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Development of antimicrobial jute packaging using chitosan and chitosan–metal complex

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ABSTRACT

Scoured jute fabrics were treated with chitosan (pre-dissolved in 1% acetic acid) under a variety of conditions. The latter were included chitosan concentration, fixation temperature and time. The chitosan-treated jute fabrics were subjected to five washing cycles after each cycle the fabrics were monitored for antimicrobial activity and nitrogen content. The antimicrobial activity was evaluated using two kinds of microorganisms, namely, *Staphylococcus aureus* (*S. aureus*) and *Candida albicans* (*C. albicans*). Results obtained show that, although scoured jute fabrics contain residual nitrogen content amount 0.22% it did not shows any antimicrobial activity towards *S. aureus* or *C. albicans*. Treatment of jute fabrics with chitosan improves only the antibacterial properties towards *S. aureus* whereas, antifungal properties remain intact. A similar study was carried out using chitosan–metal complex aiming to impart the jute fabric antimicrobial properties. In this regards, Ag^{1+}, Zn^{2+} and Zr^{2+} ions were allowed separately to form a complex with chitosan. It has been found that, jute fabrics treated with chitosan–metal complex show better antimicrobial properties than those fabrics treated with either chitosan or metal salt separately. Moreover, the jute fabrics treated with chitosan–Zn complex have higher antimicrobial properties compared with those samples treated with chitosan–Zr or chitosan–Ag complexes.

1. Introduction

Jute, a lignocellulosic natural fiber, has 58–68% α-cellulose, 12–14% lignin and 21–24% hemicellulose as a major constituent (Samanta, 1995). Traditionally and due to its inherent coarseness property, jute is being used as a low cost packaging material and also to some extent for producing floor covering and decorative items.

Recent food-borne microbial outbreaks are driving a search for innovative way to inhibit microbial growth in the foods while maintaining quality, freshness and safety. One option is to use packing to provide an increased margin of safety and quality. It is so feasible that, the next generation of food packaging will have antimicrobial properties. These packaging technologies could play a role in extending shelf-life of foods and reduce the risk from pathogens. Imparting antimicrobial properties for food packaging reduces, inhibit or retard the growth of microorganisms that may be present in the packed food or packaging material itself (Brody et al., 2001; Labuza & Breene, 1989; Rooney, 1995).

Chitin is the second most abundant polysaccharide found on earth next to cellulose. Chitin is the main component in the shells of crustaceans, such as shrimp, crab and lobster. Chitin is a polysaccharide very similar in structure to cellulose being composed of poly-2-acetamido-2-deoxy-D-glucose (Pigman & Horton, 1965).

Chitosan is a well-known derivative of chitin, the major difference being the degree of deacetylation (DAC), which is the same as relative amount of free amine (Smith, Koonce, & Hudsons, 1930). Generally, DAC less than 20% is for chitin and higher for chitosan. Chitosan is capable of undergoing many chemical modifications. Because it is amino polysaccharide, chitin and chitosan have been examined for many different applications due to their biodegradability, non-toxicity to mammals (Chandy & Sharma, 1990; Muzzarelli, 1973; Sco, Kanbara, & Ijima, 1986), cationic nature and antimicrobial activity (Muzzarelli, 1977; Roberts, 1992). Consequently, they have a variety of current and potential applications in biomedical products (Allan & Hadwiger, 1979), cosmetics (Ralston, Tracey, & Wrench, 1964), food processing (Yalpani, Johnson, & Robinhson, 1992), etc.

Chitosan has the highest chelating ability in comparison with other natural polymers (Varma, Deshpanda, & Kennedy, 2004). It has been realized, in recently years, that the mechanism of chitosan–metals complex formation is manifold and probably dominated by different processes taking place simultaneously such

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Table 1
Effect of chitosan concentration on the nitrogen content and antimicrobial activity of the treated jute fabrics.

Chitosan conc. (%)	Nitrogen content (%)	Increase in nitrogen content (%)	Inhibition zone (mm)	
			S. aureus	*C. albicans*
0.00	0.22	0.00	0.0	0.0
0.25	0.24	0.02	3.5	0.0
0.50	0.27	0.05	5.0	0.0
0.75	0.30	0.08	5.0	0.0
1.00	0.32	0.11	5.0	0.0
1.50	0.37	0.16	4.0	0.0
2.00	0.43	0.21	4.0	0.0

(a) Increase in N content (%) = N (%) of the treated sample – N (%) of untreated sample (blank).
(b) Zero chitosan concentration represents the untreated jute fabrics.
Conditions used: samples were padded in an aqueous solution of chitosan pre-dissolved in 1% acetic acid squeezed to a wet pick-up of 100%, dried at 85 °C for 5 min and cured at 120 °C for 3 min.

as adsorption, ion-exchange and chelation, under different conditions (Butelman, 1991).

Butelman (1991) patented the preparation of iron and other metal complexes with sulfonated derivatives of chitosan. It has been reported that wastewater containing 7 ppm Ni^{2+} after passing through a column of chitosan, showed Ni^{2+} contents of less than 0.1 ppm. Regeneration of the chitosan may be effected by buffered ammonium chloride (Randall, Randall, & McDonald, 1979).

