Carbohydrate Polymers 96 (2013) 403–410

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

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

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

H.M. El-Rafie[a,*], M.H. El-Rafie[b], M.K. Zahran[c]

[a] Pharmacognosy Department, National Research Centre, Dokki, Cairo 12311, Egypt
[b] Textile Research Division, National Research Centre, Dokki, Cairo 12311, Egypt
[c] Chemistry Department, Faculty of Science, Helwan University, Ain-Helwan, Cairo 11795, Egypt

ARTICLE INFO

Article history:
Received 12 February 2013
Received in revised form 12 March 2013
Accepted 23 March 2013
Available online 25 April 2013

Keywords:
Biosynthesis
Silver nanoparticles
Marine macro-algae
Antimicrobial
Cotton fabrics

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).

* Corresponding author. Tel.: +20 201065021666.
E-mail address: hanaelrafie@yahoo.com (H.M. El-Rafie).

0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.03.071

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,

Table 2
Composition of the hot water extracts of the algal polysaccharides.

Algae	Yield	Moisture	Ash	Protein
U. faciata	8.40	27.5	19.7	5.3
P. capillacae	6.46	17.6	20.0	4.9
J. rubins	5.63	07.9	18.1	3.2
C. sinusa	4.33	13.1	17.4	4.2

CA/AgNPs-cotton and Binder/AgNPs–cotton were squeezed to 100% wet pick up at constant pressure, then dried at 70 °C for 3 min, followed by curing at 150 °C for 2 min.

2.2.9. Characterization of the treated cotton fabrics

2.2.9.1. Antimicrobial activity. The antibacterial activities of the untreated cotton fabric (control), fabrics treated with CA, Binder (B), Ag-NPs, CA/Ag-NPs and B/Ag-NPs were, independently, quantitatively evaluated by using plate count agar according to the AATCC test 100–1999. The species of microorganisms used were *E. coli* AATCC 2666 (gram −ve) and *S. aureus* AATCC 6538 (gram +ve). These bacteria were singly inoculated into tubes containing 5 ml BHI (Brain Heart Infusion Broth) sterile suspension. Such suspension was adjusted spectrophotometricaly according to Koo et al. (2000), who used the optimal density at 800 nm to match the turbidity of 1.5×10^8 colony forming unit (CFU) ml^{-1} (equivalent to 0.5 Mc Farland standard).

A small volume of the previous microorganisms inoculums (10 μl) was transferred to sealed jar containing 1 g of fabric sample in addition to 50 ml normal saline. The jars were incubated at 37 °C for 24 h. 10 μl of the previous suspension were transferred on nutrient and Sabouraud dextrose agar for bacterial count. Antibacterial activity was expressed as percentage of reduction (R%) as follows:

$$R(\%) = \frac{A - B}{A} \times 100$$

where R is the reduction rate in the number of colonies, A is the number of bacterial colonies from untreated fabrics, and B is the number of bacterial colonies from treated fabrics (Duran et al., 2007).

2.2.9.2. Wash durability. The washing durability method for the antibacterial treated fabrics was assessed according to the AATCC test 61–1989. 1 gm sample was soaked in 40 ml solution containing 2 g/l Egyptol PLM (non ionic detergent).Washing was conducted for 20 min at 40 °C.

3. Results and discussion

Biosynthesis of nanoparticles by plant extracts is currently under exploitation. The development of biologically inspired experimental processes for the synthesis of nanoparticles is evolving into an important branch of nanotechnology. The present study deals with the synthesis of silver nanoparticles using water soluble polysaccharides extracted from the four marine macro-algae, namely, *P. capillacae (Pc) J. rubins (Jr) U. faciata (Uf)* and *C. sinusa* (Cs) and aqueous Ag+ ions. The approach appears to be eco-friendly and cost effective alternative to conventional methods of assembling silver nanoparticles. The results along with their appropriate discussion are given below.

3.1. Chemical analysis

Chemical analysis data of the crude polysaccharides (cps) obtained from the hot water extracts of the four studied algae are presented in Tables 2 and 3. The % yield has been calculated based on the dry weight of the alga taken for extraction; other parameters have been presented as the percentage of the extracted polysaccharides.

Results of Table 2 indicate that *U. faciata* has the highest cps yield, moisture and protein contents as compared to those of the other examined algae. The ash contents of the four examined algae were relatively high and this may be attributed to the sulphate contents and the associated metals of these algae.

Table 3 reveals that the polysaccharides hydrolyzate (psh) of *C. sinusa* (*Cs*) was the only hydrolyzate which contains alcoholic sugars (sorbitol 4.35%, mannitol 13.05%). Aldohexose sugars (glucose and galactose) were found in relatively high amount in psh of *J. rubins* (glucose, 13.23% and galactose, 22.23%), *C. sinusa* (glucose, 14.98%) and *P. capillacae* (galactose, 30.25%). The psh of *U. faciata* (*Uf*) contains mainly rhammnose (46.88%) and xylose (12.89%).

