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ORIGINAL PAPER

# Green synthesized chitosan and ZnO nanoparticles for sustainable use in multifunctionalization of cellulosic fabrics

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## Abstract

A green sustainable strategy for biosynthesis of ZnONPs and chitosan nanoparticles (ZnONPs: 20–25 nm and CSNPs: 70–90 nm) has been developed, their potential applications in multifunctional finishing of cotton and viscose fabrics to impart anti-crease, anti-UV and antibacterial functions using citric acid/Na-hypophosphite CA (15 g/L)/SHP (15 g/L), as $CH_2O$-free ester-crosslinking system and the pad-dry-cure method. The obtained results signify that the extent of improvement in the imparted functional properties is governed by type of cellulosic substrate, kind and concentration of nano-additive as well as type of bio-functional additive, namely, L-ascorbic acid or vanillin (20 g/L each). Moreover, the best results show that using CSNPs (2.5 g/L)/ZnONPs (15 g/L), as an eco-friendly two component mixture, brought about an enhancement in both chemical and functional properties of treated substrates which can be ranked as follows: nitrogen content (N%): viscose (1.818) > cotton (1.592); metal content (%): viscose (1.35) > cotton (1.24); WRA°: cotton (196) > viscose (165); anti-UV (UPF): cotton (47) > viscose (40); anti-*S. aureus* (*R*%): viscose (97) > cotton (94) and anti-*E. coli* (*R*%): viscose (92) > cotton (89), keeping other parameters constant. Major characteristics of the so-prepared nanoparticles as well as developed cellulosic fabrics were analyzed by FTIR, TEM, SEM and EDX techniques, as well as %N and %Zn content analysis. Durability to wash was evaluated and fabrics modification/functionalization, mechanism was also proposed.

**Keywords** Cellulosic fabrics · Green synthesis · Chitosan and ZnO nanoparticles · Multifunctional finish · Sustainable protective textiles

Extended author information available on the last page of the article

## Introduction

Eco-friendly surface modification and multifunctionalization of cellulosic fabrics using various emerging and sustainable technologies [12, 15, 28, 57] as well as environmentally sound textile chemicals and auxiliaries are the most recent trends in textile finishing processes [16, 17, 28, 35] for imparting highly demanded, novel and outstanding functional properties such as antibacterial [2, 14, 44, 47], UV protection, self-cleaning [36, 46, 47, 49, 52], wrinkle recovery [9, 27, 38, 51], enhanced fragrance [17, 20, 25], etc., with high values added, taken into account the ever-growing consumer demands for high product and ecology quality, along with economical social concerns [48].

Chitosan (CS) and CS derivatives are currently used in textiles modification, coloration and/or functionalization for their cationic active sites, $N^+H_2$ groups, especially at acidic conditions [23, 42, 57, 62]. Antimicrobial activity of CS is attributed to the interaction between its positively charged active sites and the negatively charged sites on the microbial surface [30, 37, 43], which, in turn, results in disruption of the harmful microbial cells, changes in their metabolism and leads to cell death [37, 61].

On the other hand, ionic gelation method is widely used for obtaining CS nanocomposites via interaction of positively charged Na-tripolyphosphate (TPP) under appropriate conditions, thereby forming coacervates as a direct consequence of electrostatic interaction between the two aqueous phases along with ionic gelation via transition from liquid to gel phase [5]. The experimental results showed that the antibacterial activity against both Gram-positive and Gram-negative bacteria of CS-TPP NPs suspension was better than that of the CS solution [5].

Recently, various techniques of ZnONPs such as chemical reduction [29, 40], plant extract [1, 3, 45], fungus [55], electrochemical method [8], microwave [58] as well as *in situ* preparation [4] and their potential textile applications to impart multifunctional properties such as antibacterial, self-cleaning, flame retardant and UV protection, taking in consideration both the environmental concerns and the ever-growing consumer demands have been developed and successfully carried out [6, 7, 10, 39, 47, 50, 56]. ZnONPs have been widely utilized in textile functionalization due to its desirable physical and chemical properties, biocompatibility compared with other metal oxides and its low production cost. ZnONPs finished fabrics showed excellent antibacterial activity due to the ability of ZnONPs to destroy the growth of the microbe [41]. Moreover, ZnONPs exhibit significant activity even at neutral condition, in the absence of light as well as excellent stability under high temperature and UV. ZnONPs, as an n-type semiconductor, show photocatalytic activity which, in turn, distinguish ZnO with unique multifunctional properties [31, 32, 53, 59].

Additionally, a green biosynthesis/cost-effective routes for fabrication of metal (M) and metal-oxide (MO) nanoparticles (NPs) using Miswak-rich active phenolic constituents for promoting, reduction, formation and stabilization of the demanded MNPs or MONPs as well as their potential applications have been developed and implemented recently [33, 54]. It was observed that the antibacterial activity of the biosynthesized nanoparticles using an eco-friendly aqueous

solution of Miswak root extract was better than that prepared by non-eco-friendly conventional chemical methods [54].

To date, there are few studies focused on the positive role of eco-friendly multi-functionalization of cellulosic substrates using, (i) citric acid/$NaH_2PO_2$ (CA/SHP) as zero-$CH_2O$ ester-crosslinking system along with biosynthesized ZnONPs using Miswak extracts as bio-reductant and ii) CA/SHP CSNPs alone and in combination with L-ascorbic or vanillin as green bioactive functional additives. Herein, we reported biosynthesis and characterization of ZnONPs and CSNPs along with their potential applications in functional finishing of cotton and viscose substrates using a pad-dry-cure process. The effect of finishing bath constituents on the imparted multifunctional properties such as anti-crease, UV protection and antibacterial activity against both Gram-positive (*S. aureus*) and Gram-negative (*E. coli*) bacteria was analyzed. Furthermore, the mode of interaction among the finishing bath constituents and the cellulosic substrates was suggested, and extent of fixation was investigated.