The ability of chitosan to bind transition metal in presence of alkali and alkaline earth metal is well investigated (Deans & Dixon, 1992). The adsorption of Cu^{2+}, Hg^{2+}, Ni^{2+} and Zn^{2+} on chitosan with various particle sizes and as a function of temperature was studied at neutral pH (McKay, Blair, & Findon, 1989). Metal complexation by chitosan and its derivatives has been recently reviewed (Varma et al., 2004). Recently, chitosan–Zn complex attracted great interest for its potential use as medicament or nutriment (Paik, 2001; Tang & David, 2001; YoneKura & Suzuki, 2003). It is well known that both of chitosan and metal ions (Zn^{2+}, Zr^{2+} and Ag^{1+}) have the properties of disinfection and bactericide (Varma et al., 2004). After complexation of these metal ions with chitosan through nitrogen, oxygen, or combination of them, the binding are likely to leave some potential donor atoms which enhance its biological activity. So far, there are few reports on antimicrobial activity of chitosan–metal complex and also no work in the literature describing the use of chitosan–metal complex to impart an antimicrobial activity for jute fabric utilized as food packing. These indeed stimulate the present work, which has twofold objective: (a) studying the technical feasibility of utilization of chitosan and chitosan–metal complex to impart an antimicrobial properties to jute fabric; (b) to establish the optimum conditions for application of these compounds through detail investigation into major factors affecting this application such as chitosan or chitosan–metal complex concentration, fixation temperature and fixation time.

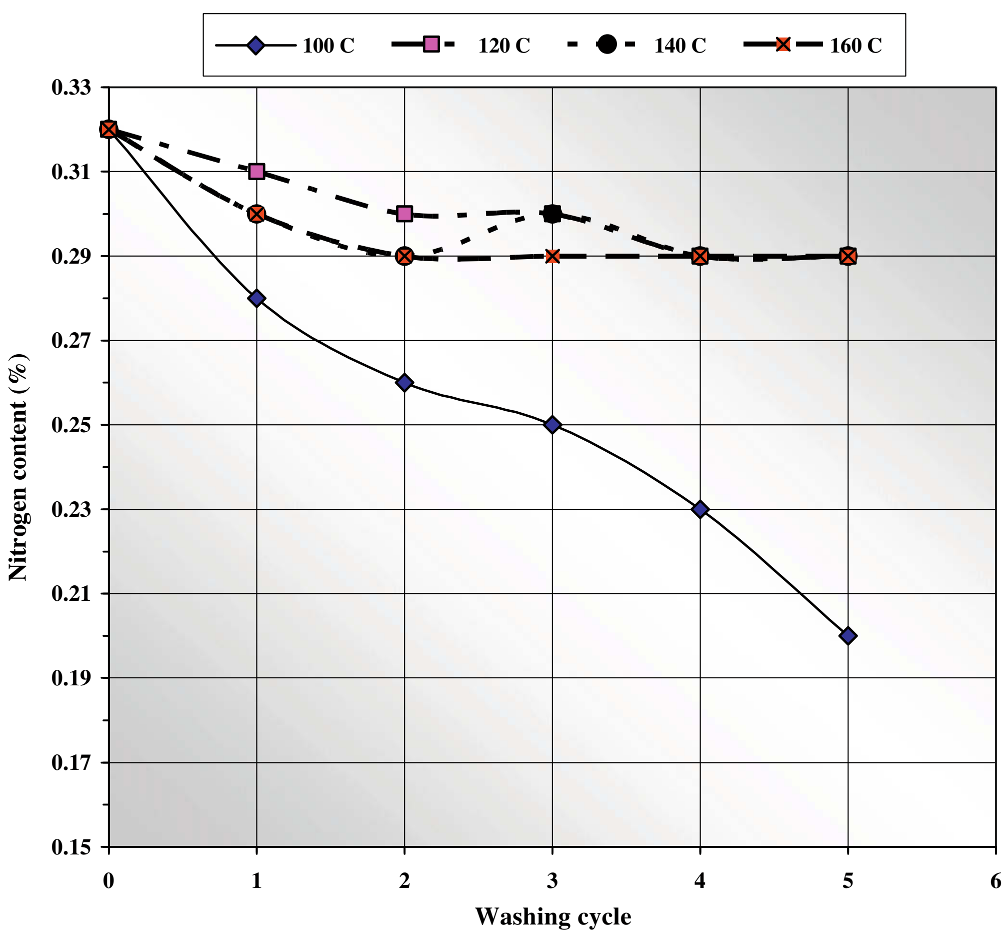


Fig. 1. Effect of curing temperature and washing cycles on the nitrogen content of chitosan-treated jute fabrics. Conditions used: jute fabrics were padded in 1% aqueous chitosan solution, squeezed to wet pick-up 100% dried at 85 °C for 5 min, cured for 3 min. Values at zero washing cycles represent the values before washing.

2. Experimental

2.1. Materials

Grey jute fabric was kindly supplied from Jute Company, Cairo, Egypt. The fabric was scoured using an aqueous solution containing NaOH, 40 g/l, Egyptol®, 5 g/L, at 95 °C for 30 min. The fabric was then washed several times with boiling water then washed with cold water and finally dried at ambient conditions. Chitosan was supplied from Vanson Inc., USA. It has a degree of deacetylation equal to 82.9%, and an average molecular weight of 160,000 Da.

Silver nitrate, zinc sulfate, zirconium sulfate tetra hydrate, hydrochloric acid, sodium hydroxide, boric acid, sulfuric acid, methylene blue, isopropyl alcohol, acetic acid, copper sulfate were of laboratory grade chemical, Egyptol® (non-ionic wetting agent based on ethylene oxide condensate) was of commercial chemicals.

2.2. Treatment of jute fabrics with chitosan

A known weight of chitosan was dissolved in an aqueous 1% acetic acid solution under mechanical stirring for 15 min. Jute fabrics were padded in two depth and nips in chitosan solution then squeezed to a wet pick-up of 100%. The jute fabrics were then dried at 85 °C for 5 min then cured at 100–160 °C for 1–5 min. Finally, the samples were washed with water at room temperature and dried at ambient conditions.

2.3. Treatment of jute fabric with chitosan–metal complex

Chitosan–metal complex was prepared according to a reported method (Hashem, El-Bisi, & Hebeish, 2003). The experimental technique was adjusted as follows.

