synthesis.

2. Experimental

2.1. Chemicals and materials

Olive tree branches were collected from olive tree farm. Sodium salt of monochloroacetic acid, propylene oxide, sodium hydroxide, sodium carbonate, potassium permanganate, potassium iodide, sodium thiosulfate and potassium bromide were all from the laboratory grade chemicals. The bleaching auxiliaries, Texamyl BL (bacterial alpha-amylase) and Texazym T (non-ionic wetting agent) were supplied by Inotex Company.

2.2. Oxidative degradation of hydroxypropyl carboxymethyl cellulose

The resulting hydroxypropyl carboxymethyl cellulose, which was obtained according to the two etherification methods mentioned above was subjected to strong oxidative treatment with 6% sodium chlorite solution, at pH value 8, for a duration of 24 h at a material to liquor ratio 1:20. To get different levels of degradation, two samples from the cellulose ether were treated, separately, keeping all treatment factors fixed and varying only the treatment temperature, to be in one sample 55 °C and in the other sample 70 °C. The resulting samples due to this treatment were found to have degrees of polymerization of 1900 and 1300, respectively.

2.3. Methods of silver nanoparticle preparation

Certain weight sample from hydroxypropyl carboxymethyl cellulose in definite volume of distilled water was stirred well by use of heating magnetic stirrer until it dissolves completely. After achieving complete dissolution of the cellulose ether, the solution pH is to be adjusted at certain value within the range of study (pH 6–pH 11). The adjustment of the pH was followed immediately by raising and fixing the temperature of the ether solution to certain degree within the range of study (30–60 °C). Definite volume of silver nitrate solution was then incorporated to the reaction medium, drop-wise, such that the total volume of the reaction medium is kept constant at 100 cm^3. The reaction mixture was stirred continuously for different time intervals within the range of study. Within few minutes after the complete addition of silver nitrate solution, the reduction medium starts to acquire a pale yellow color, which is considered as an indication for silver nanoparticles formation and the intensity of this yellow color increases as the reduction time increases until it reaches dark brown color in about 30 min. The progress of silver nitrate reduction into silver nanoparticles was monitored, not only by the change in color but also spectrophotometrically by withdrawing samples from the reaction bulk at different time intervals and evaluating them by use of UV–vis spectroscopy.

2.4. Testing and analysis

2.4.1. UV-spectroscopy

The ultra violet–visible spectroscopy have been proved to be a very efficient and quite sensitive tool for silver nanoparticles formation due to the intense absorption peak exhibited by the formed silver nanoparticles. This intense absorption peak represents the collective excitation of the conduction electrons present in the silver metal, i.e. this peak appears due to the surface plasmon excitation. The silver nanoparticles were prepared in our study through reduction of silver nitrate by means of hydroxypropyl carboxymethyl cellulose. The nanoparticles were accordingly embedded in the ether and their UV–vis spectra were recorded by means of a 50 ANALYTIKA JENA Spectrophotometer from 300 to 550 nm. A solution of pure hydroxypropyl carboxymethyl cellulose in distilled water without any additives was used as a blank for the UV–vis spectroscopy measurements.

2.5. Transmission electron microscopy

Transmission electron microscopy is the second tool used for characterizing the formed silver nanoparticles. In this study, the size and shape of the formed silver nanoparticles were measured and characterized by use of a JEOL-JEM-1200 transmission electron microscope. Samples for transmission electron microscopy measurements were prepared by dropping a small portion of the formed silver nanoparticle colloidal solution on the surface of a 400 mesh carbon-coated copper grid. The water was evaporated from the colloidal solution just by air at room temperature to precipitate the silver nanoparticles on the surface of the grid. The average diameter of the formed silver nanoparticles was calculated by finding the diameters of about 100 nanoparticles distributed in several areas in the micrographs.

3. Results and discussion

3.1. Hydroxypropyl carboxymethyl cellulose as reductant and stabilizer in silver nanoparticles synthesis

Different samples from hydroxypropyl carboxymethyl cellulose having different degrees of substitution and different degrees of polymerization were prepared and used to perform dual role in silver nanoparticles synthesis as both reducing agent for silver nitrate to silver nanoparticles and also as stabilizing agent for the formed nanoparticles during the silver nanoparticles synthesis process. Factors which govern the efficiency of hydroxypropyl carboxymethyl cellulose as reducing and stabilizing agent in silver nanoparticle synthesis, as well as the morphology and particle size of the formed nano silver along with the involved mechanisms are discussed below.

3.1.1. Mechanisms involved in silver nanoparticles synthesis

Many authors reported previously that the polymeric solutions, especially those of natural polymers can be successfully used in synthesizing and stabilizing metal nanoparticles [33–35]. Both dendritic polymers and linear polymers have been used successfully

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