3.2. Silver nanoparticles

In this work, a well-stabilized Ag-NPs solution with a concentration of 108 ppm were prepared using 30 mg of the prepared polysaccharides from *C. sinusa*, *J. rubins*, *U. faciata* and *P. capillacae* algae as reducing agents for silver ions as well as stabilizing agents for the formed Ag-NPs. It is well known that the Ag-NPs exhibit brownish color in aqueous solution due to excitation of surface plasmon vibration in silver nanoparticles (Mulvaney, 1996). Therefore, reduction of silver ions to nanoparticles during experiments could be followed by color change from pale yellow to dark brown which was checked periodically by UV–vis spectroscopy, as illustrated in Fig. 1.

3.3. UV–vis spectroscopy

The UV–vis spectrum of silver nanoparticles (Fig. 1) was recorded from the reaction medium as a function of time (15, 30, 45, 60 min) using 30 mg of CHWPS extract of each alga with 0.1 mM $AgNO_3$. The samples showed similar behavior with maximum absorption peak ranging between 407–424 nm. As is evident the increase in intensity of brownish color during incubation time (15-60mn) at about 407–424 nm absorbance is due to increase in number of nanoparticles formed as a result of reduction of silver ions present in experimental solution. With increasing incubation time till 1 h, color change stopped, which suggested that almost all of silver ions altered to silver nanoparticles. As shown in Fig. 1, the plasmon bands are relatively broad with an absorbance tail in the longer wavelengths due to the size distribution of the particles. The broadening of the peak indicated that the particles are polydispersed. The stability of the formed Ag-NPs was proved by measuring its UV–vis absorbance after six months where no change in absorbance or shapes of peaks was noticed.

3.4. FT-IR spectroscopy

FT-IR measurements were carried out to identify the possible biomolecules accountable for the stabilization and for the reduction of the Ag+ ions and the capping of the bioreduced silver nanoparticles synthesized.

Fig. 2a–h show the FT-IR spectra of the polysaccharides extracted from *P. capillacae, J. rubins, U. faciata* and *C. sinusa* and their prepared Ag-NPs. Fig. 2a, c, e and g impart broad intense bands at 3419, 3424, 3421 and 3422 cm^{-1} which characterize the polysaccharides from *J. rubins*, *P. capillacae*, *U. faciata* and *C. sinusa*, respectively. These absorption frequencies are assigned to the OH group of the algal polysaccharides. The bands at 2926, 2925, 2928 and 2923 cm^{-1} can be assigned to the alkane C—H stretching or assigned to the secondary amine. The bands appearing at 1418, 1457, 1430 and 1428 cm^{-1} are assigned to the—C—O—O—group. The absorption bands observed at 1655,1636,1624 and 1617 cm^{-1}

Table 3
Constituents of sugars calculated as area percentage from the total chromatogram of GLC.

Algae	Xylose	Glucose	Mannose	Ribose	Fucose	Rhaminose	Arabinose	Galactose	Fructose	Sorbitol	Mannitol	Galacturonic	Glucoronic
U. faciata	12.89	7.92	0.24	0.58	–	46.88	4.04	1.07	–	–	–	0.46	2.93
P. capillacae	2.26	5.95	–	0.51	–	0.50	1.15	30.25	3.77	–	1.79	–	–
J. rubins	9.59	13.23	0.85	1.11	0.72	13.95	3.71	22.23	0.15	0.13	3.30	0.30	–
C. sinusa	0.98	14.98	3.21	–	19.96	5.99	1.73	4.38	10.96	4.35	13.05	7.84	–

can be assigned to the amide groups of protein or to the carbonyl stretching groups of the algal polysaccharides. The two bands at 1049 and 1078 cm^{-1} in the polysaccharides extracts of *J. rubins* and *P. capillacae* are corresponded to the S=O stretch of the sulphated polysaccharides or the C—N stretching of aromatic amine group whereas the bands at 1105 and 1104 cm^{-1} in polysaccharides extracts of *U. faciata* and *C. sinusa* are allocated to—C—O—groups of polyols of polysaccharides. The absorption bands at 875, 876, 863 and 870 cm^{-1} are assigned to—C—O—SO_4 of sulphated polysaccharides.

Previous studies have confirmed the fact that the carbonyl group from amino acid residues and proteins has the stronger ability to bind metal indicating that the proteins could possibly form a layer covering the metal nanoparticles (i.e. capping of silver nanoparticles) to prevent agglomeration and thereby stabilize the medium (Kanchana, Agarwal, Sunkar, Nellore, & Namasivayam, 2011).Besides, the extracted polysaccharides contain reducing sugars that possess the ability to reduce silver and synthesis the nanoparticles through biogenic routes

3.5. Transmission electron microscopy (TEM)

The transmission electron microscope has provided further insight into the morphology and size details of the formed silver nanoparticles. Representative TEM images and histograms of particle size distribution recorded from silver nanoparticle solutions are shown in Figs. 3 and 4. It is obvious that the formed nanoparticles are polydispersed and predominantly spherical with the maximum diameter size of 7,7,12 and 20 nm for those prepared from the polysaccharides of *U. faciata*, *P. capillacae*, *J. rubins* and *C. sinusa*, respectively. All the nanoparticles are well separated and no agglomeration was noticed.