A known weight of chitosan was dissolved in an aqueous 1% acetic acid solution under mechanical stirring at room temperature for 15 min. An exact known concentration from metal salt pre-dissolved in distilled water was added to the chitosan solution, and the stirring was continued for another 30 min at room temperature to allow the formation of chitosan–metal complex. Scoured jute fabric was padded in two depth and nips in solution then squeezed to a wet pick-up 100%. The treated jute fabrics were then dried at 85 °C for 5 min then cured at (100–140 °C) for different time interval (3–10 min). The samples were then washed several times with distilled water at room temperature and finally dried at ambient conditions.

In this regard, three kind of metal salts were used in our investigation, namely, silver nitrate [$AgNO_3$], zinc sulfate [$ZnSO_4$] and zirconium sulfate [$Zr(SO_4)_2 \cdot 4H_2O$].

2.4. Testing and analysis

2.4.1. Nitrogen analysis

Nitrogen content of treated and untreated jute fabric was determined according to Kjeldahl method (Vogel, 1975).

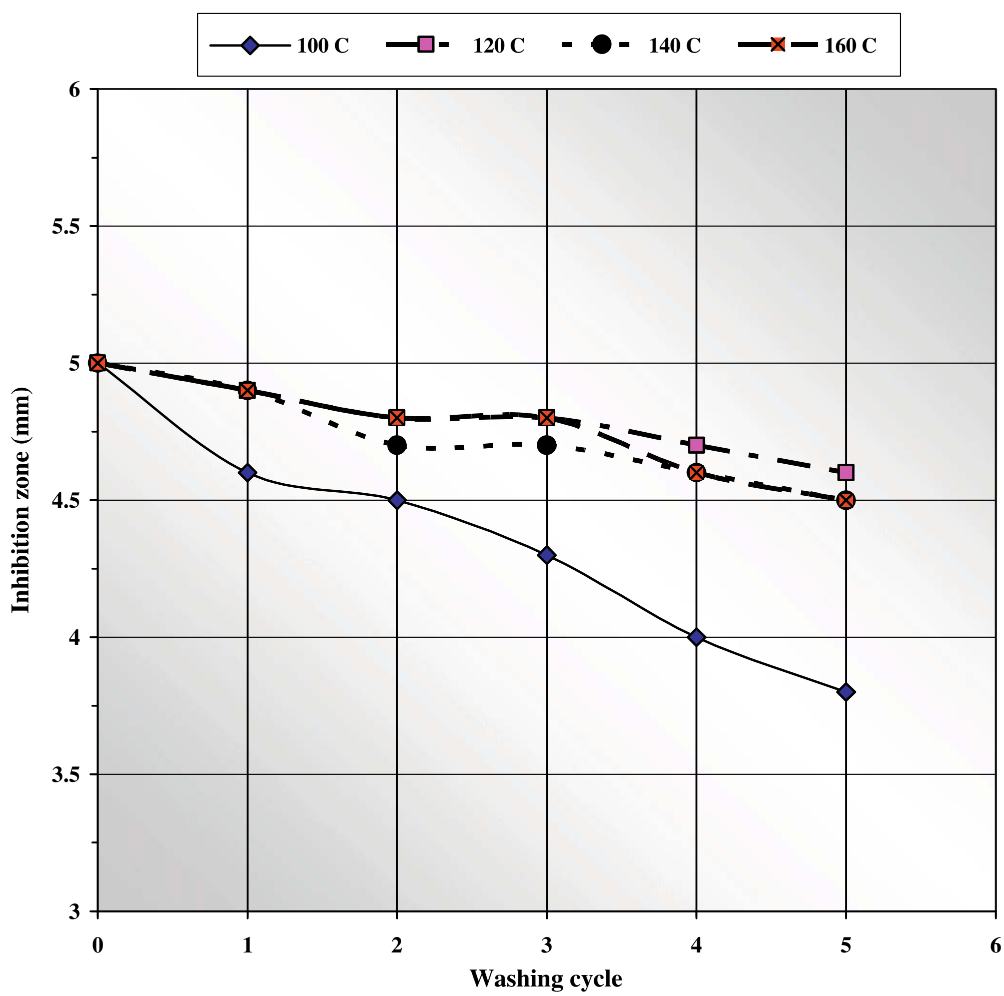


Fig. 2. Effect of curing temperature and washing cycles on the inhibition zone of chitosan-treated jute fabric against *S.a* (mm). Conditions used: jute fabrics were padded in 1% aqueous chitosan solution, squeezed to wet pick-up 100% dried at 85 °C for 5 min, cured for 3 min. Values at zero washing cycles represent the values before washing.

2.4.2. Antimicrobial activity test

Control and treated jute samples were tested for their antimicrobial activities against *Staphylococcus aureus* as Gram-positive bacteria and *Candida albicans* as a fungus. Microorganisms were supplied from the Department of Microbial Chemistry, Division of Genetic Engineering and Biotechnology, National Research Centre, Cairo, Egypt. The cultural medium used was prepared by mixing the following constituents: glucose, 10 g/L; yeast extract, 3 g/L; meat extract, 1.5 g/L; NaCl, 0.5 g/L and agar 20 g/L. The pH of the cultural medium was adjusted at 7 then sterilized at 120 °C for 30 min under pressure (Koneman, Allen, Jonda, & Win, 1994, chap. 19).

Antimicrobial activity was estimated according to AATCC Standard Test Method. The previously mentioned medium was poured in sterile Petri dishes (20 ml for each plate) and left to cool. These plates were inoculated with the test organism and left for 2 h. Discs of jute fabric samples (10 mm in diameter) were introduced to the plates with a sterile forceps and gently pressed to insure good contact with the solid medium. The plates were then kept in the refrigerators at 5 °C for 1 h to permit good diffusion before transferring them to an incubator at 37 °C for 24 h. The inhibition zones (mm) were then measured.

