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TEMPO OXIDATION AS A TOOL FOR IMPROVING ANTIBACTERIAL PROPERTIES OF VISCOSE FABRIC FUNCTIONALIZED WITH CHITOSAN BASED NANOPARTICLES

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ABSTRACT: *TEMPO oxidation of viscose fabric was used as a pretreatment to introduce carboxyl and aldehyde groups for irreversible binding of chitosan and to improve antibacterial activity and washing durability of viscose fabrics functionalized with chitosan nanoparticles without (NCS) and with embedded zinc (NCS+Zn). Carboxyl and aldehyde group content, electrokinetic properties, elemental analysis, inductively coupled plasma optical emission spectrometry and antibacterial testing were used to evaluate the influence of TEMPO oxidation on subsequent NCS and NCS+Zn binding and antibacterial properties of chitosan functionalized viscose fabrics. Antibacterial activity of NCS and NCS+Zn functionalized viscose fabrics was preserved after multiple washing.*

Keywords: *Viscose fabric, TEMPO oxidation, chitosan nanoparticles, chitosan nanoparticles with embedded zinc, antibacterial properties.*

TEMPO OKSIDACIJA U FUNKCIJI POBOLJŠANJA ANTIBAKTERIJSKIH SVOJSTAVA VISKOZNE TKANINE FUNKCIONALIZOVANE NANOČESTICAMA NA BAZI HITOZANA

APSTRAKT: *TEMPO oksidacija viskozne tkanine sprovedena je kao predtretman za uvođenje karboksilnih i aldehidnih grupa za ireverzibilno vezivanje hitozana i poboljšanje antibakterijske aktivnosti i postojanosti na pranje viskoznih tkanina* *funkcionalizovanih sa nanočesticama hitozana bez (NCS) i sa inkorporiranim cinkom (NCS+Zn). Sadržaj karboksilnih i aldehidnih grupa, elektrokinetička svojstva, elementalna analiza, induktivno kuplovana plazma sa optičkom emisionom spektrometrijom i antibakterijsko testiranje upotrebljeni su radi proučavanja uticaja TEMPO oksidacije na naknadno vezivanje NCS i NCS+Zn i antibakterijska svojstava viskoznih tkanina funkcionalizovanih sa hitozanom. Antibakterijska aktivnost viskoznih tkanina funkcionalizovanih sa NCS i NCS+Zn očuvana je nakon višestrukih pranja.*

Ključne reči: *Viskozna tkanina, TEMPO oksidacija, nanočestice hitozana, nanočestice hitozana sa inkorporiranim cinkom, antibakterijska svojstva.*

1. INTRODUCTION

Viscose is traditionally used as medical textiles for first aid, many clinical and hygienic purposes. Its molecular structure offers excellent possibilities for the design of biocompatible and bioactive medical textiles, with considerable variations in terms of performance and unit value [1]. In recent years, many efforts have been made in obtaining of medical textiles based on viscose fibers with antibacterial properties. However, the drawback of commonly used compounds for antibacterial functionalization of viscose, such as inorganic salts, phenols, antibiotics, iodine derivatives, nitro compounds, formaldehyde derivatives and amines, is their toxicity and poor biodegradability which are unacceptable from standpoint of current environmental and health protection legislation. For these reasons, non-toxic, biodegradable and environmentally-friendly compound chitosan is very favourable to be included in new strategies for development of contemporary antibacterial textiles based on viscose [2].
Chitosan is a natural amino polysaccharide with antimicrobial, antiviral, antitumour and haemostatic properties as well as a low immunogenicity, which provide ample opportunities for development of different medical applications [3]. Newest researches demonstrated the advantage of using chitosan nanoparticles instead of bulk chitosan, to impart enhanced antibacterial activity. Further, much effort has been devoted to the development of chitosan nanoparticles/metal ions hybrids, in order to link the chelating capacity of chitosan with the antibacterial properties of metal ions. The chelation of chitosan nanoparticles/metal ion increases the positive charge density of chitosan, which is expected to lead to enhanced adsorption onto the negatively charged cell surface of bacteria, causing the inhibition of bacteria growth [4]. Zinc is one of these metals, showing great antimicrobial properties. Based on the available evidence from clinical trials, zinc is also an effective antiseptic agent showing neither the purported harmful effects nor a delay in the wound-healing process, particularly in chronic and burn wounds and other infections [5].
Similarities between the chemical and molecular structures of viscose and chitosan enable high affinity between them, mainly based on H-bonds and Van der Waals forces. However, for more intense and irreversible binding between viscose and chitosan, it is necessary to introduce carboxyl and/or aldehyde groups into/onto the viscose. Carboxyl