3.6. Antimicrobial activity

The antimicrobial effect of the treated cotton fabrics on the gram +ve bacteria *S. aureus* and the gram −ve bacteria *E. coli* was investigated. For comparison purposes, the cotton fabrics were severally treated with CA, Binder (B), Ag-NPs, CA/Ag-NPs, and B/Ag-NPs, as

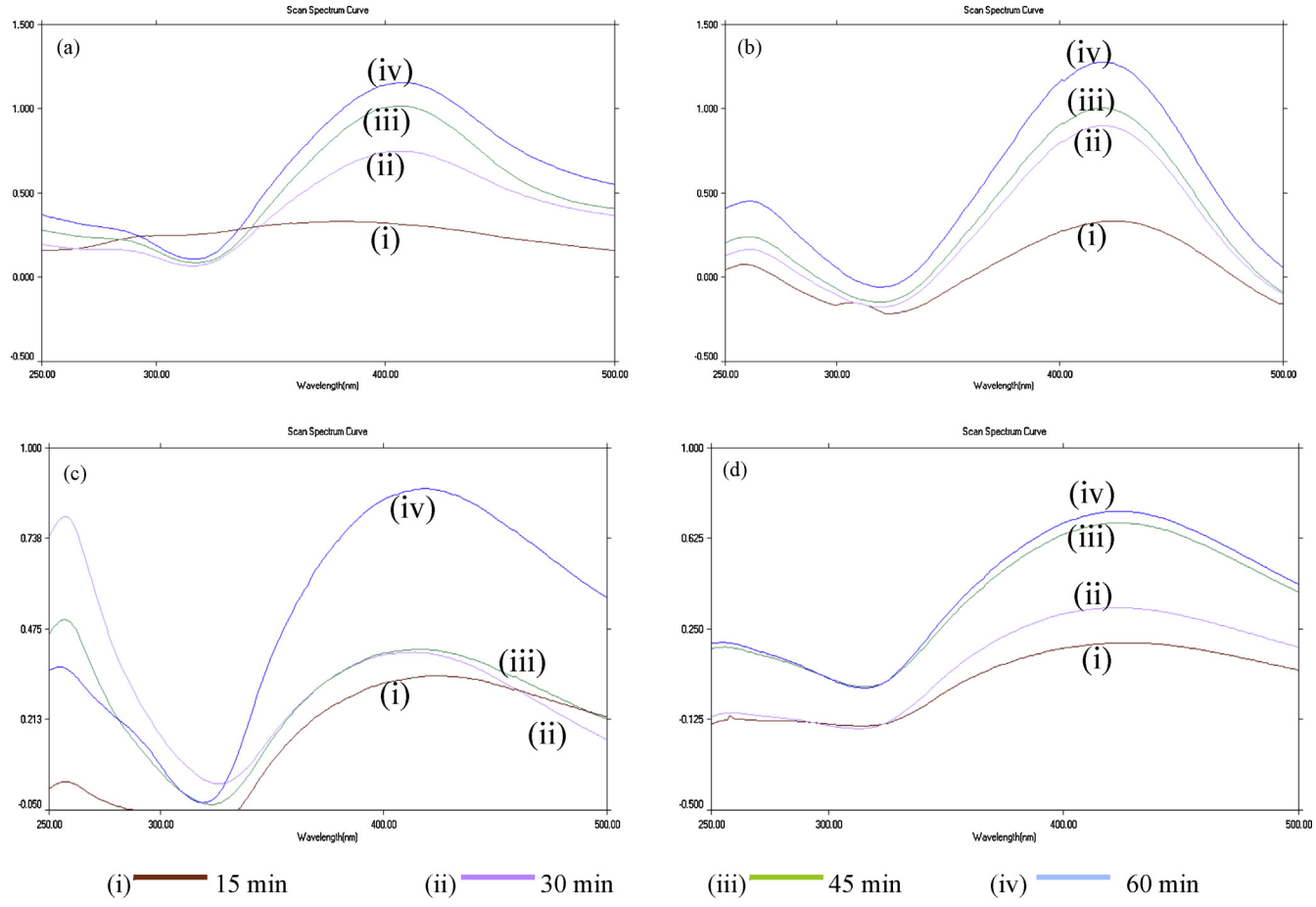

Fig. 1. UV–visible spectra of the prepared Ag-NPs as a function of the reaction time by polysaccharides of (a) *U. faciata*, (b) *P. capillacae, (c) J. rubins and (d) C. sinusa.*