2.4.3. Metal ion determination

Metal ion content of jute fabric before and after treatment with chitosan–metal complex as well as those treated with metal salts were evaluated using "Flame Atomic Absorption Spectrometer", Varian Spectra A220. The experimental technique was adopted as follows: 0.5 g of dried jute fabric was dissolved in 50 ml 72% H_2SO_4 at 3 °C. The solution was completed to 250 ml using distilled water. Ten milliliters from this solution was diluted to 500 ml using distilled H_2O. Aliquot from the latter was subjected to "Flame Atomic Adsorption" determination. The metal ion content [C (ppm)] of jute fabrics was determined from the following equation:

$$C(\text{ppm}) = 2500A$$

where A is the value obtained from flame atomic adsorption spectrophotometer.

3. Results and discussion

3.1. Treatment of jute fabric with chitosan: effect of process parameters

3.1.1. Effect of chitosan concentration

Scoured jute fabrics were treated with chitosan (dissolved in 1% acetic acid) under a variety of conditions. The later were included chitosan concentration, fixation temperature and time. The fabrics were monitored for nitrogen content and antimicrobial activity and the durability of these properties on washing was also investigated. The latter was evaluated using two kinds of microorganisms,

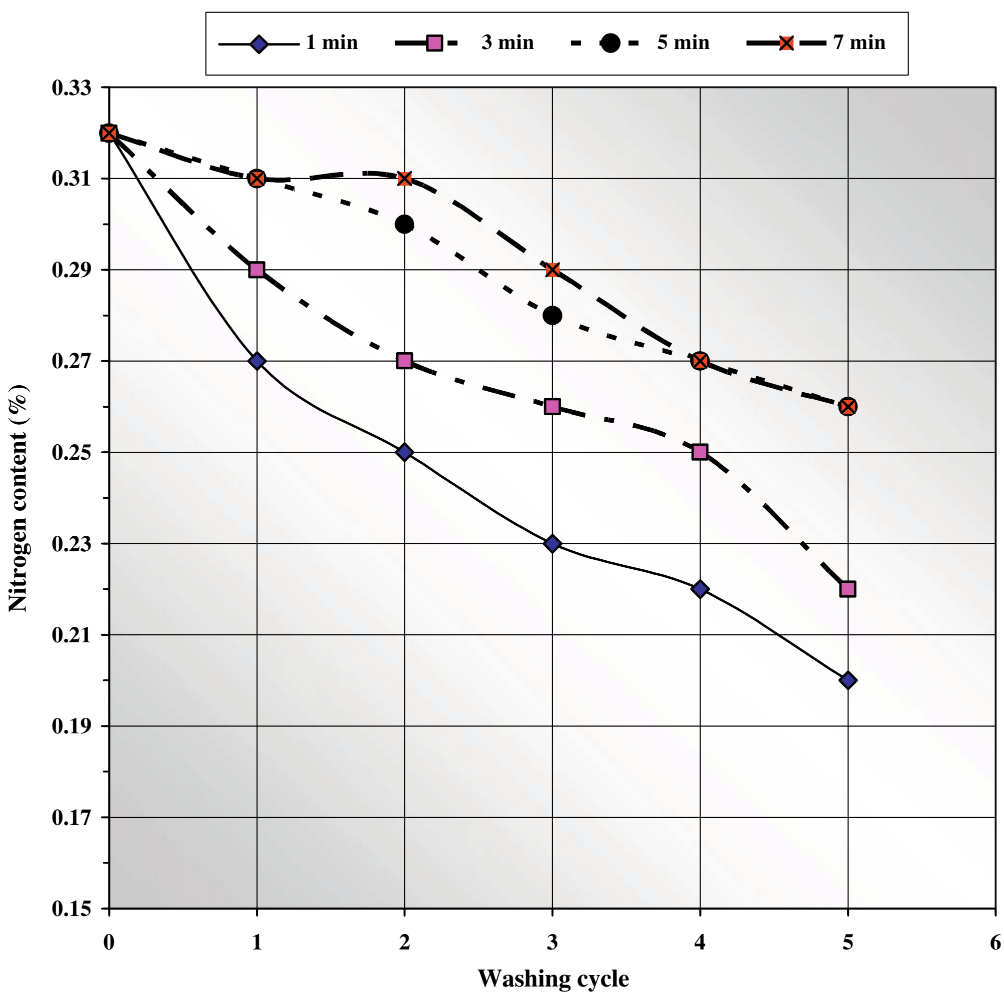


Fig. 3. Effect of curing time and washing cycles on the nitrogen content of chitosan-treated jute fabrics. Conditions used: jute fabrics were padded in 1% aqueous chitosan solution, squeezed to wet pick-up 100% dried at 85 °C for 5 min, cured at 120 °C. Values at zero washing cycles represent the values before washing and just after treatment.

namely *Staphylococcus aureus* (*S. aureus*) and *Candida albicans* (*C. albicans*). The diameter of inhibition zone (mm) formed around the test sample was taken as a measure of antimicrobial activity. Results obtained are set-out in Table 1. Results obtained with the untreated (blank) jute fabric are set-out in the same table for comparison.

It is seen from Table 1 that:

(i) Although scoured and untreated jute fabrics contained residual nitrogen content amounted 0.22%, it did not show any antimicrobial properties towards *S. aureus* or *C. albicans*. This could be attributed to that; the residual nitrogen content originally present in scoured jute fabric are not in chemical form that can impart an antimicrobial activity for jute fabric towards *S. aureus* or *C. albicans*.

(ii) The added nitrogen on chitosan-treated jute fabrics increases as the concentration of chitosan increases.

