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Antibacterial property and characterization of cotton fabric treated with chitosan/AgCl–TiO_2 colloid

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ABSTRACT

The antibacterial activity of cotton fabric was studied by using chitosan/AgCl–TiO_2 colloid. Different blend ratios of chitosan to AgCl–TiO_2 colloid were used to investigate the efficacy of antibacterial activity against *Staphylococcus aureus* (gram positive) and *Escherichia coli* (gram negative) and its effect on physical properties of cotton fabric. Our study shows that the combination of chitosan with AgCl–TiO_2 colloid produced better antibacterial activity than the fabric treated without chitosan; 100% bacterial reduction against *S. aureus* and *E. coli* obtained with chitosan/AgCl–TiO_2 colloid at concentrations of 4 g/L and 10 g/L respectively. Moreover, the treated cotton indicates improved tensile strength and wrinkle recovery angle (WRA). Increasing chitosan concentration slightly affected the fabric stiffness and whiteness. The treated cotton fabrics were further characterized by Fourier Transform Infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM), energy dispersive X-ray (EDX) and wide angle X-ray (WAXD). We can expect a direct industrial application of our proposed work because it is simple one go pad-dry-cure method and the low cost commercial grades of chitosan and AgCl–TiO_2 are conveniently available in the market.

1. Introduction

Owing to a growing demand for clean and hygienic textile fabric, an urgent need for production of antibacterial textile fabric has arisen (Fouda, Abdel-Halim, & Al-Deyab, 2013; Gao & Cranston, 2008; Purwar & Joshi, 2004; Simoncic & Tomsic, 2010). Therefore, the number of different antibacterial agents suitable for textile application on the market has radically increased (Lam, Kan, & Yuen, 2012). Good antibacterial agent must be safe for the manufacturer to apply, the consumer to wear and have a minimal environmental impact. The antibacterial finish must be easily applied at the textile mill, economical and should be compatible with other finishing agents, and have little, if any, adverse effects on other fabric properties including wear comfort, fabric handle and tensile strength (Fouda et al., 2013; Schindler & Hauser, 2004).

Chitosan has attracted a great deal of interest recently due to having a very good antibacterial property (El-Tahlawy, El-Bendary, Elhendawy, & Hudson, 2005; Fahmy & Fouda, 2008; Fouda, El Shafei, Sharaf, & Hebeish, 2009; Gupta & Haile, 2007; Periolatto, Ferrero, & Vineis, 2011; Raafat & Sahl, 2009; Reicha, Sarhan, Abdel-Hamid, & El-Sherbiny, 2012). Chitosan, the linear and partly acetylated (1-4)-2-amino-2-deoxy-β-D-glucan, is isolated from marine chitin (Muzzarelli, 2011; Muzzarelli et al., 2012). As a natural renewable antibacterial agent, chitosan exhibits non-toxicity, biocompatibility, biodegradability, antimicrobial or antifungal activity and chemical reactivity (Lim & Hudson, 2003). Because of its polycationic nature, chitosan shows good antibacterial activity against various bacteria and fungi (Ye, Xin, Li, Lee, & Kwong, 2006). The only limitation of this antibacterial agent is that it shows high activity against microbes at relatively high concentration which adversely affects the fabric handle (Joshi, Ali, Purwar, & Rajendran, 2009). In previous study, chitosan shows 72% bacterial reduction at 5 g/L concentration (Ortega-Ortiz, Gutiérrez-Rodríguez, Cadenas-Pliego, & Jimenez, 2010).

A substantial research has been carried to explore the antibacterial property of silver (Dubas, Kumlangdudsana, & Potiyaraj, 2006; Gorenšek & Recelj, 2007; Kozicki et al., 2012; Maneerung, Tokura, & Rujiravanit, 2008; Son, Youk, & Park, 2006; Tomšič et al., 2009). Among different metals, silver is by far the most widely used antibacterial agent in textile applications because of its effectiveness against many forms of both gram-positive and gram-negative bacteria, but it is not effective against fungi, mold or mildew (Lam et al., 2012; Purwar & Joshi, 2004). Silver has been described as being 'oligodynamic' because of its ability to exert a bactericidal effect on products containing silver (Fouda et al., 2013; Textor,

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Fouda, & Mahltig, 2010). Silver shows superior and effective functionality against microbes among others as bacteria could not build resistance against silver (Chopra, 2007). However, some of the silver particles dispersed as a rough layer on the surface of cotton fibers are visible on the white fabrics. The dark yellowish color of silver is a problem in its application on textile products (Hu, Zhang, Chan, & Szeto, 2006).