groups of viscose provide electrostatic attraction between viscose and chitosan, while aldehyde groups of viscose allow covalent binding of chitosan via Schiff base formation [2]. In recent years, the N-oxyl radical-mediated oxidation using, for example, 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO) was found to be the most promising chemical modification for efficient conversion of primary hydroxyl groups of cellulose based metrials to carboxylates via aldehydes [6, 7].
In the present work, viscose fabric was TEMPO oxidized in order to obtain viscose fabrics functionalized with chitosan nanoparticles (NCS) as well as chitosan nanoparticles with embedded zinc (NCS+Zn) with improved antibacterial activity and its washing durability. By TEMPO oxidation carboxyl and aldehyde groups, necessary for irreversible binding of chitosan, were introduced into/onto the viscose fabric. Influence of TEMPO oxidation on NCS and NCS+Zn binding into/onto the viscose fabric and antibacterial properties of NCS and NCS+Zn functionalized viscose fabrics were evaluated by determination of carboxyl and aldehyde group content, elemental analysis, inductively coupled plasma optical emission spectrometry and antibacterial testing. Washing durability of NCS/NCS+Zn functionalized viscose fabrics was monitored through changes in the electrokinetic and antibacterial properties after 1, 3 and 5 washing cycles.

2. MATERIALS AND METHODS

2.1. Materials

Regenerated cellulose fabric, (15A23 viscose uni Sandy–white), as provided by IGR Agence, was used as a base material. The surface mass of the fabrics was 82 g/m^2, yarn count of 9.6 tex × 9.9 tex, fabric count of 400 warp threads/10 cm and 350 weft threads/10 cm. Chitosan from crab shells with low molecular weight (Aldrich, 448869), 75%–85% deacetylated, purchased from Sigma-Aldrich (Vienna, Austria). 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO), sodium bromide (NaBr), zinc acetate dihydrate ($ZnAc{\cdot}2H_2O$), sodium tripolyphosphate (TPP), sodium hypochlorite (NaClO), sodium chlorite ($NaClO_2$), sodium hydroxide (NaOH) and 13% sodium hypochlorite (NaClO) solution were from Sigma-Aldrich (Vienna, Austria), and applied without further purification.

2.2. TEMPO oxidation of viscose fabric

TEMPO oxidation of viscose fabric was performed according to a method described by Korica et al. [2].

2.3. Preparation of chitosan nanoparticles dispersion

Chitosan nanoparticles dispersion (NCS) were prepared according to a modified ionic gelation method described by Gan et al. [8].

2.4. Preparation of chitosan nanoparticles with embedded Zn dispersion

Chitosan nanoparticles with embedded Zn dispersion were prepared by dropping 3% solution of ZnAc into dispersion of chitosan nanoparticles prepared according above described method (2.3) in a ratio of 10:1 (w/w). The final pH of the chitosan nanoparticles with embedded Zn dispersion was adjusted to pH 5.5 with 0.5 M NaOH.

2.5. Functionalization of pristine and TEMPO oxidized viscose fabrics with chitosan nanoparticles without and with embedded Zn

Pristine and TEMPO oxidized viscose fabrics were immersed into the:

a) Chitosan nanoparticles dispersion or
b) Chitosan nanoparticles with embedded Zn dispersion.

The treatment lasted for 30 min at room temperature using a material-liquid bath ratio of 1:50, with a wet pick up of 100%. Samples were then squeezed onto a laboratory padder (Rapid, Istanbul, Turkey) at a pressure of 2 bars. After the excess liquid was removed, fabrics were dried at 40°C for 30 min in a laboratory oven (Instrumentaria, Zagreb, Croatia). Fabrics were then conditioned (T=20±2°C; RH=65±5%) before being analyzed further.