(iii) Treatment of jute fabrics with chitosan enhances its antimicrobial activity towards *S. aureus*. The inhibition zone increases from zero to 5 mm as the concentration of chitosan increases from zero to 1%. Further increase in chitosan concentration has approximately no effect on antimicrobial activity of the chitosan-treated jute fabric towards *S. aureus*. On the other hand, treatment of jute fabric with chitosan had absolutely no effect on the growth of *C. albicans* as evidenced by zero inhibition zone even at higher chitosan concentrations and under our experimental conditions used. State in other words, chitosan showed moderate bactericidal effect and shows no fungicidal effect.

3.1.2. Effect of fixation temperature

Scoured jute fabrics were treated with 1% aqueous chitosan solution (dissolved in 1% acetic acid) then squeezed to a wet pick-up of 100%, dried at 85 °C for 5 min, curing at different temperature (100–160 °C). The fabrics were then washed with water at 60 °C five times (cycles). After each cycle, the fabric was monitored for nitrogen content and antimicrobial activity. Results obtained are represented in Fig. 1. It is seen from Fig. 1 that, at curing temperature 100 °C, the nitrogen content of chitosan-treated jute fabric gradually decreases from 0.32% to 0.20% after five washing cycles. Consequently, the inhibition zone decreases from 5 to 4 mm after five washing cycles. Raising the curing temperature to 120 °C, enhances the durability of chitosan-treated jute fabrics as evidenced by marginally decrease in the nitrogen content by increasing the number of washing cycles. The same holds true for the antimicrobial activity of the jute fabrics as shown in Fig. 2, the inhibition zone marginally decreases as the number of washing cycles increase. Raising the curing temperature above 120 °C exerts no effect approximately on the inhibition zone.

Results of Figs. 1 and 2 make it clear that, 120 °C represents optimal curing temperature of chitosan onto jute fabrics.

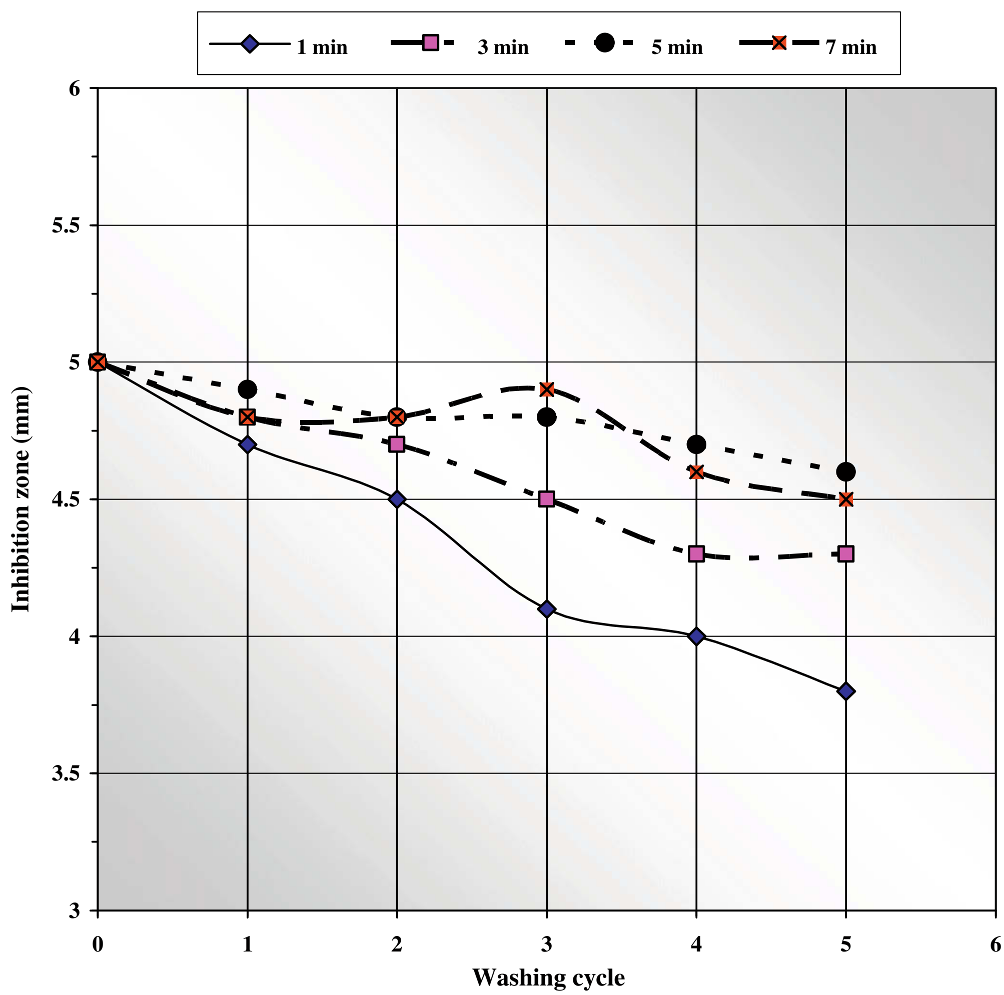


Fig. 4. Effect of curing time and washing cycles on the inhibition zone of chitosan-treated jute fabrics against *S.a* (mm). Conditions used: jute fabrics were padded in 1% aqueous chitosan solution, squeezed to wet pick-up 100% dried at 85 °C for 5 min, cured at 120 °C. Values at zero washing cycles represent the values before washing.

3.1.3. Effect of curing time

Chitosan-treated jute fabrics were cured at 120 °C for different time intervals. The fabrics washed five times after each wash the fabrics were subjected to nitrogen content and antimicrobial analysis. Results obtained are represented in Figs. 3 and 4. Results of Figs. 3 and 4 make it clear that 5 min, curing at 120 °C represents the optimal time for fixation of chitosan onto jute fabrics. Prolonged time exerts no effect on durability or antimicrobial activity of chitosan-treated jute fabrics.