## Materials and methods

### Materials

Mill scoured and bleached cotton (140 g/$m^2$) and viscose (130 g/$m^2$) woven fabrics were used in this study. Miswak (*Salvadora persica* root) was purchased from the local market. Chitosan (CS, Mol. Wt. $2.4\times10^4$ Da and 89.2% deacetaylated), Na-tripolyphosphate monohydrate (TPP) and L-ascorbic acid are purchased from Sigma-Aldrich. Citric acid, glacial acetic acid, Na-hypophosphite monohydrate (SHP, $NaH_2PO_2.H_2O$), vanillin, zinc acetate, ($Zn(CH_3COO)_2$) $0.2H_2O$ and sodium hydroxide were of laboratory reagent grade.

### Methods

#### Preparation of Miswak extract

Freshly obtained roots were cut into small pieces, then grounded. Subsequently, 10 g of the powder were immersed in 100 ml of distilled water and refluxed for 5 h. The obtained extract was filtered by using Whatman No. 1 filter paper, then stored in a refrigerator at 4 °C for biosynthesis of ZnONPs.

#### Biosynthesis of ZnONPs

ZnONPs were fabricated by adding of 4 ml of freshly prepared Miswak aqueous extract to 100 ml of Zn-acetate aqueous solution (0.225 M), stirred for 12 h, and pH was maintained at 12 by adding 0.02 M NaOH solution and mixing for 1 h, after which it was centrifuged at 6000 rpm for 30 min. The obtained precipitate was washed several times with bi-distilled water to get pH 7 dried at 90 °C for 8 h.

### Preparation of CS/TPP NPs suspension

Preparation of CS/TPP NPs was carried out successfully according to the method given by Bangun et al. [5] with some modifications. Briefly, 3 g of CS were dissolved in 600 ml of 1% acetic acid and stirred continuously for 30 min. Subsequently, an aqueous solution of TPP (1.4 g/600 ml) was then slowly added and stirred for 2 h at room temperature and sonicated for 1 h.

### Functional finishing of cellulosic fabrics

Cotton and viscose fabric samples were padded twice in various functional finishing formulations containing:

(i) Citric acid (30 g/L), as ester-cross linker, and SHP (15 g/L), as a catalyst, CS-TPP NP (2.5 g/L), as a polycationic agent, and ZnONPs (0–15 g/L), as a multifunctional agent, or
(ii) CA/SHP (30 g/L/15 g/L), CS-TPP NPs (2.5 g/L) and L-ascorbic acid (0–20 g/L) or vanillin (0–20 g/L), as environmentally sound functional additive, to give wet pick-up of 85%, followed by drying at 100 °C/3 min and curing at 150 °C/3 min, thoroughly washed to remove unfixed/non-reacted constituents and finally dried and conditioned before evaluation.

## Testing and analysis

### Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared (FTIR) spectroscopy was carried out using a Nicolet 380 spectrophotometer (Thermo Scientific), and the IR spectra were scanned 32 times over the wavenumber range of 4000–400 $cm^{-1}$. The sample (0.002 g) was mixed with KBr to reach (0.2 g) to form around disk suitable for measurements.

### Transmission electron microscopy (TEM)

TEM images of the samples were obtained using a JEOL (JEM-1400 TEM, Japan), with an accelerating voltage of 100 kV. The CSNPs and ZnONPs suspension sample was ultrasonically dispersed in deionized water. Then, a small droplet of the diluted CSNPs and ZnONPs suspension was deposited on a 300-mesh copper grid coated with holey carbon film.

### Particle size analysis

The average size and size distribution of the CSNPs and ZnONPs were estimated by dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS (Malvern

Instruments Ltd., UK) equipped with a He–Ne laser (0.4 m W; 633 nm) and a temperature-controlled cell holder. The mean intensity weighted diameter was recorded as the average of three measurements.

### Scanning electron microscopy (SEM)

SEM images for surface morphology of the samples were taken using SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy-Dispersive X-ray Analyses), with accelerating voltage 30 KV, magnification 14×up to 1,000,000 and resolution for Gun.1n. The surfaces of all the samples were coated with a gold thin layer under vacuum before SEM studies.

### Textile testing

The amount of metal content in the post-treated fabric samples was determined by a flame atomic absorption spectrophotometer (GBC-Avanta, Australia).

Nitrogen content of fixed finished fabric was estimated as per a standard Kjeldahl method [60] using instrument model DNP-3000 (Raypa-SPAIN) using standard reference materials [60].

UPF was determined according to the Australian/New Zealand Standard (AS/NZS 4399-1996). Fabric can be rated as providing good, very good and excellent protection if their UPF values range 15–24, 25–39 and above 40, respectively.

The antimicrobial activity assessment against Gram-positive, *Staphylococcus aureus* (*S. aureus*) and Gram-negative, *Escherichia coli* (*E. coli*) bacteria was determined quantitatively according to AATCC 100 test method. The reduction of colonies was calculated using the following equation: $R = 100\ (B-A)/B$, where $R$: % reduction, $A$: the number of bacterial colonies survived after contacting with treated sample and $B$: the number of colonies present in untreated control sample (blank).

Dry wrinkle recovery was determined according to AATCC Test Method 66-2008 using iron recovery apparatus type FF-07 (Metrimpex).

## Results and discussion

### Synthesis of CS-TPP, TEM morphology and DLS analysis

Incorporation of CS–$NH_2$, acetic acid and Na-TPP in aqueous solution under appropriate conditions would be expected to enable the following interactions [5]. On the other hand, TEM and DLS analysis (Fig. 1a and b) of the fabricated CS-TPP NPs demonstrated that the obtained NPs have uniform, well disperse and capped structure with particle size in the range of 70–90 nm.