2.6. Washing of functionalized viscose fabrics

Washing of NCS and NCS+Zn functionalized viscose fabrics was performed according to standard ISO 105-C10. The sample notations of viscose fabrics before and after washing are presented in Table 1.

2.7. The carboxyl and aldehyde group content

The carboxyl and aldehyde group content in pristine and TEMPO oxidized viscose fabrics determined by method described by Korica et al. [2].

2.8. Elemental analyses

The chitosan content in NCS and NCS+Zn functionalized viscose fabrics was calculated from the nitrogen percentage, determined by the elemental analysis performed on a Vario EL III C,H,N,S/O Elemental Analyzer (Elementar Analysensysteme GmbH, Langenselbold, Germany).

Table 1: Notation of the prepared samples

Description of samples	Washing cycles			
	0	1	3	5
Pristine viscose	CV			
TEMPO oxidized viscose	TEMPO CV			
CV+ chitosan nanoparticles	CV/NCS	CV/NCS-1	CV/NCS-3	CV/NCS-5
TEMPO CV+ chitosan nanoparticles	TEMPO CV/NCS	TEMPO CV/NCS-1	TEMPO CV/NCS-3	TEMPO CV/NCS-5
CV+ chitosan nanoparticles with embaded zinc	CV/NCS+Zn	CV/NCS+Zn-1	CV/NCS+Zn-3	CV/NCS+Zn-5
TEMPO CV+ chitosan nanoparticles with embaded zinc	TEMPO CV/NCS+Zn	TEMPO CV/NCS+Zn-1	TEMPO CV/NCS+Zn-3	TEMPO CV/NCS+Zn-5

2.9. ICP-OES analyses

The content of Zn in NCS+Zn functionalized fabrics was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). ICP-OES measurement was performed using Thermo Scientific iCAP 6500 Duo ICP (Thermo Fisher Scientific, Cambridge, United Kingdom) spectrometer equipped with RACID86 charge injector device (CID) detector, standard glass concentric nebulizer, quartz torch, and alumina injector.

2.10. The streaming potential measurement

The zeta potential of all viscose fabrics presented in Table 1. was determined by method described by Korica et al. [2].

2.11. Antibacterial testing

The antibacterial activity of NCS and NCS+Zn functionalized viscose fabrics before and after washing was tested against Gram-negative bacteria *Escherichia coli* ATCC 25922 and Gram-positive bacteria *Staphylococcus aureus* ATCC 25923, using a standard test method for determining the antimicrobial activity of immobilized antimicrobial agents under dynamic contact conditions ASTM E 2149-01 (2001).

3. RESULTS AND DISCUSSION

3.1. Carboxyl and aldehyde group content in pristine and TEMPO oxidized viscose fabrics

Conversion of the primary hydroxyl groups of pristine viscose fabric into carboxyl groups through aldehyde intermediates during TEMPO oxidation leads to an increase in the carboxyl and aldehyde groups content of TEMPO oxidized viscose fabric. Carboxyl group content was increased from 64 mmol/kg for pristine to 438 mmol/kg for TEMPO oxidized viscose fabric, and aldehyde group content was increased from 18 mmol/kg for pristine to 440 mmol/kg for TEMPO oxidized viscose fabric.

3.2. Chitosan and zinc content in the NCS and NCS+Zn functionalized viscose fabrics

Chitosan and zinc content in pristine and TEMPO oxidized viscose fabrics after functionalization with NCS and NCS+Zn were quantified; the results are presented in Table 2. Compared to pristine, the TEMPO oxidized viscose fabric bounded increased amount of chitosan (2.7 and 1.6 times for TEMPO CV/NCS and TEMPO CV/NCS+Zn, respectively) probably due to higher functional group content. Consequently, in TEMPO oxidized viscose fabric after functionalization with NCS+Zn increased amount of zinc was present (1.8 times higher for TEMPO CV/NCS+Zn compare to CV/NCS+Zn).