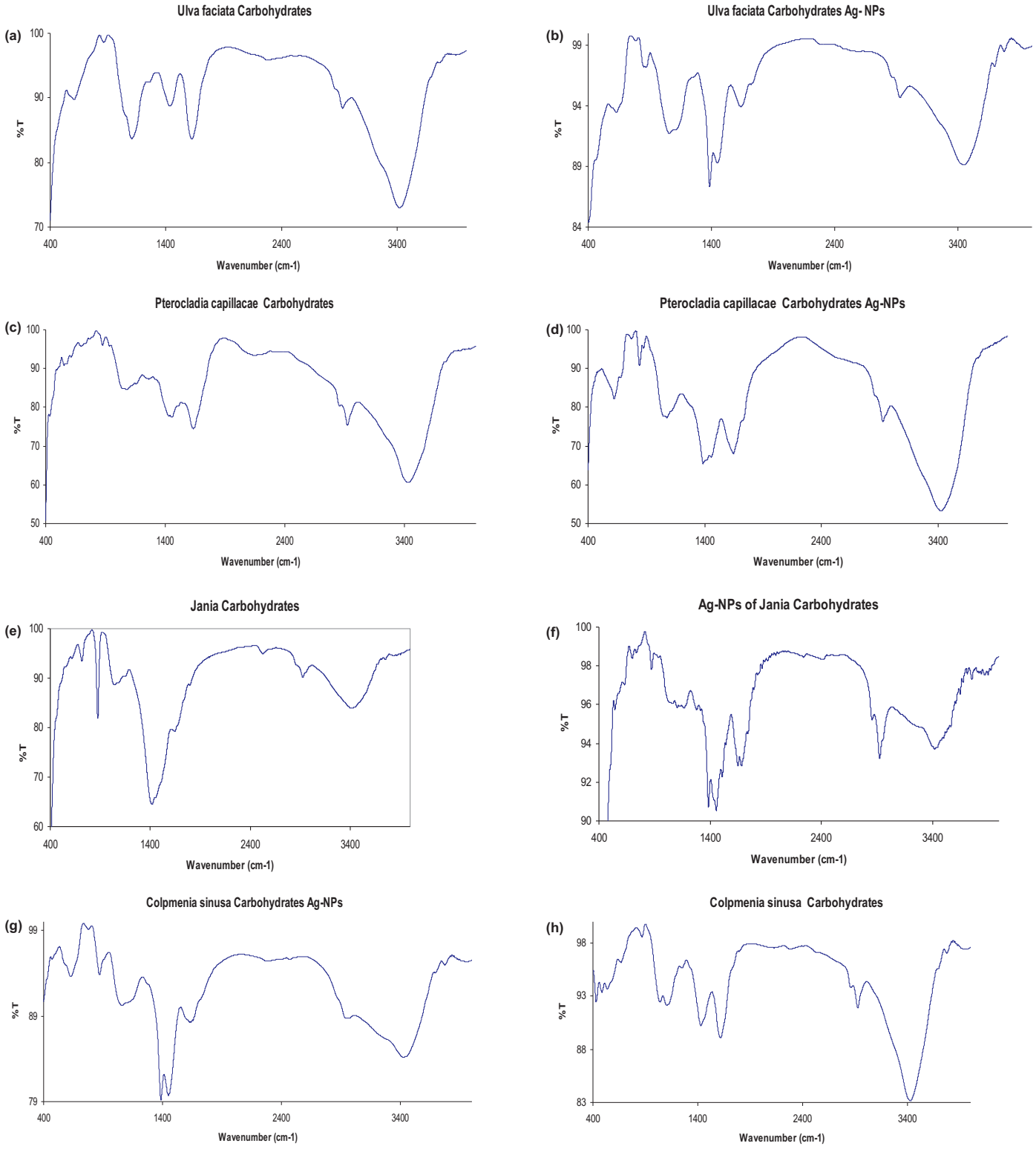

Fig. 2. FT-IR spectra of the polysaccharides and their prepared Ag-NPs.

mentioned earlier in the experimental section. The quantitative antibacterial assessment by the plate count agar shows that the cotton fabric sample displays different situations according to type of the fabric treatment. The results are summarized in Table 4. This table discloses that: (a) the AgNPs-treated fabrics have excellent antimicrobial activity, however it diminishes by increasing number of washing cycles. This holds true with all samples, irrespective of the algal and bacterial type used; (b) the CA-treated fabrics have better antibacterial effect before washing, however after 5 washing cycles they loss about 64% and after 10 cycles, they have no antibacterial activity; (c) the antibacterial activity of the Binder-treated fabrics was absent; and (d) presence of CA or Binder