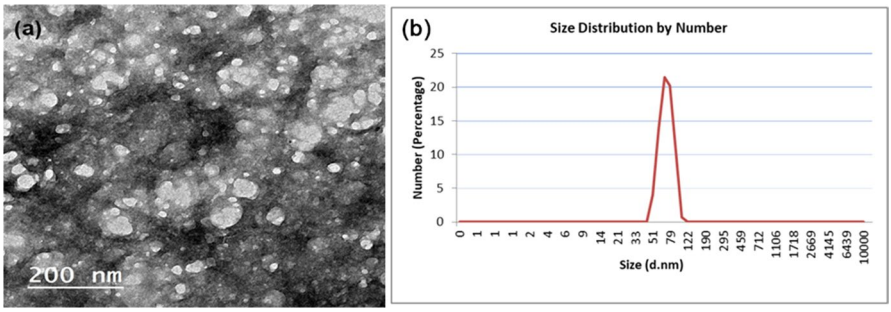



**Fig. 1** TEM morphology of chitosan nanoparticles (CNPs) (**a**) and particle size analyzer from DLS (**b**)

$$\text{CS-NH}_2 + \overset{+}{\text{H}} \longrightarrow \text{CS-}\overset{+}{\text{N}}\text{H}_3 \quad (1)$$

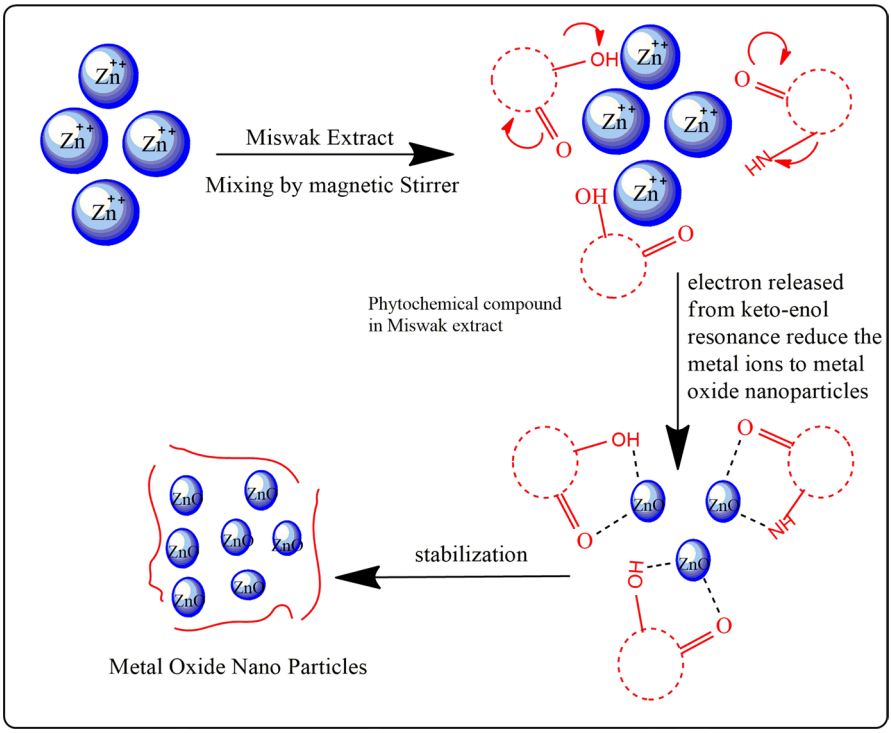
$$\text{CS-}\overset{+}{\text{N}}\text{H}_3 + \text{NaO-P}(\text{ONa})\text{-O-P}(\text{ONa})\text{-O-P}(\text{ONa})\text{-ONa} \xrightarrow{\text{Ionic gelate}} \text{CS-TPP NPs suspension} \quad (1)$$

## Green biosynthesis and characterization of ZnONPs using Miswak extract

The suggested mechanism of interaction among $(Zn(CH_3COO)_2)0.2H_2O$, as a precursor and phenolic constituents of Miswak extract under appropriate pH and stirring conditions are given in Scheme 1. On the other hand, Fig. 2a and b shows the TEM image and DLS analysis of biosynthesized ZnONPs using the phenolic constituents of Miswak root extract to promote both the reduction process and stabilization of the fabricated ZnONPs under the given conditions. Both Fig. 2a and b demonstrate well-distributed NPs within a range of 20–25 nm.

FTIR spectra of (a) Miswak extract and produced ZnONPs are shown in Fig. 3. Figure 3a shows broadband corresponding to the –OH functional group and N–H stretch at 3545 $cm^{-1}$. The band at 2919.17 $cm^{-1}$ is attributed to C–C stretch of alkynes triple bond. Moreover, a strong peak at 1720.32 $cm^{-1}$ is related to C=O stretching along with two bands at 1640.24 $cm^{-1}$, 1413.24 $cm^{-1}$ and 1124.34 $cm^{-1}$ attributed to C–C, C–N and C–O stretching, respectively [5]. Additionally, the formation of NPs is a direct consequence of the presence of different reducing functional groups such as oxygen and nitrogen-containing groups, as shown in Fig. 3a, which facilitate reduction of metal to the nanosized scale.

Furthermore, FTIR spectrum of biosynthesized ZnONPs (Fig. 3b) also indicates that all the aforementioned peaks which correspond to Miswak extract constituents (Fig. 3a) are presented with a slight shift in a few peaks. Also, FTIR data of green fabricated ZnONPs confirm the presence of new bands near the region of 500 $cm^{-1}$, which assigned to Zn–O stretching [11]. On the other hand, the peak detected around 500 $cm^{-1}$ confirmed the presence of metal-oxide bond, Zn–O, which confirms the biosynthesis of ZnONPs using Miswak.