3.2. Performance of chitosan–metal complexes as antimicrobial agent vis-à-vis uncomplexed chitosan and metal ions separately

Among several heavy metal ions; zinc (Zn), silver (Ag) and zirconium (Zr) are environmentally safe biocidal metal ions and possess nutritional features important to human health and health care (David & Tang, 2000; Varma et al., 2004). Moreover, these metal ions are easily to complex with chitosan (Varma et al., 2004).

Results discussed above show that, treatment of jute fabrics with chitosan impart the fabrics moderate bactericidal properties (especially towards *S. aureus*), whereas no obvious activity was observed towards *C. albicans* under our experimental conditions used. The objective of the study in this part is to investigate the antimicrobial activity of jute fabrics treated with chitosan–metal complex. Three metal ions were chosen to form complex with chitosan, namely Zn^{2+}, Ag^{1+} and Zr^{2+}. In order to discover the optimum fixation condition of chitosan–metal complexes onto jute fabrics; chitosan–Ag complex was chosen for treatment of jute fabrics under a varieties of conditions. The fabrics were monitored for antimicrobial activity and the durability towards washing. Results obtained when the jute fabrics treated with uncomplexed chitosan and metal ions separately were also monitored for comparison.

3.2.1. Effect of curing temperature on fixation of chitosan–Ag complex onto jute fabrics

To start with, samples of scoured jute fabrics were treated with chitosan–Ag complex under different curing temperature. The samples were washed five times (cycles) with water at 60 °C for 15 min. After each cycle the samples were monitored for nitrogen content, antimicrobial activity and Ag^{1+} ions content. Table 2 summarizes the effect of curing temperature on fixation of chitosan–Ag complex onto jute fabrics. The results bring into focus the following features:

(i) Jute samples treated with chitosan–Ag complex then cured at 100 °C undergo sharp decrease in the antimicrobial activity towards *S. aureus* or *C. albicans* as the number of washing cycle increases. This was evidenced by sharp decrease in inhibition zone from 2.5 and 1.8 mm before washing to 1.6 and 1 mm for *S. aureus* and *C. albicans*, respectively, after washing cycle number 5. The same holds true for the nitrogen content and silver ion content of the treated jute samples, where the nitrogen content and silver ion content sharply decreased from 0.32% and 125 ppm to 0.16% and 80 ppm, respectively, as the number of washing cycle increases up to 5 cycles.

(ii) Raising the curing temperature to 120 °C improves the durability of jute fabrics treated with chitosan–Ag complex. Although there is a marginally decrease in nitrogen content, silver ion content and antimicrobial activity it is rather better than those obtained at 100 °C. Raising the curing temperature above 120 °C exerts practically no marginally effect on the change of nitrogen and silver ion content as well as antimicrobial activity. It is, therefore, concluded that, 120 °C can be regarded the optimal temperature for fixation of chitosan–Ag complex onto jute fabrics.

Table 2
Effect of curing temperature on durability of jute fabrics treated with chitosan–Ag complex.

Temp. (°C)	Parameter	Before washing	Washing cycle				
			Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
100	I.Z (mm)	2.5[a] (1.8)[b]	2.2 (1.5)	2.0 (1.1)	1.8 (1.1)	1.6 (1.1)	1.6 (1.0)
	N (%)	0.32	0.28	0.26	0.23	0.20	0.16
	[Ag^{1+}] (ppm)	125	110	104	97.5	86	80
120	I.Z (mm)	2.6 (2.1)	2.5 (2.0)	2.5 (2.0)	2.4 (2.0)	2.4 (1.8)	2.4 (1.7)
	N (%)	0.32	0.31	0.30	0.30	0.30	0.29
	[Ag^{1+}] (ppm)	125	121	119	118	118	116
140	I.Z (mm)	2.6 (2.2)	2.5 (2.0)	2.5 (2.0)	2.4 (2.0)	2.4 (2.0)	2.2 (2.0)
	N (%)	0.32	0.32	0.30	0.31	0.29	0.29
	[Ag^{1+}] (ppm)	125	123	119	118	117	115
160	I.Z (mm)	2.6 (2.2)	2.5 (2.2)	2.5 (2.0)	2.5 (1.9)	2.4 (1.9)	2.3 (1.8)
	N (%)	0.32	0.31	0.32	0.31	0.30	0.29
	[Ag^{1+}] (ppm)	125	122	120	119	117	116

I.Z, inhibition zone.
Conditions used: 1% chitosan dissolved in 1% acetic acid, 0.05 g $AgNO_3$ drying at 85 °C for 5 min, curing for 3 min.
[a] I.Z value of the treated fabric against (*S.a*) bacteria.
[b] I.Z value of the treated fabric against (*C.a*) fungi.

3.2.2. Effect of fixation time

Table 3 shows the effect of curing time on durability of jute fabric treated with chitosan–Ag complex against repeated laundering. The durability includes the change in antimicrobial activity, nitrogen content and silver ion content of treated jute fabrics after five washing cycles. The results make it evident that increasing the curing time from 1 to 3 min enhances the fixation of chitosan–Ag complex towards repeated washing as evidenced by the marginally decrement in the antimicrobial activity, nitrogen content as well as silver ion content. Further increase in the curing time has no effect on these properties.