Table 2: Chitosan and zinc content in pristine and TEMPO oxidized viscose fabrics after their functionalization with NCS or NCS+Zn

Sample	Chitosan, mg/100 g cellulose	Zinc, mg/100 g cellulose
CV/NCS	430	
TEMPO CV/NCS	1180	
CV/NCS+Zn	630	1860
TEMPO CV/NCS+Zn	1040	3400

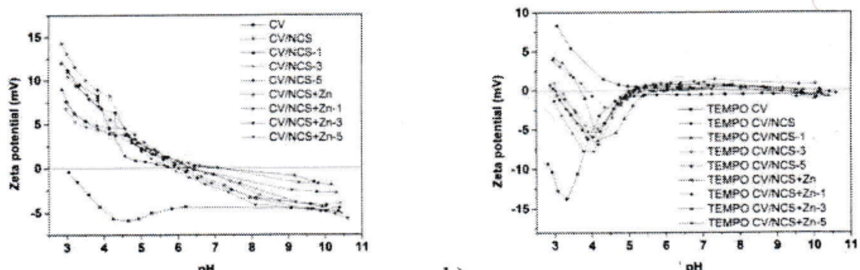
3.3. Antibacterical properties of NCS and NCS+Zn functionalized viscose fabrics

The antibacterial properties of NCS and NCS+Zn functionalized pristine and TEMPO oxidized viscose fabrics were evaluated against Gram-positive (*S. aureus*) and Gram-negative (*E. coli*) bacteria. In accordance with the used standard, the fabrics show antibacterial activity if the bacterial reduction is greater than 75 %. Maximum bacterial reduction was achieved by all functionalized fabrics against *S.aureus*: 99.9% for CV/NCS, TEMPO CV/NCS, CV/NCS+Zn, and TEMPO CV/NCS+Zn; as well as against *E.coli*: 98.8% for CV/NCS, and 99.9% for TEMPO CV/NCS, CV/NCS+Zn, and TEMPO CV/NCS+Zn.

3.4. Washing durability of NCS and NCS+Zn functionalized viscose fabrics

Washing durability of NCS and NCS+Zn functionalized pristine and TEMPO oxidized viscose fabrics was monitored through changes in their electrokinetic surface properties and antibacterial activity after multiple washing, i.e. 1, 3 and 5 washing cycles.

The changes of the electrokinetic surface properties of NCS and NCS+Zn functionalized pristine and TEMPO oxidized viscose fabrics before and after multiple washing cycles are presented in Figure 1. For all functionalized samples, after each washing cycle the zeta potential–pH curves were phase-shifting to a lower pH, i.e. to a lower isoelectric point, indicating release of reversibly bound NCS and NCS+Zn during washing. Comparing the zeta potential-pH curves of pristine and TEMPO oxidized viscose fabrics before functionalizations and functionalized fabrics after 5 washing cycles, it is clear that NCS and NCS+Zn are still present onto fabrics' surfaces.



a) b)

Figure 1: Zeta potential of pristine (a) and TEMPO oxidized viscose fabrics (b) functionalized with NCS and NCS+Zn before and after 1, 3 and 5 washing cycles

Bacterial reduction of pristine and TEMPO oxidized viscose fabrics functionalized with NCS and NCS+Zn before and after 1, 3 and 5 washing cycles against *S. aureus* and *E. coli* is presented in Figure 2. NCS functionalized pristine viscose fabric provided effective bacterial reduction against *S. aureus* up to tree washing cycles, while TEMPO oxidized viscose fabrics up to five washing cycles. For both NCS functionalized viscose fabrics the effective bacterial reduction against *E. coli* was provided only before washing. Compared to the NCS, NCS+Zn functionalized viscose fabrics showed more washing durable effective bacterial reduction: against *S. aureus* for pristine, and against *E. coli* for TEMPO oxidized. NCS+Zn functionalized pristine as well as TEMPO oxidized viscose fabrics provided effective bacterial reduction against *S. aureus* up to five washing cycles, while NCS+Zn functionalized TEMPO oxidized viscose fabric provided effective bacterial reduction against *E. coli* up to one washing cycle. Generally, better antibacterial activity of NCS as well as NCS+Zn functionalized viscose fabrics against Gram-positive (*S. aureus*) compared to Gram-negative bacteria (*E. coli*) can be explained by the presence of outer membrane in Gram-negative bacteria which acts as a barrier towards the environmental impact, which is already reported [9]. Comparing the results obtained for pristine and TEMPO oxidized viscose fabrics functionalized either with NCS or NCS+Zn, it was evident that TEMPO oxidized viscose fabric showed more effective and durable antibacterial activity against both types of bacteria.