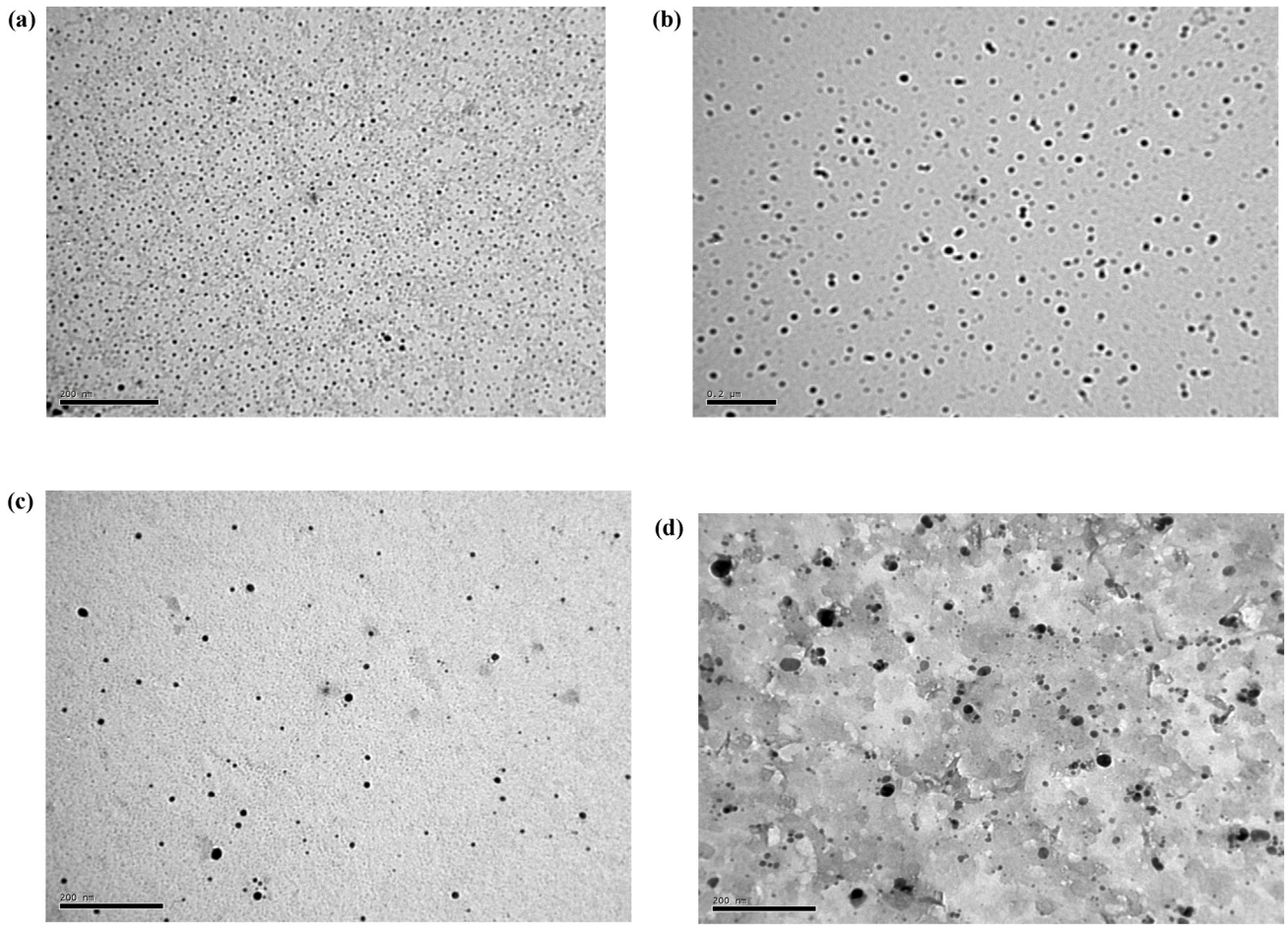

Fig. 3. TEM micrograph of Ag-NPs with a concentration of 100 ppm prepared by the polysaccharides of (a) *U. faciata*, (b) *P. capillacae*, (c) *J. rubins*, and (d) *C. sinusa*.

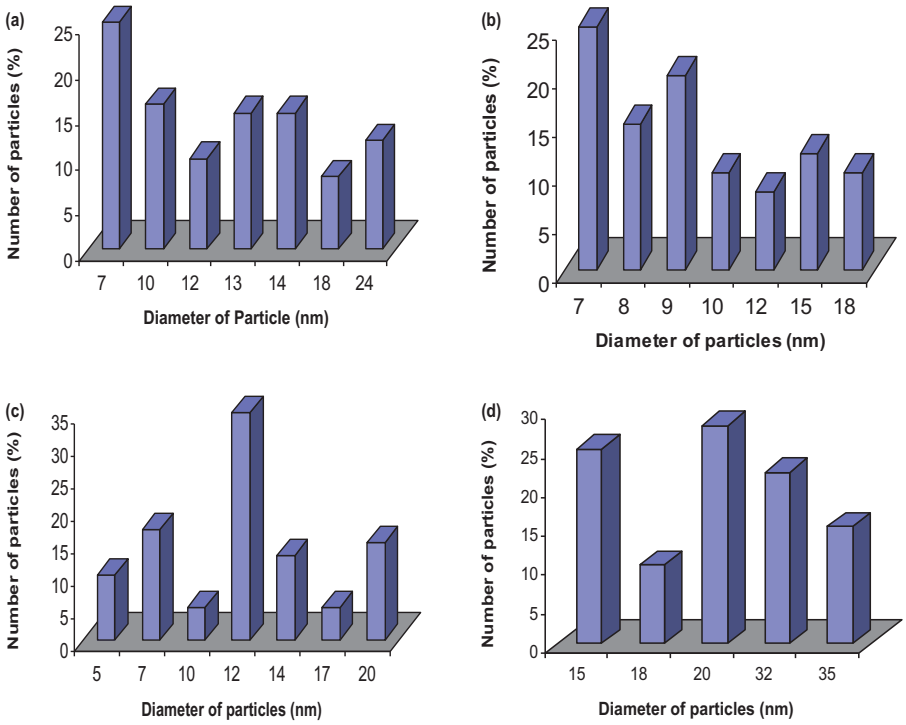

Fig. 4. Histogram of Particles Size Distribution of Ag-NPs Prepared by Polysaccharides of (a) *U. faciata*, (b) *P. capillacae*, (c) *J. rubins*, and (d) *C. sinusa*.