**Scheme 1** Schematic diagram for fabrication of ZnONPs

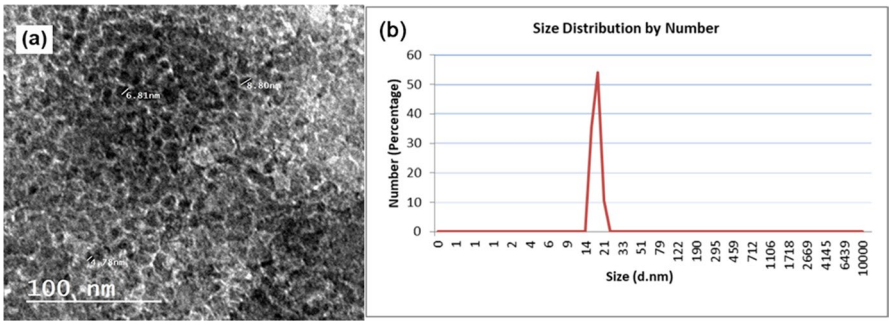



**Fig. 2** TEM morphology of zinc oxide nanoparticles (ZnONPs) (**a**) and particle size analyzer from DLS (**b**)

## Multifunctionalization of cotton and viscose cellulosic fabrics using the bio-fabricated ZnONPs

Effect of inclusion of the biosynthesized ZnONPs (0–15 g/L) into the finishing formulation along CA/SHP (30/15 g/L) and CS-TPP (2.5 g/L) on the N%, Zn% content, WRA, UPF and antibacterial activity, expressed as (%R), of

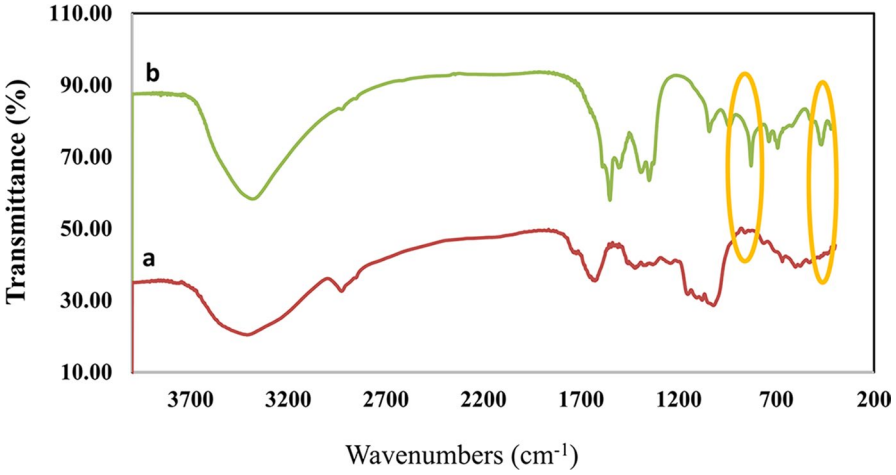



**Fig. 3** FTIR analysis of **a** Miswak root extract and **b** ZnONPs

ester-crosslinked cellulosic substrates is presented in Table 1. The experimental results in Table 1 demonstrate that: (i) increasing ZnONPs concentration up to 15 g/L results in an increase in the %N, %Zn content, a reasonable increase in WRA, a significant improve in UV protection efficiency and a remarkable increase in the imparted antibacterial activity against the harmful *S. aureus* and *E. coli* bacteria, regardless of the treated substrate.

**Table 1** Effect of inclusion of ZnONPs into the finishing formulation on some performance and functional properties of treated substrates

| ZnONPs (g/L) | Substrate | *N* (%) | Metal content (%) | WRA (*W*+*F*)° | UPF | Antimicrobial activity *R* (%) | |
|---|---|---|---|---|---|---|---|
| | | | | | | *S. aureus* | *E. coli* |
| 0.0 | Cotton | 0.577 | 0.00 | 162 | 15 | 50 | 47 |
| | Viscose | 0.809 | 0.00 | 130 | 11 | 60 | 58 |
| 10 | Cotton | 0.804 | 0.94 | 179 | 38 | 77 | 74 |
| | Viscose | 1.020 | 1.33 | 146 | 32 | 85 | 81 |
| 15 | Cotton | 1.592 | 1.24 | 196 | 47 | 94 | 89 |
| | Viscose | 1.818 | 1.35 | 165 | 40 | 97 | 92 |

Finishing formulation: citric acid 30 g/L; $NaH_2PO_2$ 15 g/L; CSNPs 2.5 g/L; ZnONPs (0–15) g/L; wet pick-up (80%); drying at 100 °C/3 min and curing at 150 °C/2 min

*N* nitrogen content, *WRA* wrinkle recovery angle (warp + weft), *UPF* UV protection factor and *R*% reduction in percentage of bacterial colonies *S. aureus* and *E. coli*

Properties of untreated cotton: %*N* = 0.00, metal content % = 0.00, WRA = 110, UPF = 6 and antibacterial activity against *S. aureus* and *E. coli* bacteria = 0%

Properties of untreated viscose: %*N* = 0.00, metal content % = 0.00, WRA = 97, UPF = 3 and antibacterial activity against *S. aureus* and *E. coli* bacteria = 0%

The increase in %N is a direct consequence of enhancing the extent of CS-TPP fixation onto/within the cellulose structure [23]. The increase in %Zn content is a direct consequence fixation of $Zn^{+2}$ onto/within the ester-crosslinked structure via its –COOH groups [23] and $–NH_2$ active sites of loaded CS-TPP NPs.

The reasonable improve in WRA of finished substrates reflects the positive role of ZnONPs in enhancing the extent of ester-crosslinking along with the positive role of NPs in minimizing the slipping of cellulosic chains, i.e., high anti-crease property [27].

The remarkable increase in UV protection functionality, expressed as UPF value, of ZnO immobilized onto/within the ester-crosslinked cellulose structure is attributed to its ability to block and shield the harmful UV-B radiation and hinder its transmittance through the modified cellulose structure to the textile consumer skin [19, 47].

