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# Preparation of cellulose composites with *in situ* generated copper nanoparticles using leaf extract and their properties

V. Sadanand [a], N. Rajini [b], A. Varada Rajulu [c,*], B. Satyanarayana [a]

[a] Department of Chemistry, Osmania University, Hyderabad 500007, India
[b] Department of Mechanical Engineering, Kalasalingam University, Anand Nagar, Krishnan Kovil 626126, India
[c] Centre for Composite Materials, International Research Centre, Kalasalingam University, Anand Nagar, Krishnan Kvoil 626126, India

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ABSTRACT

In the present work, copper nanoparticles (CuNPs) were in *situ* generated in cellulose matrix using *Ocimum sanctum* leaf extract as a reducing agent and aq. $CuSO_4$ solution by diffusion process. Some CuNPs were also formed outside the film in the solution which were separated and viewed by Transmission electron microscope and Scanning electron microscope (SEM). The composite films showed good antibacterial activity against *Escherichia coli* bacteria when the CuNPs were generated using higher concentrated aq. $CuSO_4$ solutions. The cellulose, matrix and the composite films were characterized by Fourier transform infrared spectroscopic, X-ray diffraction, thermogravimetric analysis and SEM techniques. The tensile strength of the composite films was lower than that of the matrix but still higher than the conventional polymers like polyethylene and polypropylene used for packaging applications. These biodegradable composite films can be considered for packaging and medical applications.



## 1. Introduction

The usage of synthetic polymers in general and polymer composites in particular is ever increasing. But unfortunately, the synthetic polymers and their composites are non-biodegradable and at the time of disposal pose many environmental problems. Moreover, the synthetic polymers are derived from petroleum sources which are fast depleting. In order to avoid this white pollution and to save precious petroleum sources, the present trend is switched towards using biodegradable polymers from renewable sources. In this direction, some workers developed completely biodegradable polymer composite films for packaging and medical applications. Some of the developed completely biodegradable polymer composites include wheat protein isolate/*Hildegardia populifolia* natural fabric (Jagadeesh, Jeevan Prasad Reddy, Varada Rajulu, & Li, 2011), soy protein isolate (Jeevan Prasad Reddy, Varada Rajulu, Arumugam, Naresh, & Muthukrishnan, 2009), polypropylene carbonate/short lignocelllose fiber *H. populifolia* (Li, Meng, Wang, Varada Rajulu, & Tjong, 2004), Polylactic acid/*Sterculia urens* uniaxial fabric biocomposites (Jayaramudu et al., 2013a), Polypropylene carbonate/Eggshell powder (Feng, Ashok, Madhukar, Zhang, Zhang, Obi Reddy & Varada Rajulu, 2014) etc. But among all the renewable matrices, cellulose is an abundantly available natural source. Further, cellulose has good tensile strength and modulus compared to conventional synthetic polymers like polyethylene and polypropylene. In this direction, some researchers prepared the composites using cellulose as matrix and different fillers like curcumin (Luo, Varaprasad, Venkata Subba Reddy, Varada Rajulu, & Zhang, 2012), *S. urens* short fibers (Jayaramudu et al., 2013a,b), spent tea leaf powder (Duan et al., 2016) and *Thespesia lampas* short fibers (Ashok et al., 2015). For medical applications, composite films with antibacterial activity are required. In this direction, in general, silver nanoparticles are preferred as they have good antibacterial activity. Unfortunately, silver salts used for generating nano silver particles are expensive. As an alternative, some workers tried to generate copper nanoparticles which are cheaper. In this direction, flexible cellulose-copper nanoparticles composite films through in situ coating were prepared which showed highly single-side conductive performance but lower tensile strength than the cellulose matrix (Jia, Dong, Zhou, & Zhang, 2014). There are many methods of generating metal nanoparticles and among them chemical and biological methods are simple. Recently many workers generated copper nanoparticles using extracts of different leaves such as tea leaf and coffee powder (Sutradhar, Saha, & Maiti, 2014), plant tea for genera-

* Corresponding author.
*E-mail addresses:* avaradarajulu@gmail.com, arajulu@rediffmail.com (A. Varada Rajulu).

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tion of ultrasmall copper nanoparticles (Brumbaugh, Cohen, & Angelo, 2014), *Cassia alata* flowers (Jayalakshmi & Yogamoorthi, 2014), *Eucalyptus* plant leaves (Kulkarni, Suryawanshi, & Kulakarni, 2015), *Gymnema sylvestre* (Heera, Shanmugam, & Ramachandran, 2015), *Ocimum sanctum* (Kulkarni & Kulkarni, 2013) etc. Most of the workers concentrated in generating the metal nanoparticles which can be later dispersed in polymer matrices. The antibacterial activity and broad spectrum biocide effects of CuNPs and their oxides was already established (Candy, Behnke, & Strickland, 2011; Jamshidi & Jahangiri-red, 2014). In another work, CuNPs were synthesized using modified polyol method and their antibacterial activity against *Micrococcus luteus*, *Staphylococcus aureus*, *Escherichia coli*, *Klebsiella pneumoniae*, and *Pseudomonas aeruginosa* was reported (Ramyadevi, Jeyasubramanian, Marikani, Rajkumar, & Rahuman, 2014). CuNPs were also synthesized by ginger extract and their antimicrobial activity was reported (Subhankari & Nayak, 2013).