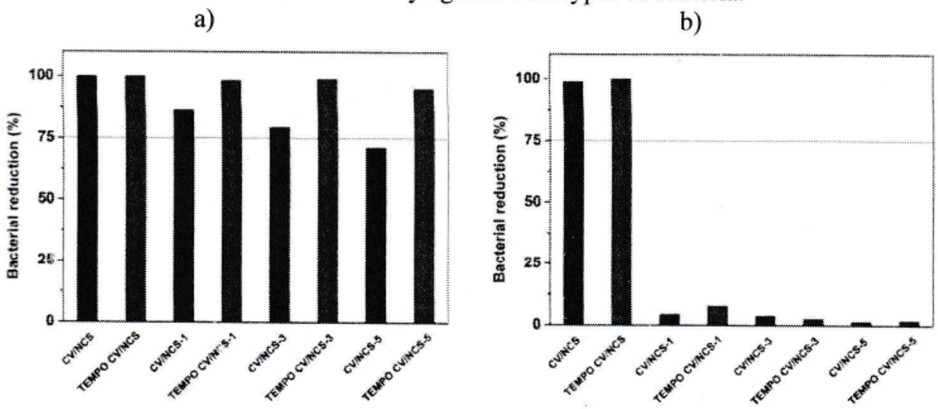
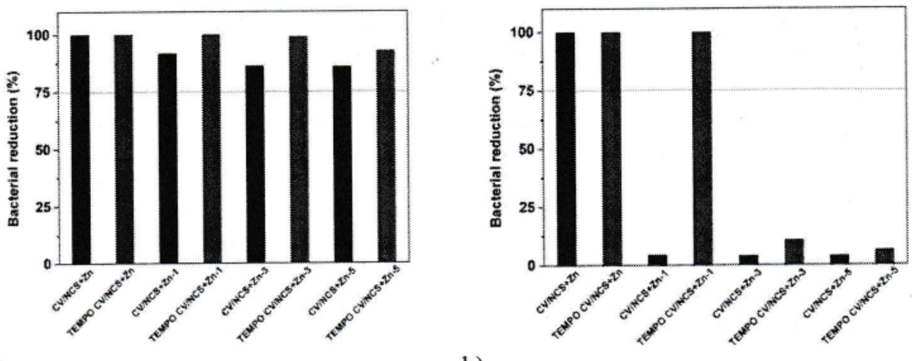


Figure 2: Bacterial reduction of pristine and TEMPO oxidized viscose fabrics functionalized with NCS after 1, 3 and 5 washing cycles against *S. aureus* (a) and *E. coli* (b)



a) b)

Figure 3: Bacterial reduction of pristine and TEMPO oxidized viscose fabrics functionalized with NCS+Zn after 1, 3 and 5 washing cycles against *S. aureus* (a) and *E. coli* (b)

3. CONCLUSION

In this study TEMPO oxidation was used to improve antibacterial properties of viscose fabric functionalized with NCS as well as NCS+Zn, by introducing carboxyl and aldehyde groups into/onto viscose fabric for irreversible binding of NCS and NCS+Zn. TEMPO oxidation contributes to the increase in the content of carboxyl and aldehyde groups, and thus the ability of the viscose fabrics to bind NCS and NCS+Zn. As a consequence of a higher amount of irreversibly bound NCS and NCS+Zn, TEMPO oxidation contributes to more efficient and durable antibacterial activity. NCS functionalized TEMPO oxidized viscose fabric preserve antibacterial activity against *S. aureus* after five washing cycles, while antibacterial activity against *E. coli* was lost after first wasing cycle. Compared to NCS functionalized, NCS+Zn functionalized TEMPO oxidized viscose fabric prolonged antibacterial activity against *E. coli* up to one washing cycle. Owing to the obtained antibacterial properties, the NCS and NCS+Zn functionalized TEMPO oxidized viscose fabrics do have a very high potential to be applied in manufacturing of washable antibacterial textiles for a vast number of healthcare and hygiene products.

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