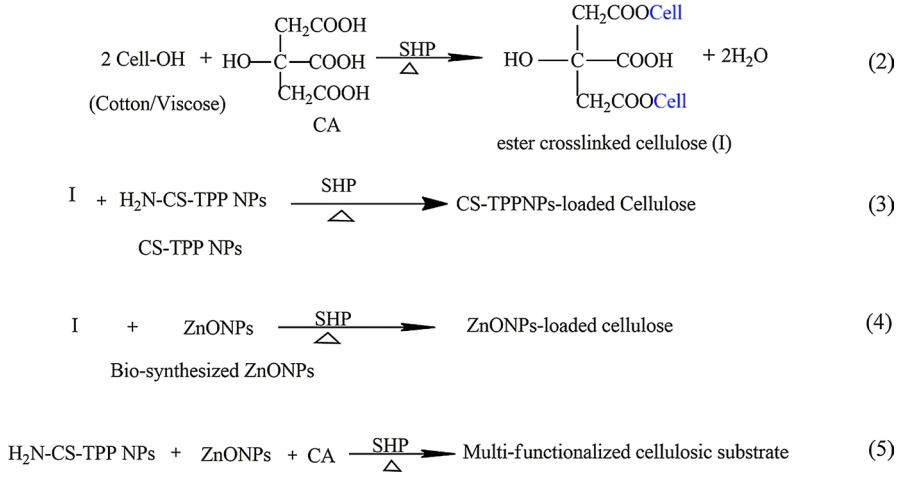
The data in Table 1 also signify that incorporation of the biosynthesized ZnONPs up to 15 g/L along with CS-TPP NPs in the finishing formulation is accompanied by a remarkable increase in the imparted antibacterial activity against both the *S. aureus* and *E. coli* bacteria regardless of the used substrate. The higher the ZnONPs concentration, the more efficient the imparted antibacterial functionality is [34, 49].

Moreover, the remarkable enhancement in the imparted antibacterial activity by increasing ZnONPs concentration up to 15 g/L along with the presence of CS-TPP NPs as bioactive agent could be discussed in terms of: (i) the synergistic antibacterial effect of the loaded ZnONPs via destruction of bacterial cell integrity/liberation of $Zn^{2+}$ ions/generation of reactive oxygen species ($^{\cdot}OH$, $^{\cdot}O_{2-}$, $^{\cdot}HO_2$ and $H_2O_2$) that capable to penetrate through the cell thereby inhibiting or killing the pathogenic microorganisms [23], (ii) the polycationic nature, $–NH_2$ groups, of chitosan and its ability to inhibit the growth of harmful bacteria via: interaction with negatively charged moieties at its surface [37] and (iii) the phytochemical constituents of Miswak bark extract [18].

Additionally, the improvement in the imparted antibacterial activity against *S. aureus* bacterium is better than *E. coli* bacterium, as a direct consequence of variation in cell constitution and physiology as well as the metabolism [13, 22].

The data in Table 1 also demonstrate that the variation in the imparted functional properties, i.e., easy care, anti-UV and antibacterial functionalities, as well as both the %N and %Zn content are governed by type of the finished substrate and reflected the differences between the viscose and cotton substrates in: fabric weight, structure, amorphous/crystalline ratio, availability and accessibility of –OH active sites, location and extent of distribution of bio- and nano-active agents onto and/or within finished cellulose structure, as well as degree of fixation and immobilization of the used nano-active ingredients [21, 24].

Inclusion of CS-TPP NPs into ester-crosslinking formulation along with biosynthesized ZnONPs as functional nano-additive, followed by padding, drying and curing at appropriate fixation conditions would be expected to facilitate multifunctionalization of the viscose and cotton cellulosic substrates simultaneously in one step as shown in Scheme 2 [21, 23] as follows:




**Scheme 2** Simplified reaction scheme for multifunctionalization of cellulosic substrates using CS and ZnONPs

## Multifunctionalization of cotton and viscose cellulosic fabrics using CSNPs along with L-ascorbic acid or vanillin additives

As far as the change in %N, WRA, UPF and antibacterial activity of treated cellulosic substrates as a function of type and concentration of function of type and concentration of functional additive, the data in Table 2 clearly demonstrate that inclusion of L-ascorbic or vanillin (0–20 g/L) additive along with CSNPs (2.5 g/L) and CA/SHP ester-crosslinking system (30/15 g/L) in the finishing formulation followed by padding and curing is accompanied by an increase in %N, WRA and UPF values as well as in the imparted antibacterial activity against both the *S. aureus* and *E. coli* pathogenic bacteria, irrespective of the treated substrate. The higher the functional additive concentration, the better are the imparted functionalities, i.e., fabric resiliency, anti-UV capability and antibacterial efficacy [26].

The enhancement in the imparted functional properties reflects the positive role of functional properties reflects the positive role of functional additive in: increasing the extent of CSNPs fixation, expressed as % N, enhancing the UV shielding and blocking capability, expressed as UPF value, along with supporting the imparted antibacterial activity to the treated substrates, expressed as % R, against the tested pathogens. On the other hand, the positive changes in the aforementioned properties are governed by type of functional additive and follows, the decreasing order: L-ascorbic acid < vanillin, as well as kind of cellulosic substrate as discussed earlier, keeping other parameters constant [20, 25, 26].