The polymer nanocomposites can be made mainly by two methods—(1) dispersion of already prepared metal nanoparticles in a suitable polymer matrix and (2) i*n situ* generation of the metal nanoparticles inside the matrices. Dispersion of metal nanoparticles in polymer matrices often lead to their agglomeration and hence whenever possible, *in situ* generation inside the matrices is preferable (He, Kunitake & Nako, 2003; Maneerung, Tokura, & Rujiravanit, 2008; Dallas, Sharma, & Zboril, 2011). In the present work, the authors made an attempt to generate the copper nanoparticles (CuNPs) *in situ* in the cellulose matrix by a simple two step process at ambient conditions. In the first stage, the regenerated cellulose wet films were immersed in 10 wt.% *O. sanctum* (locally known as Tulasi) leaf extract and allowed some of it to diffuse into the wet films. In the second step, the leaf extract diffused wet films were immersed in different concentrated aq. copper sulfate solutions and allowed the copper sulfate solution to react with leaf extract inside the film to generate CuNPs *in situ*. Besides the formation of stable CuNPs inside the composite films, the metal nanoparticles were also found to form outside the films in the solution. The authors selected *O. sanctum* leaves in the present study because they possess many medicinal properties. The therapeutic uses of *O. sanctum* and its pharmacological actions were already reported in the literature (Prakash & Gupta, 2005). Eugenol (l-hydroxy-2-methoxy-4-allylbenzene), the active constituent present in *O. sanctum* L., was found to be largely responsible for its therapeutic potentials. Eugenol and the essential oils have been found to reduce raised blood sugar, triglyceride and cholesterol levels. Further, these have also been observed to possess membrane stabilizing properties on synaptosomes, erythrocytes and mast cells which account for the therapeutic potentials of *O. sanctum* in management of neurological such as convulsions and epilepsy, inflammatory and allergic disorders. The CuNPs generated outside the film were observed with transmission electron microscope (TEM) and scanning electron microscope (SEM) and those formed inside the composite films by SEM for the particle size distribution. The dried cellulose/CuNP composite films were characterized by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA), Tensile and antibacterial tests.

## 2. Materials and methods

### 2.1. Materials

In the present work, cotton linter pulp (with a degree of polymerization Dp of 620) supplied by Hubei Chemical Fiber Co., Ltd. (Xiangfan, China) was used. LiOH, $CuSO_4{\cdot}5H_2O$ and urea were supplied by S.D. Chemicals, India and were used without further purification. Ethyl alcohol was supplied by Jebsen & Jessen Co., Germany. The *O. sanctum* leaves were collected from local area and washed thoroughly with distilled water before the extract was made.

### 2.2. O. sanctum *leaf extraction*

The cleaned *O. sanct*um leaves were cut into small pieces and 10 wt.% leaves were added to distilled water and heated to 80 °C for 20 min. The decant was separated, filtered and stored till further use.

### 2.3. *Dissolution of cellulose*

For dissolving cellulose, we followed the procedure described elsewhere (Cai & Zhang, 2005). The solution of aqueous (8 wt.% LiOH + 15 wt.% urea) was prepared and cooled to −12.5 °C. To this pre cooled solution, 4 wt.% cotton linter pulp was added and stirred vigorously at room temperature. Within a period of 2 min, a clear solution of cellulose was obtained. The undissolved pulp and other impurities if any were removed by centrifuging the solution at a speed of 7200 rpm and temperature of 5 °C for 15 min. This stock solution was stored at 5 °C till it was used.

### 2.4. *Preparation of cellulose wet films with diffused leaf extract*

The cellulose solution was cast on glass plates and regenerated with alcohol bath. The regenerated wet films were washed thoroughly in distilled water to remove the alcohol and salts remaining in them if any. These wet films were then kept in leaf extract in a beaker for about two hours to ensure its uniform diffusion into the films.

### 2.5. *Preparation of Cellulose/CuNP composite films*

Copper sulfate solutions of different concentrations in the range of aq.1 mM to 250 mM were prepared. Each concentrated solution was taken in separate beakers and to each, the leaf extract diffused wet films were added and stirred with the help of a magnetic stirrer at 100 rpm for about 2. During this period, the color of the wet films gradually changed from light brown to dark brown indicating the *in situ* generation of CuNPs in the matrix. These films were washed thoroughly with water and dried at room temperature. The dark brown color of the composite wet films remained unchanged in spite of washing thoroughly with distilled water indicating the formation of stable nanoparticles inside the films.

### 2.6. *FTIR spectroscopic analysis*

The FTIR spectra of cellulose, cellulose with leaf extract (matrix) and the composite films were recorded on a Smart iTR ATR Nicolet is 10 FTIR spectrophotometer. All the spectra were recorded in the 4000–500 $cm^{-1}$ range with 32 scans in each case at a resolution of 4 $cm^{-1}$.

### 2.7. *Morphology*

One mg/ml of aqueous suspension of CuNPs was prepared and sonicated for half an hour. Then the suspension was drop casted onto copper coated carbon grids and kept for drying overnight. Then the images were captured using Hitachi electron microscope model H-800 at an accelerating voltage of 300 kV. The CuNPs formed outside the film were also observed in Zeiss O 18 scanning electron microscope operated at an accelerating voltage of 10 kV. In order to observe the distribution and size range of the nanoparticles formed inside the films, their cryogenically fractured surfaces