Table 4
Antibacterial effect of the treated cotton fabrics against *S. aurous* and *E. coli*[a].

Type of cotton fabric treatment	Bacterial Reduction (%)					
	S. aurous			*E. coli*		
	A	B	C	A	B	C
Ag-NPs of *U. faciata*	98	76.7	64.5	96	73	56
Ag-NPs of *P. capillacae*	98	75.5	63	95.7	71	52
Ag-NPs of *J. rubins*	96.4	71	59	92.5	68	50
Ag-NPs of *C. sinusa*	95.6	69	52	94	65	49.5
2% Citric acid (CA)	78	50	0	73	46	0
2%CA/Ag-NPs of *U. faciata*	100	100	87	100	95	83
2%CA/Ag-NPs of *P. capillacae*	100	100	86	100	91	78
2%CA/Ag-NPs of *J. rubins*	100	100	86	100	86	74
2%CA/Ag-NPs of *C. sinusa*	100	100	84	100	83	73
1% Binder (B)	0	0	0	0	0	0
1%B/Ag-NPs of *U. faciata*	100	100	100	100	95	95
1%B/Ag-NPs of *P. capillacae*	100	100	100	100	94	94
1%B/Ag-NPs of *J. rubins*	100	100	100	100	92	92
1%B/Ag-NPs of *C. sinusa*	98	98	98	93	93	93

[a] A, B and C represent the bacterial reduction (%) of the fabric samples before washing, after 5 and 10 cycles of washings respectively. For untreated fabric: A, B and C = zero, [Ag-NPs] = 108 ppm

with Ag-NPs overall the fabric surfaces and within the fiber pores and crevices greatly ameliorate its antibacterial potency. The latter reached 100%, in most instances.

The above findings are expected as both CA and Ag-NPs have antibacterial effects (Bischof, Flinčec, Budimir, & Kalenić, 2011; El-Rafie, Mohamed, Shaheen, & Hebeish, 2009; El-Rafie, Shaheen Th., Mohamed, & Hebeish, 2012; Eswaranandam, Hettiarachchy, & Johnson, 2004). The antimicrobial activity of CA, in general, is attributed to pH reduction, depression of internal pH of microbial cell by ionization of undissociated acid molecules, and disruption of substrate transport by altering cell membrane permeability or reduction of proton motive force (Beuchat, 1998). On the other hand, the bactericidal effect of Ag-NPs can be attributed to the attachment of Ag-NPs to the surface of the cell membrane disturbing permeability and respiration functions of the cell (Kvitek et al., 2008). It is also possible that Ag-NPs not only interact with the surface of membrane, but can also penetrate inside the bacteria (Morones et al., 2005). Additionally reports suggest that ionic silver strongly interacts with the thiol group of vital enzymes and inactivates them (Jeong, Yeo, & Yi, 2005; Lee, Park, Lee, Kim, & Park, 2007). The differences between gram −ve and gram +ve bacteria essentially rest in the structure of their respective cell walls. The gram −ve bacteria have a layer of lipopolysaccharide at the exterior, followed underneath by a thin (about 7–8 nm) layer of peptidoglycan consisting of linear polysaccharide chains cross-linked by hort peptides to form a three dimensional rigid structure (Madigan & Martinko, 2005). Although, the lipopolysaccharides are composed of covalently linked lipids and polysaccharides, they lack strength and rigidity. Negative charges on the lipopolysaccharides are attracted towards weak positive charges available on silver nanoparticle (Sui et al., 2006) thereby contributing to the sequestration of free Ag+ ions. Thus the relations between nanoparticles and the cell wall of bacteria would be facilitated by the relative wealth of negative charges on the gram-ve bacteria, which was amiable to the fact that growth of gram −ve bacteria was supplementary. Once inside the cell, nanoparticles would impede with the bacterial growth signaling pathway by amending tyrosine phosphorylation of putative peptide substrates decisive for cell viability and division. Thus, gram +ve bacteria may allow less Ag+ to reach the cytoplasmic membrane than the gram −ve bacteria.

Moreover, the Binder (B) used in the current work, although it has no antibacterial activity; it binds and/or traps the Ag-NPs overall the cotton fabric surfaces as well as within the fiber pores and crevices. This explains why the B/AgNPs-treated fabrics retains its highest antibacterial activity after the maximum washing cycles (Table 4).

