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Green synthesis of silver nanoparticles using polysaccharides extracted from marine macro algae

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ABSTRACT

Green synthesis of nanoparticles that have environmentally acceptable solvent systems and eco-friendly reducing agents is of great importance. The aim of this work was to synthesis of silver nanoparticles (AgNPs) using water soluble polysaccharides extracted from four marine macro-algae, namely, *Pterocladia capillacae (Pc)*, *Jania rubins (Jr)*, *Ulva faciata (Uf)*, and *Colpmenia sinusa* (Cs) as reducing agents for silver ions as well as stabilizing agents for the synthesized AgNPs. The formed Ag-NPs have been confirmed by UV–Vis spectroscopy, FTIR analysis and TEM. The resultant Ag-NPs colloidal solutions were applied to cotton fabrics in presence and absence of citric acid (CA) or a binder (B). The antimicrobial activity of the treated fabrics was evaluated. The results revealed that the antimicrobial activity depends on type of the fabric treatment, size of the synthesized Ag-NPs and the algal species used for polysaccharides extraction.

1. Introduction

Synthesis of metal nanoparticles has been demonstrated by many physical and chemical means (Gao & Cranston, 2008; Rodriguez-Sanchez, Blanco, & Lopez-Quinetela, 2000; Sailaja, Amareshwar, & Chakravarty, 2011). Because most of these methods are capital intensive, toxic, non eco-friendly and have low productivity, it is a need of today's nanotechnology to adopt a variety of green routes for synthesis of nanoparticles. Amongst these are those concerned with plant extract (Gilaki, 2010), bacteria (Saifuddin, Wong, & Nur Yasumira, 2009), fungi (Balaji, Basavaraja, Bedre, Prabhakar, & Venkataraman, 2011), enzymes (Schneidewind et al., 2012) and algae (Sahayaa, Rajesh, & Rahi, 2012). These biosynthesis routes are currently under wide exploration (Bansal et al., 2005). Due to their amenability to biological functionalization, the biosynthesized nanoparticles are finding important applications in the field of medicine, in particular that related to the antimicrobial activity (Dykman & Khlebtsov, 2012). The antimicrobial potential of metal-based nanoparticles has led to its incorporation in consumer, health-related and industrial products (Albrecht, Evans, & Raston, 2006; Khanna, 2008; Wiechers & Musee, 2010). Among all the metal nanoparticles, silver nanoparticles (SNPs) have high inhibitory and bactericidal effects (Cho, Park, Osaka, & Park, 2005). Kim et al. (2007) reported that the antimicrobial mechanism of SNPs is due to the formation of free radicals and subsequent free radical induced membrane damage. Antibacterial activity of SNPs largely has been studied with human pathogenic bacteria, mainly *Escherichia coli* and *Staphylococcus aureus* (Shrivastava et al., 2007).

The application of nanoparticles to textile materials has been the object of several studies aimed at producing finished fabrics with different performances. For example nano-Ag has been used for imparting antibacterial properties (Durán, Marcato, De Souza, Alves, & Esposito, 2007), nano-TiO2 for UV-blocking and self-cleaning properties (Qi et al., 2007; Xin, Daoud, & Kong, 2004) and ZnO nanoparticles for antibacterial and UV-blocking properties (Vigneshwaran, Kumar, Kathe, Varadarajan, & Prasad, 2006; Wang, Xin, & Tao, 2005). In the last few years, the market for antimicrobial textiles has shown double digit growth. This growth has been fuelled by the increased need of consumers for fresh, clean, and hygienic clothing. Extensive research is taking place to develop new antimicrobial finishes. The Nanosilver is a powerful and natural antimicrobial agent that has been proven highly effective in fighting a whole range of microbes. Acting as a catalyst, it reportedly disables the enzyme that one-celled bacteria, viruses, and fungi need for their oxygen intake without causing corresponding harm to human enzymes or other parts of the human body chemistry. The result is the destruction of disease-causing organisms without any detrimental effects on the surrounding human tissue (Papaspyrides, Pavlidou, & Vouyiouka, 2009).

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Based on the fact that utilization of plants in synthesis of nanoparticles is quite novel leading to truly green chemistry which provide advancement over chemical and physical method as it is cost effective and environment friendly easily scaled up for large, the present work aims to establish a novel environmentally safe method for preparation of silver nanoparticles using polysaccharides extracted from marine macro-algae. These polysaccharides have a dual effect as they act as reducing agents of silver ions and as stabilizing agents for the formed silver nanoparticles. The so-prepared nano-sized silver colloids were applied onto cotton fabrics in absence and presence of citric acid or a Binder and the antimicrobial efficacy of the treated samples was evaluated.

2. Experimental

2.1. Materials

2.1.1. Algae

The red {*P. capillacae (Pc) and J. rubins (Jr)*}, brown {*C. sinusa* (Cs)}, and green {*U. faciata (Uf)*} algae were collected from along the coast of Abo-Qire, Alexandria, Cairo, Egypt, in March, May and September 2011, respectively. The algal samples were brought to the laboratory in an ice box and cleaned thoroughly with fresh water, the epiphytes were removed. The cleaned algae were dried in shade at room temperature and well grinned.