The imparted anti-UV and antibacterial effects of L-ascorbic could be discussed in terms of: the presence of antioxidant and flavonoids constituents, its ability to lower the pH, its anti-quorum sensing activity, its oxygen absorption characteristics thereby acting as a barrier for oxygen availability for tested

**Table 2** Effect of combined phenolic compound and chitosan nanoparticles with citric acid on some performance and functional properties of cellulose fabrics

| Additives | Additives conc. (g/L) | Substrate | *N* (%) | WRA (*W* + *F*)° | UPF | Antibacterial activity *R* % | |
|---|---|---|---|---|---|---|---|
| | | | | | | *S. aureus* | *E. coli* |
| L-ascorbic | 0 | Cotton | 0.577 | 162 | 15 | 50 | 47 |
| | | Viscose | 0.809 | 130 | 11 | 60 | 58 |
| | 10 | Cotton | 0.832 | 179 | 40 | 75 | 67 |
| | | Viscose | 1.322 | 157 | 35 | 85 | 76 |
| | 20 | Cotton | 0.864 | 200 | 54 | 82 | 77 |
| | | Viscose | 1.337 | 183 | 48 | 91 | 86 |
| Vanillin | 0 | Cotton | 0.577 | 162 | 15 | 50 | 47 |
| | | Viscose | 0.809 | 130 | 11 | 60 | 55 |
| | 10 | Cotton | 0.844 | 173 | 30 | 69 | 60 |
| | | Viscose | 0.949 | 145 | 25 | 78 | 71 |
| | 20 | Cotton | 0.869 | 192 | 40 | 80 | 73 |
| | | Viscose | 0.998 | 160 | 36 | 90 | 80 |

Finishing formulation: citric acid 30 g/L; $NaH_2PO_2$ 15 g/L; CSNPs 2.5 g/L; phenolic compound (0–20) g/L; wet pick-up (80%); drying at 100 °C/3 min and curing at 150 °C/2 min

*N* nitrogen content, *WRA* wrinkle recovery angle (warp + weft), *UPF* UV protection factor and *R*% reduction in percentage of bacterial colonies, G + ve *S. aureus* and G − ve *E. coli*

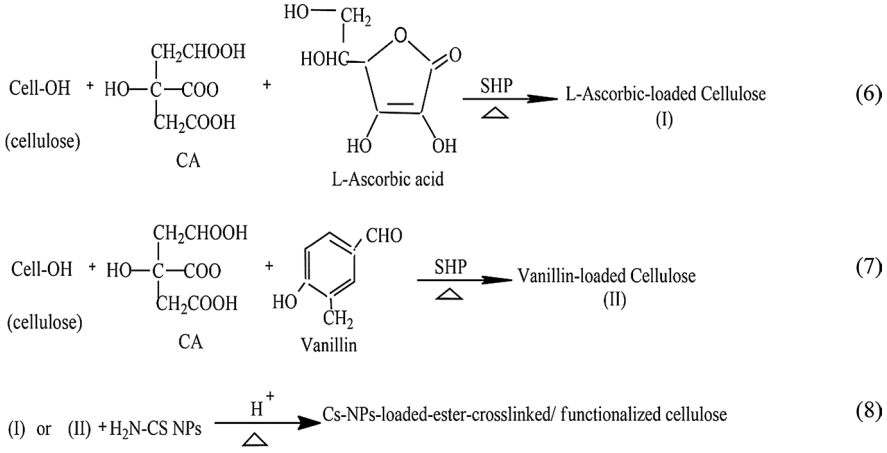
Properties of untreated cotton are: %*N* = 0.00, metal content % = 0.00, WRA = 110, UPF = 6 and antibacterial activity against *S. aureus* and *E. coli* bacteria = 0%

Properties of untreated viscose are: %*N* = 0.00, metal content % = 0.00, WRA = 97, UPF = 3 and antibacterial activity against *S. aureus* and *E. coli* bacteria = 0%

microorganisms, as well as due to the significant synergistic antibacterial effects of CSNPs, L-ascorbic acid at low pH against the tested *S. aureus* and *E. coli* bacteria [26].

On the other hand, the significant improvement in antibacterial functionality against both *S. aureus* and *E. coli* harmful bacteria by fixation and immobilization of vanillin, as a safe and effective anti-UV and antibacterial agent onto/within the ester-crosslinked substrates most probably is due to its ability as phenolic aldehyde to damage and disrupt the bacterial cell which, in turn, adversely affects its growth and survival, along with its ability to absorb the harmful UV-B radiation [20].

The variation in the imparted antibacterial functionality is governed by chemical composition, molecular size, bioactive constituents, extent of loading and release, mode of action, as well as, the synergistic effect of the functional additives and other finishing bath constituents [20]. Moreover, simplified reaction Scheme 3 for fixation and immobilization of the functional additives onto and for within the ester-crosslinked cellulose structure during the thermofixation step could be suggested as follows [20].




Fixation of Cs-NPs via the free-COOH groups of ester crosslinked cellulose and/or via-CHO group of grafted vanillin or via-C=O group of grafted L-Ascorbic acid

**Scheme 3** Simplified reaction scheme for multimodification of the treated cellulosic substrates using L-ascorbic acid or vanillin as additive

## SEM and EDX analysis

Figure 4 demonstrates the changes in surface morphology and elemental composition of selected untreated cotton (a, b) and viscose (e, f) samples as well as treated cotton (c, d) and viscose (g, h) fabric samples using CA/SHP (30/15 g/L), CSNPs (2.5 g/L) and ZnONPs (15 g/L) finishing formulation. SEM of the selected fabrics samples clearly shows that ester-crosslinking of the cellulosic substrates in the presence of CSNPs and ZnONPs forms surface deposits as a direct consequence of loading the functional additives onto the ester-crosslinked cotton (Fig. 4c) and viscose (Fig. 4g) compared with the untreated ones (Fig. 4a and e), respectively. The change in surface morphology reflects the differences between cotton and viscose substrates in fabric surface, extent of modification as well as post-coating and deposition of the thermofixed ingredients onto the fabric during the thermofixation step.