4. Conclusion

Nanoparticles is an emerging field that has made its contribution to all spheres of human life. There is an ever-increasing need to develop environmentally benign processes in place of synthetic protocols involving toxic ingredients. As a result researcher in the field of nanoparticle synthesis and assembly focusing their attention on biological systems.

Here we described a rapid, low-cost, green approach and easily amenable for large-scale method for reducing silver nitrate solution to form Ag nanoparticles using polysaccharides extracted from marine macro algae. The biosynthesized Ag nanoparticles are stable for six months and have the ability to be immobilized on the cotton fibers bringing a good antimicrobial property to the final textile product and rendering it to be used as an antiseptic dressing or bandage, which is in high demand for biomedical applications.

References

Albrecht, M. A., Evans, C. W., & Raston, C. L. (2006). Green chemistry and the health implications of nanoparticles. *Green Chemistry*, *8*, 417–432.

American Association of Textile Chemists Colorists (1989). AATCC Test Method 61-1989, colorfastness to Laundering, Home and Commercial: Accelerated, AATCC Technical Manual, Vol. 68, 1993, p.94.

American Association of Textile Chemists Colorists. (1999). . *AATCC test method 100-1999, antibacterial finishes on textile materials: Assessment of AATCC technical manual* (Vol. 75) NC: 2000 Technical Manual of the American Association of Textile Chemists and Colorists, AATCC, Research Triangle Park.

AOAC. (1990). *Official methods of analysis* (15th edn., pp.). Washington DC: Association of Official Analytical Chemists.

Balaji, D. S., Basavaraja, S., Bedre, M. D., Prabhakar, B. K., & Venkataraman, A. (2011). Biosynthesis of silver nanoparticles by fungus *Trichoderma Reesei*. *Insciences Journal*, *1*(1), 65–79.

Bansal, V., Rautaray, D., Bharde, A., Ahire, K., Sanyal, A., Ahmad, A., et al. (2005). Fungus mediated biosynthesis of silica and titania particles. *Journal of Materials Chemistry*, *15*, 2583–2589.

Beuchat, L. R. (1998). Surface decontamination of fruits and vegetables eaten raw: A review. Geneva (Switzerland): Food Safety Unit/World Health Organization. WHO/FSF/FOS/98.2. Available at: http://www.who.int/fsf/fos982~1.pdf

Bischof, V. S., Flinčec, G. S., Budimir, A., & Kalenić, S. (2011). Cotton textiles modified with citric acid as efficient anti-bacterial agent for prevention of nosocomial infections. *Croatian Medical Journal*, *52*, 68–75.

Cho, K., Park, J., Osaka, T., & Park, S. (2005). The study of antimicrobial activity and preservative effects of nanosilver ingredient. *Electrochimica Acta*, *51*, 956–960.

Durán, N., Marcato, P. D., De Souza, G. I. H., Alves, O. L., & Esposito, E. (2007). Antibacterial effect of silver nanoparticles produced by fungal process on textile fabrics and their effluent treatment. *Journal of Biomedical Nanotechnology*, *3*, 203–208.

Dykman, L., & Khlebtsov, N. (2012). Gold nanoparticles in biomedical applications: Recent advances and perspectives. *Chemical Society Reviews*, *41*, 2256–2282.

El-Rafie, M. H., Mohamed, A. A., Shaheen, T. I., & Hebeish, A. (2009). Antimicrobial effect of silver nanoparticles produced by fungal process on cotton fabrics. *Carbohydrate Polymers*, *3*, 279–290.

El-Rafie, M. H., Shaheen Th., I., Mohamed, A. A., & Hebeish, A. (2012). Bio-synthesis and applications of silver nanoparticles onto cotton fabrics. *Carbohydrate Polymers*, *90*, 915–920.

Eswaranandam, S., Hettiarachchy, N. S., & Johnson, M. G. (2004). Antimicrobial activity of citric, lactic, malic, or tartaric acids and nisinincorporated soy protein film against *Listeria monocytogenes*, *Escherichia coli* O157:H7, and *Salmonella gaminara*. *Journal of Food Science*, *69*(3), FMS79–FMS84.

Gao, Y., & Cranston, R. (2008). Recent advances in antimicrobial treatments of textiles. *Textile Research Journal*, *78*(1), 68–72.

Gilaki, M. (2010). Biosynthesis of silver nanoparticles using plant extracts. *Journal of Biological Sciences*, *10*(5), 465–467.

Jeong, S. H., Yeo, S. Y., & Yi, S. C. (2005). The effect of filler particle size on the antibacterial properties of compounded polymer/silver fibers. *Journal of Materials Science*, *40*, 5407–5411.

Kanchana, A., Agarwal, I., Sunkar, S., Nellore, J., & Namasivayam, K. (2011). Biogenic silver nanoparticles from *spinacia oleracea* and *lactuca sativa* and their potential antimicrobial activity. *Digest Journal of Nanomaterials and Biostructures*, *6*, 1741–1750.

Khanna, A. S. (2008). Nanotechnology in high performance paint coatings. *Asian Journal of Experimental Sciences*, *21*, 25–32.