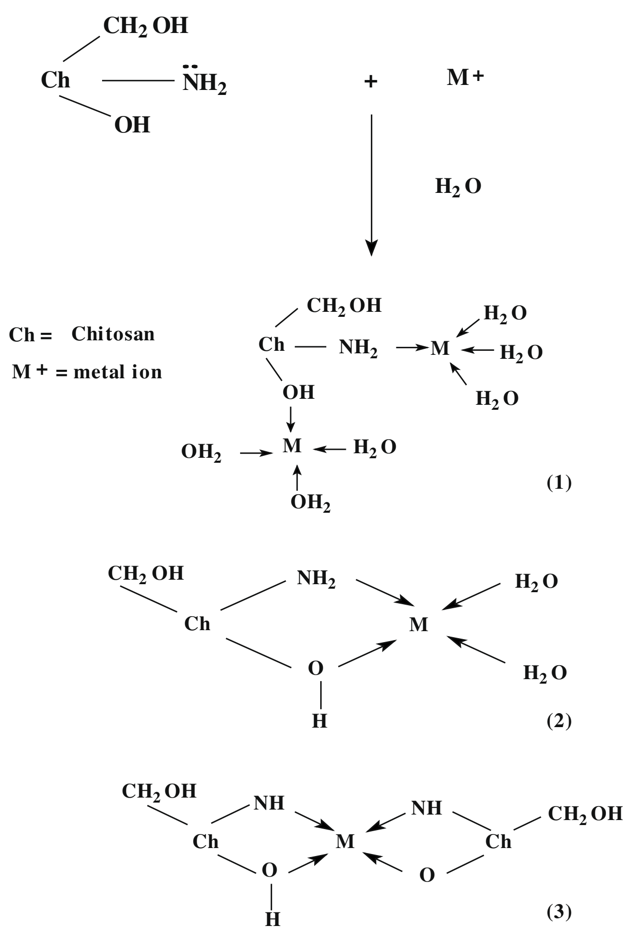
It could be emphasized that, fixation of chitosan–Ag complex onto scoured jute fabrics can be successfully carried out at 120 °C for 3 min. Empirically these conditions can be regarded as optimum conditions for fixation of other chitosan–metal complexes (like chitosan–Zn or chitosan–Zr complexes) onto jute fabric and will be applied in the treatment of jute fabric with chitosan–Zn or chitosan–Zr complexes.

3.2.3. Proposed mechanism of complex formation between chitosan and metal ions and the inherent antimicrobial properties

Chitosan macromolecule contains great deal of amine and hydroxyl groups which give the chitosan the ability to form metal complexes. Zn^{2+}, Ag^{1+} and Zr^{2+} are d^{10} element and usually form a tetra-coordinate structure with several ligands.

Complex formation between chitosan and metal ions could be described based on Lewis acid–base theory which state that acid is electron acceptor substance and the base is an electron donor substance. In case of chitosan–metal complexes metal ions acting as the acid which accept a pair of electron given by chitosan macromolecules which act as base. Several hypotheses were postulated to elucidate the structure of chitosan–metal complexes. Among these hypotheses, only two models have been experimentally proved (Wang, Yumin, & Liu, 2004). The first is pendant structure, in which metal ions were coordinate to one amino group or hydroxyl groups of chitosan (structure 1 or 2). The second is the bridge structure in which metal ions coordinate to two or more amino groups and/or hydroxyl groups of one or more chitosan chain as a bridge (structure 3).

Generally, the structure of chitosan–metal complexes depends on, chitosan/metal ion molar ratio, type of metal ion, molecular weight and degree of deacetylation of chitosan as well as the conditions of preparation.



The antimicrobial properties of chitosan ensuing from its polycationic nature. The cationic sites interact with the outer membrane of bacteria or anionic components of the bacteria (e.g., lipopolysaccharides, proteins). This interaction causes alternation of outer membrane structure leading to releasing of major proportion of proteinaceous material from the cells and finally disturbs the bacteria cell metabolism and inhibits its growth (Helander, Kala, & Lounatmaa, 1998; Helander, Lassila, Ahvenainen, Rhoades, & Roller, 2002; Vaara & Vaara, 1983). However, because chitosan is a macromolecule, its mobility is very limited compared with those encountered with metal ions. Hence, its antibacterial and antifungal properties will be lower than metal ions. On the other hand, when chitosan is cheated with metal ion, the positive charge on its amino group is strengthened and the interaction with anionic components of microorganism cells is therefore, much stronger and exhibit higher antimicrobial activity.

Table 3
Effect of curing time on durability of jute fabrics treated with chitosan–Ag complex.

Time (min)	Parameter	Before washing	Washing cycle				
			Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
1	I.Z (mm)	2.5[a] (1.8)[b]	2.3 (1.6)	2.0 (1.4)	1.8 (1.1)	1.6 (1.1)	1.4 (1)
	N (%)	0.32	0.26	0.22	0.21	0.21	0.19
	$[Ag^{1+}]$ (ppm)	125	105	97	89	85	80
3	I.Z (mm)	2.5 (2.0)	2.5 (2.0)	2.5 (2.0)	2.4 (2.0)	2.4 (1.8)	2.4 (1.7)
	N (%)	0.32	0.31	0.30	0.30	0.30	0.29
	$[Ag^{1+}]$ (ppm)	125	121	119	118	118	116
5	I.Z (mm)	2.5 (2.0)	2.5 (2.0)	2.5 (2.0)	2.3 (1.9)	2.4 (1.7)	2.4 (1.7)
	N (%)	0.32	0.31	0.30	0.29	0.29	0.28
	$[Ag^{1+}]$ (ppm)	125	120	118	119	118	115
7	I.Z (mm)	2.5 (2.0)	2.5 (2.0)	2.5 (2.0)	2.3 (1.9)	2.4 (2.0)	2.4 (1.7)
	N (%)	0.32	0.31	0.31	0.30	0.29	0.29
	$[Ag^{1+}]$ (ppm)	125	121	119	118	117	117

I.Z, inhibition zone.
Conditions used: the fabrics were padded in an aqueous solution containing 1% chitosan complexed with 0.05% $AgNO_3$ then squeezed to wet pick-up of 100% drying at 85 °C for 5 min then cured at 120 °C for different time intervals (1–7 min).
[a] I.Z value of the treated fabric against (*S.a*) bacteria.
[b] I.Z value of the treated fabric against (*C.a*) fungi.