Additionally, EDX spectra of multifunctionalized cotton (Fig. 4d) and viscose (Fig. 4h) demonstrated new peaks of N, P and Zn elements in their pattern confirming the fixation and immobilization of CSNPs, SHP and ZnONPs onto the ester-crosslinked substrates in comparison with the untreated ones (Fig. 4b and f), respectively. The extent of ester-crosslinking and simultaneous fixation of the used functional additives is determined by type of cellulose, kind of functional additive as well as degree of fixation and immobilization during the curing step.

Fixation and immobilization of ZnONPs onto the modified cellulose structure could be discussed in terms of the availability of both $–NH_2$ groups and free –COOH groups in the crosslinked cellulose structure which can help in coordination and immobilization of ZnONPs [23].

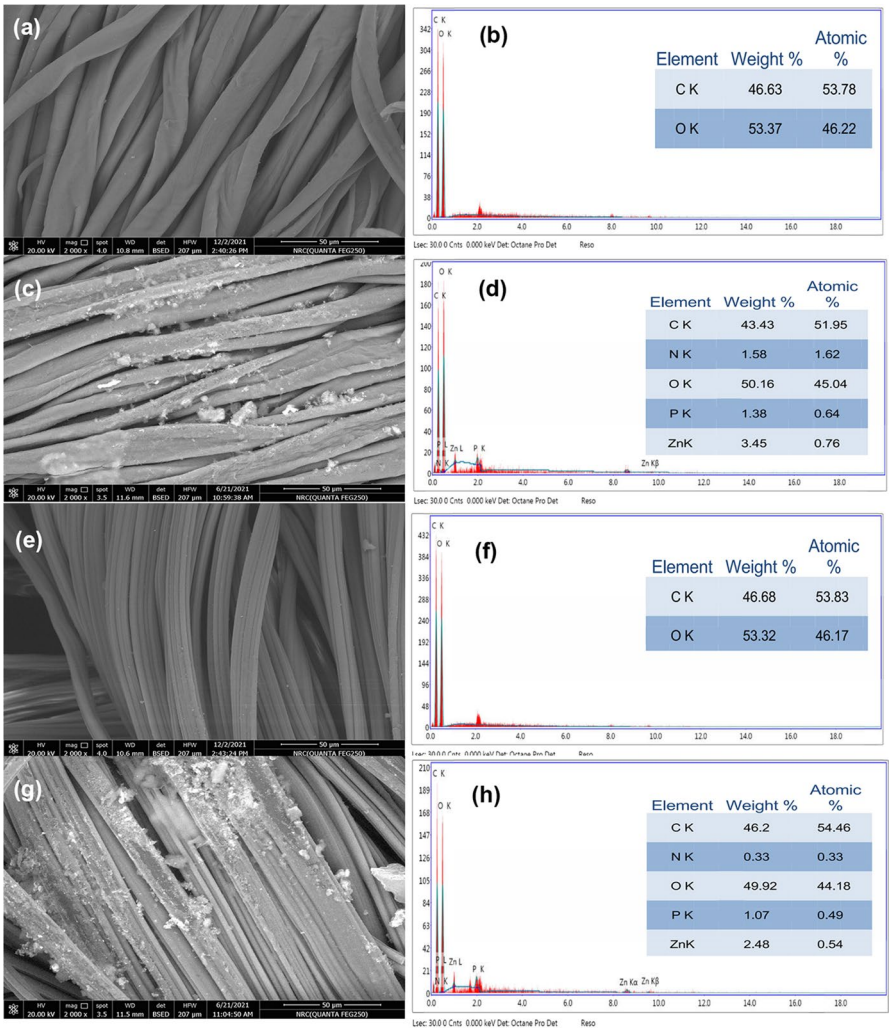



**Fig. 4** SEM image and EDX spectra of untreated cotton **a**, **b**, treated cotton with ZnONPs, CSNPs, CA and SHP **c**, **d**, untreated viscose **e**, **f**, treated viscose with ZnONPs, Cs, CA and SHP and **g**, **h** fabrics

## Durability to wash

The washing durability of multifunctionalized cellulosic substrates was also evaluated, and the experimental results are given in Table 3. The data in Table 3 demonstrate that increasing the washing cycles up to 10 results in a reasonable decrease in both the chemical and functional properties of the developed fabrics. The extent of decrease in the aforementioned properties is governed by type of cellulosic substrate and functional additives. The reasonable decrease in the evaluated properties is a direct consequence of the partial removal of unreacted and

**Table 3** Durability to wash

| Additive | Substrate | Washing cycle | Chemical and functional properties | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | *N* (%) | Metal content (%) | WRA ($W+F$)° | UPF | *R* (%) | |
| | | | | | | | *S. aureus* | *E. coli* |
| CSNPs (2.5 g/L) + ZnONPs (15 g/L) | Cotton | 1 | 1.592 | 1.24 | 196 | 47 | 94 | 89 |
| | | 10 | 1.580 | 1.10 | 186 | 45 | 90 | 83 |
| | Viscose | 1 | 1.818 | 1.35 | 165 | 40 | 97 | 92 |
| | | 10 | 1.80 | 1.20 | 151 | 36 | 92 | 85 |
| CSNPs (2.5 g/L) + L-ascorbic (20 g/L) | Cotton | 1 | 0.864 | – | 200 | 54 | 82 | 77 |
| | | 10 | 0.850 | – | 191 | 50 | 78 | 73 |
| | Viscose | 1 | 1.337 | – | 183 | 48 | 91 | 86 |
| | | 10 | 1.317 | – | 170 | 42 | 84 | 80 |
| CSNPs (2.5 g/L) + Vanillin (20 g/L) | Cotton | 1 | 0.869 | – | 192 | 40 | 80 | 73 |
| | | 10 | 0.851 | – | 180 | 35 | 75 | 70 |
| | Viscose | 1 | 0.998 | – | 160 | 36 | 90 | 80 |
| | | 10 | 0.979 | – | 145 | 30 | 83 | 75 |

Finishing conditions are shown in Tables 1 and 2, respectively

non-fixed active ingredients and confirms the high degree of fixation of the finishing formulation constituents during the thermofixation step.