Kim, J. S., Kuk, E., Yu, K. N., Kim, J., Park, S. J., & Lee, H. J. (2007). Antimicrobial effects of silver nanoparticles. *Nanomedicine: Nanotechnology, Biology, and Medicine*, *3*, 95–101.

Koo, H., Gomes, B., Rosalen, P., Ambrosano, G., Park, Y., & Cury, J. (2000). In-vitro antimicrobial activity of propolis and *Arnica montana* against oral pathogens. *Archives of Oral Biology*, *45*, 141–148.

Kvitek, L., Panacek, A., Soukupova, J., Kolar, M., Vecerova, R., & Prucek, R. (2008). Effect of surfactant and polymers on stability and antibacterial activity of silver nanoparticles (NPAS). *The Journal of Physical Chemistry C*, *112*, 5825–5834.

Lee, H. Y., Park, H. K., Lee, Y. M., Kim, K., & Park, S. B. (2007). A practical procedure for producing silver nanocoated fabric and its antibacterial evaluation for biomedical applications. *Chemical Communications*, 2959–2961.

Madigan, M., & Martinko, J. (2005). *Brock biology of microorganisms* (11th edn., pp.). Englewood Cliffs, NJ: Prentice Hall.

Morones, J. R., Elechiguerra, J. L., Camacho, A., Holt, K., Kouri, J. B., Ramirez, J. T., et al. (2005). The bactericidal effect of silver nanoparticles. *Nanotechnology*, *16*, 2346–2353.

Mulvaney, P. (1996). Surface plasmon spectroscopy of nanosized metal particles. *Langmuir*, *12*, 788–800.

Papaspyrides, C. D., Pavlidou, S., & Vouyiouka, S. N. (2009). Development of advanced textile materials: Natural fibre composites, antimicrobial, and flame-retardant fabrics. *Journal of Materials: Design and Applications*, *223*, 91–102.

Pearson, D. (1976). *Chemical analysis of foods* (7th ed., pp.). London: Chuchill Livingstone., pp7-11

Qi, K., Chen, X., Liu, Y., Xin, J. H., Mak, C. L., & Daoud, W. A. (2007). Facile preparation of anatase/SiO_2 spherical nanocomposites and their application in self cleaning textiles. *Journal of Materials Chemistry*, *17*, 3504–3508.

Rodriguez-Sanchez, L., Blanco, M. C., & Lopez-Quinetela, M. A. (2000). Electrochemical synthesis of silver nanoparticles. *The Journal of Physical Chemistry B*, *104*, 9683.

Ronald, S. K., & Ronald, S. (1991). *Composition and analysis of foods*. England: Longman Scientific & Technical publishers., pp.182-235.

Sahayaa, K., Rajesh, S., & Rahi, J. M. (2012). Silver nanoparticles biosynthsis using marine Alga *Padina pavonica (Linn.)* and its microbicidal activity. *Digest Journal of Nanomaterials and Biostructures*, *7*(7), 1557–1567.

Saifuddin, N., Wong, C. W., & Nur Yasumira, A. A. (2009). Rapid biosynthesis of silver nanoparticles using culture supernatants of bacteria with microwave irradiation. *E-Journal of Chemistry*, *6*, 61–70.

Sailaja, A. K., Amareshwar, P., & Chakravarty, P. (2011). Different techniques used for the preparation of nanoparticles using natural polymers and their application. *International Journal of Pharmacy and Pharmaceutical Sciences*, *3*(Suppl. (2)), 45–50.

Schneidewind, H., Schüler, T., Strelau, K. K., Weber, K., Cialla, D., Diegel, M., et al. (2012). The morphology of silver nanoparticles prepared by enzyme-induced reduction. *Beilstein Journal of Nanotechnology*, *3*, 404–414.

Shrivastava, S., Bera, T., Roy, A., Singh, G., Ramachandrarao, P., & Dash, D. (2007). Characterization of enhanced antibacterial effects of novel silver nanoparticles. *Nanotechnology*, *18*, 225103.

Sui, Z. M., Chen, X., Wang, L. Y., Xu, L. M., Zhuang, W. C., Chai, Y. C., et al. (2006). Capping effect of CTAB on positively charged Ag nanoparticles. *Physica E.*, *33*, 308–314.

Vigneshwaran, N., Kumar, S., Kathe, A. A., Varadarajan, P. V., & Prasad, V. (2006). Functional finishing of cotton fabrics using zinc oxide-soluble starch nanocomposites. *Nanotechnology*, *17*, 5087–5095.

Wang, R. H., Xin, J. H., & Tao, X. M. (2005). UV-blocking property of dumbbell-shaped ZnO crystallites on cotton fabrics. *Inorganic Chemistry*, *44*, 3926–3930.

Wiechers, J. W., & Musee, N. (2010). Engineered inorganic nanoparticles and cosmetics – facts, issues, knowledge gaps and challenges. *Journal of Biomedical Nanotechnology*, *6*, 408–431.

Xin, J. H., Daoud, W. A., & Kong, Y. Y. (2004). A new approach to UV-blocking treatment for cotton fabrics. *Textile Research Journal*, *74*, 97–100.