2.1.2. Fabrics

Desized, scoured, and bleached 100% cotton fabric, was kindly supplied from El-Mahalla Company for Spinning and Weaving, El-Mahalla El-Kubra, Egypt.

2.2. Methods

2.2.1. Extraction of water soluble polysaccharides

5 g of dry algal powder were extracted in distilled water at 80 °C for 3 h. The extracts were filtered and concentrated under reduced pressure at temperature not exceed 40 °C. The hot water soluble polysaccharides were precipitated by the addition of 4-fold volume of 95% (v/v) ethanol and the precipitated polysaccharides were filtered, washed twice with absolute ethanol and dried at 40 °C to obtain the crude hot water soluble polysaccharides (CHWPS).

2.2.2. Chemical analysis of CHWPS

Moisture and total ash were estimated using the method reported by AOAC (1990). The protein content was estimated as total nitrogen by the procedure adopted by Pearson using micro-Kjeldahl method (Pearson, 1976). Crude protein was subsequently calculated by multiplying the nitrogen content (expressed as % N) by a factor of 6.25. Sugars were determined by the GLC analysis according to Ronald method (1991).

2.2.3. Acid hydrolysis of polysaccharides

The precipitated polysaccharides (0.1 g) were added to 10 ml 1 N H_2SO_4 and heated in a boiling water bath for 5 h to hydrolyze polysaccharides. $BaCO_3$ was added then centrifuged and the precipitate was washed twice by water, then the solution was evaporated until the volume reached 2 ml hydrolyzate.

2.2.4. Silylation of the polysaccharide hydrolyzate (Ronald, 1991)

A part of the hydrolyzate solution (0.5 ml) was evaporated in a small screw-topped septum vials to dryness under stream of nitrogen at 40 °C. When almost dry, 0.5 ml isopropanol was added and the drying was completed under stream of nitrogen until a dry solid residue remained. 0.5 ml of 2.5% hydroxylamine hydrochloride in pyridine was added, mixed and heated for 30 min at 80 °C then allowed to cool. One ml of trimethylchlorosilane: N,O-bis-(trimethylsilyl) acetamide (1:5 by volume) was added, mixed and heated for 30 min at 80 °C.

Table 1
Conditions of GLC analysis of the polysaccharide hydrolyzate.

Column	ZB-1701, 30 m × 0.25 m × 0.25 μm,
Stationary	14% cyanopropyl phenyl methyl
Carrier gas	Helium at 1.2 ml/min,10.6 psi
Temperature programming	Initial temperature: 150 °C for 2 min with a rate 7 °C/min, final temperature: 200 °C for 20 min.
Injector chamber temperature	250 °C
Detector	FID at 250 °C

2.2.5. GLC analysis of the polysaccharide hydrolyzate

1 μl of the silylated sugars was subjected to GLC analysis adopting the conditions listed in Table 1.

2.2.6. Synthesis of silver nanoparticles (Ag-NPs)

30 mg of CHWPS extract of each alga was dissolved in 90 ml of sterile distilled water with continuous stirring at 70 °C. 1 ml of 0.1 mM $AgNO_3$ solution was added to the obtained solution dropwise with continuous stirring and the solution pH was adjusted at 10. The final volume was completed to 100 ml by sterile distilled water and kept in a magnetic stirrer at 70 °C under constant stirring for 20 min. The reduction of silver ions to silver nanoparticles was routinely monitored by visual inspection of the solution as well as by UV–vis spectra and TEM.

2.2.7. Characterization of silver nanoparticles

2.2.7.1. UV–visible spectral analysis. The color change of the reaction medium from pale yellow to dark brown was checked periodically and the bioreduction of silver ions was monitored by periodic sampling of solution and subsequently measuring UV Visible spectra of the samples. UV–vis spectra of these samples were monitored as a function of the reaction time on UV–vis spectrophotometer (T80 UV/vis, PG Instruments Ltd, England).

2.2.7.2. TEM analysis. The structural characterization of Ag-NPs was carried out by Transmission electron microscopy (TEM) (JEOL-JEM-1200, Japan). The sample placed on the carbon coated copper grid, making a thin film of sample on the grid and extra sample was removed using the cone of a blotting paper and kept in grid box sequentially.

2.2.7.3. FTIR analysis. To remove any free biomass residue or compound that is not the capping ligand of the nanoparticles, the residual solution of 100 ml after reaction was centrifuged at 5000 rpm for 10 min and the resulting suspension was redispersed in 10 ml sterile distilled water. Thereafter, the purified suspension was freeze dried to obtain dried powder. Finally, the dried nanoparticles were analyzed by using JASCO, FT/IR-b 100 spectrophotometer (Japan).

2.2.8. Treatment of cotton fabrics

Before being used, cotton fabrics were washed and dried. Experiments were performed on samples with maximum dimension of 30 cm × 15 cm. The dried cotton samples were subjected to two separate treatments. In the first one, the fabrics were, individually, treated with 2% citric acid (CA) and 1% Binder (printo® FX based on acrylate) solutions as well as Ag-NPs colloidal solution at concentration of 108 ppm using pad/dry technique. The second treatment embraced padding of cotton fabrics with Ag-NPs colloidal solution containing either 2% CA or 1% Binder. After padding, all treated samples, encompassing, CA-cotton, Binder-cotton, AgNPs-cotton,