## FTIR features of finished substrates

Figures 5 and 6 show the results of FTIR analysis of untreated and finished of some selected samples.

Untreated cotton (Fig. 5a) showed the following peaks: nearly 3339.42 $cm^{-1}$, around 2897.32 $cm^{-1}$ and 1600 $cm^{-1}$ attributed to O–H stretching, C–H stretching and due to the adsorbed water molecule, respectively. While the IR spectra of finished cotton fabric sample with CA/SHP, CSNPs and ZnONPs (Fig. 5b) showed an additional peak at 1730 $cm^{-1}$ corresponded to C=O stretching for ester linked cellulose with citric acid and a new peak at 500 $cm^{-1}$ attributed to the bio-prepared ZnONPs.

Regarding finished cotton fabric samples with L-ascorbic acid and vanillin, respectively, Fig. 6b and c, the C=C stretching in the L-ascorbic and vanillin overlaps with the OH bending in untreated fabric samples at 1600.42 $cm^{-1}$. Moreover, additional new peaks were observed at 1313.35 $cm^{-1}$ and 1311.42 $cm^{-1}$ for the C–O stretching bands in L-ascorbic and vanillin, respectively.

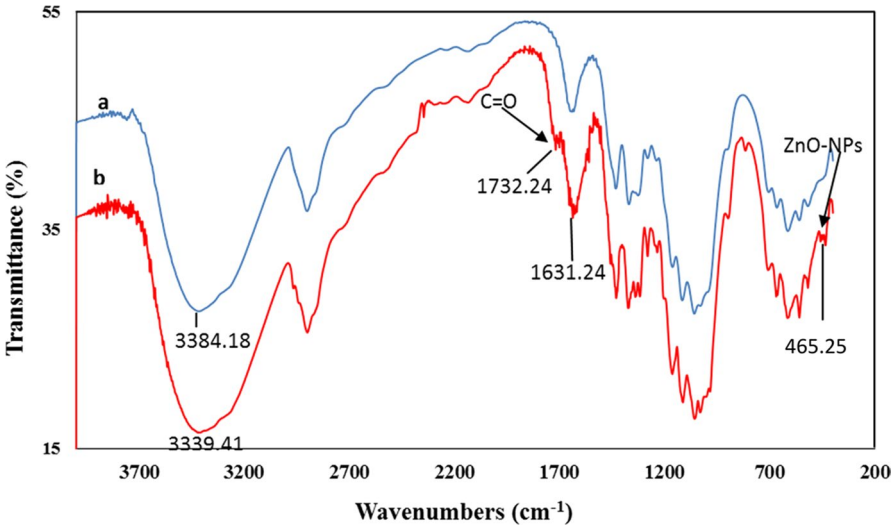



**Fig. 5** FTIR of the untreated and finished cotton fabric samples with ZnONPs, CS, CA and SHP **a** untreated fabrics and **b** finished fabrics

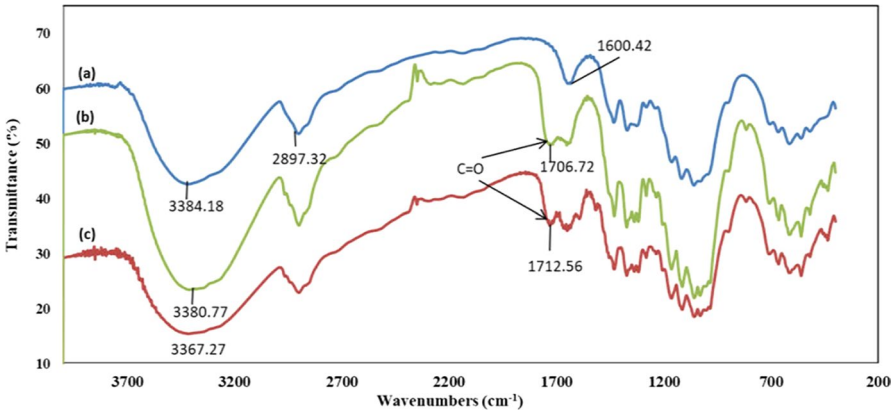



**Fig. 6** FTIR of the untreated and finished cotton and viscose fabrics **a** untreated fabric, **b** L-ascorbic finished fabric and **c** vanillin finished fabric

## Conclusion

The main task of the present research work is to a develop a single-stage multifunctional treatment of cotton and viscose cellulosic substrates to impart anti-crease, UV blocking and antibacterial functions using environmentally sound and sustainable finishing formulations. Green synthesis of ZnONPs and CSNPs and their positive role in the development of multifunctionalized cotton and viscose fabrics using CA/SHP as ester-crosslinking system and pad-dry-cure thermofixation method are reported. Inclusion of ZnONPs (15 g/L) or a synergistic constitutions of CSNPs (2.5 g/L)/L-ascorbic acid (20 g/L) or CSNPs (2.5 g/L)/vanillin (20 g/L) in the ester-crosslinking formulations resulted in a remarkable improvement in the imparted anti-crease, UV protection and antibacterial efficacy of the finished fabrics, irrespective of the treated substrate.

The extent of improvement in the imparted functional properties is determined by the kind of cellulosic substrate as well as type of finishing formulation constituents. Moreover, FTIR, SEM and EDX analysis confirm surface modification and functionalization of the treated fabric samples. The results obtained further signify that increasing washing cycles up to 10 cycles resulted in a slight decrease in the imparted functional properties. Thus, it can be concluded that developing of durable multifunctionalized textile products using an eco-friendly, and facile single-step finishing regime greatly supports the possibility of a wide range of potential and practical applications.

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## Declarations

**Conflict of interest** The authors have declared that they have no conflict of interest.



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