3.2.4. Relation between type and concentration of metal ion before and after complexation with chitosan and the antimicrobial properties of thereof treated jute fabric

Table 4 summarizes the antimicrobial properties of jute fabric treated with Ag^{1+}, Zn^{2+} and Zr^{2+} ions in its native form or complexed with 1% chitosan. The inhibition zones formed with those samples treated with 1% aqueous chitosan solution are also setout in the same table for comparison. Results of Table 4 reveal that:

(i) Jute fabrics treated with uncomplexed chitosan (zero metal ion concentration) show an antimicrobial properties towards *S. aureus* and the observed inhibition zone amounted 4.5 mm, whereas no observed antifungal properties was observed against *C. albicans*.
(ii) Jute samples treated with metal ions show antibacterial and antifungal properties, both of them depend on the type and concentration of metal salts used. It is further observed from

Table 4
Effect of metal salt type and concentration in the form of complex with chitosan or uncomplex form on the antimicrobial properties of thereof treated jute fabrics.

Metal ion conc. (%)	Inhibition zone (mm)					
	$AgNO_3$		$ZnSO_4$		$Zr(SO_4)\cdot 4H_2O$	
	Free ions	Complex with chitosan	Free ions	Complex with chitosan	Free ions	Complex with chitosan
0[a]	–	4.5 (0)	–	4.5 (0)	–	4.5 (0)
0.05	1[b] (3.5)[c]	4 (3.5)	3.5 (2)	4 (3.5)	1.5 (2.5)	4 (3.5)
0.1	2 (4)	4.5 (4)	4 (3)	5.8 (4.5)	3.5 (3)	5.5 (3.8)
0.15	2.5 (4)	5.5 (4.5)	6 (4)	7.5 (6)	4 (4)	6.5 (5.5)
0.25	4 (4)	6.5 (4.5)	7 (5)	8.5 (6.5)	4.5 (4)	7.5 (6)

Preparation of chitosan–metal complex as descried in the experimental part.
[a] Zero metal ions conc. represent the values obtained with jute fabrics treated with chitosan.
[b] I.Z value of the treated jute fabrics against (*S.a*) bacteria.
[c] I.Z value of the treated jute fabrics against (*C.a*) fungi.

Table 4 that, regardless of the metal type of salts, increasing the concentration of metal salts enhance the antimicrobial activity of the treated jute fabrics as evidenced by increase in the inhibition zone. It is also seen from Table 4 that; at the same metal salt concentration. The antimicrobial properties of the treated jute fabrics show the following order: $Zn^{2+} > Zr^{2+} > Ag^{1+}$.

(iii) The antimicrobial properties of the jute fabrics treated with chitosan–metal complex prepared using very low concentration of metal salts (0.05%) show marginally decrease in the antibacterial properties towards *S. aureus*, this was evidenced by decrement in the inhibition zone from 4.5 mm in case of using chitosan to 4 mm when using chitosan–metal complex containing 0.05% metal ions. This was observed irrespective to the metal ion used. It is also observed that, although jute fabric treated with 1% aqueous chitosan did not show antifungal properties; the treatments with chitosan–metal complex succeed in affecting antifungal properties; and the inhibition zone ranged from 3 to 3.2 mm depending on the type of metal salt used.

(iv) It is further observed that, jute fabric treated with chitosan–metal complex prepared at higher concentration from metal salts showed an increase in the antimicrobial properties and exceeds that obtained either with chitosan or metal salts separately. This result was observed regardless of the type of metal salt used.

(v) At the same metal salts concentration, the antimicrobial properties of jute fabrics treated with chitosan–metal complex vary according to the type of metal salt used. Results of Table 4 would reveal also that, at the same metal salt concentration (0.15%), the antibacterial the antifungal properties of the jute fabrics treated with chitosan–metal complex follow the order: chitosan–Zn > chitosan–Zr > chitosan–Ag > chitosan.

(vi) Results abstracted from Table 4 show also that, at the same metal salt type and concentration, the antimicrobial properties of jute fabric treated with metal salts, chitosan or chitosan–metal complex show the following order: chitosan–metal complex > metal salt > chitosan.

(vii) It can be concluded from results obtained above, that jute fabric treated with chitosan–metal complexes have better antimicrobial properties than those fabrics treated with either chitosan or metal salts separately. Moreover, treatment of jute fabric with chitosan–Zn complex gives higher antimicrobial activity compared with the antimicrobial activity obtained with either chitosan–Zr or chitosan–Ag complexes or their uncomplexed form.

4. Conclusions

Although scoured jute fabrics contain residual nitrogen content amount 0.22% it did not shows any antimicrobial activity towards *S. aureus* or *C. albicans*. Treatment of jute fabric with chitosan enhances the nitrogen content of the fabric and improves only the antibacterial properties towards *S. aureus* whereas, antifungal properties remain intact. Moreover, maximum antibacterial properties of chitosan-treated jute fabrics were observed when the fabrics were treated with 1% aqueous chitosan solution (pre-dissolved in 1% acetic acid), then squeezed to a wet pick-up of 100%, dried at 85 °C for 5 min then cured at 120 °C for 3 min.

A similar study was carried out using chitosan–metal complex aiming at impart the jute fabrics antimicrobial properties. In this regards, Ag^{+1}, Zn^{+2} and Zr^{+2} ions were allowed separately to form a complex with chitosan. It has been found that, jute fabrics treated with chitosan–metal complex show better antimicrobial properties than those fabrics treated with either chitosan or metal salt separately. Moreover, the jute fabrics treated with chitosan–Zn complex have higher antimicrobial properties compared with those samples treated with chitosan–Zr or chitosan–Ag complexes.

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