Hence, there exists a need to develop antibacterial cotton fabric which exhibit satisfactory antibacterial property without affecting fabric handle and degree of whiteness. In the present study, various blends of chitosan/AgCl–TiO_2 colloid have been applied on to cotton fabric by simple pad-dry-cure method. The amino (NH_2) and hydroxyl (OH) groups of chitosan can form a chelate complex with the silver (Gouda & Keshk, 2010; Guibal, 2004; Tankhiwale & Bajpai, 2009; Thomas, Bajpai, & Bajpai, 2011). Advantages of this synergistic effect of the colloid containing chitosan and AgCl result in excellent antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* (Gouda & Keshk, 2010; Hu, Chan, & Szeto, 2008; Thomas et al., 2011). Moreover, the synergy of chitosan and AgCl colloid enables a very low add-on process so that the treatment does not affect the handle of the cotton fabric (Hu et al., 2008). The colloid used in this study is a mixture of AgCl and TiO_2, where TiO_2 has an additional antibacterial activity. It is well known that the photocatalytic reaction using TiO_2 in aqueous media has been found to be effective for killing bacteria and inactivating viruses (Dastjerdi & Montazer, 2010; Fouda et al., 2013; Lam et al., 2012; Mihailović et al., 2010; Wang, Zhu, Li, Fu, & Shi, 2012; Yang, Liang, Xu, Gao, & Xu, 2009; Yuan, Ding, Xu, Deng, & Guo, 2010). In fact, TiO_2 has a relatively high-energy band gap and it can only be excited by high-energy UV irradiation. This shortcoming may be overcome by addition of noble metals, such as silver in this case, which increase the photocatalytic activities of TiO_2 by extending the range of light absorption from UV to visible light; for example, silver can act as an electron trap, aiding electron–hole separation and can also facilitate electron excitation by creating a local electric field (Dastjerdi & Montazer, 2010; Lam et al., 2012; Perelshtein, Applerot, Perkas, Grinblat, & Gedanken, 2012).

Based on the literature reported, antibacterial finishing of cotton fabric with composite finishes have obvious advantages in terms of better antibacterial and physical properties. Therefore, the present study has dealt with the application of chitosan/AgCl–TiO_2 colloid by simple pad-dry-cure method. The proposed finish offers better antibacterial property against *S. aureus* and *E. coli* without affecting fabric whiteness and fabric handling. The finished cotton was characterized by FTIR, SEM and EDX analysis.

2. Materials and methods

2.1. Materials

A bleached 100% cotton fabric (250 g/m^2) was used. Commercially available AgCl–TiO_2 colloid provided by Clariant Pakistan Ltd., under trade name of Sanitized T 27-22 Silver and was used as received. The average particle size of silver in the colloid was around 5 μm, measured by Generic latex measurement method. Chitosan (85% de-acetylated) purchased from Marine Chemicals, India and solubilized in acetic acid (pH 4) before use.

2.2. Methods

Antibacterial cotton was prepared by one-step treatment with chitosan/silver colloid (AgCl–TiO_2) blend. The cotton fabric was treated by pad-dry-cure method as followed by other researchers (El-Rafie, Mohamed, Shaheen, & Hebeish, 2010). Briefly, cotton fabric was dipped into antibacterial solutions and nipped through the padder at 70% pickup and dried at 120 °C for 2 min followed by curing at 150 °C for 3 min using laboratory mini-dryer. The antibacterial solutions were prepared by blending chitosan (1–5 g/L) with AgCl–TiO_2 colloid (1–25 g/L).

2.3. Measurements

Antibacterial activity of treated samples was evaluated according to AATCC-100 method and followed as described by Tomšič et al. (2009). Two bacteria *S. aureus* (gram positive) bacteria and *E. coli* (gram negative) bacteria were used as the test organisms. Briefly, treated and control (untreated) fabric swatches were inoculated with the test organisms. After incubation for 24 h, the bacteria were collected from the swatches by shaking in neutralizing solution. Number of bacteria's present in this liquid was determined and Bacteria Reduction percentage (*%BR*) in the treated swatches was calculated using Eq. (1) as described by other researchers (Ali, Rajendran, & Joshi, 2011).

$$\%\mathrm{BR} = \frac{B - A}{B} \times 100 \quad (1)$$

where A is the number of bacteria recovered from the inoculated treated test specimen swatches incubated over the desired period of time and B is the number of bacteria recovered from the inoculated untreated test specimen swatches immediately after incubation (zero contact time).

Tensile strength of treated samples was measured according to ASTM D 5035 strip test method using UTR-4 (Uster) and the fabric Bending length was measured according to ASTM D 1388-96 using stiffness tester (SDL International). CIE Degree of whiteness (Whiteness Index) of treated samples was assessed using an X-rite Color-Eye 7000A Spectrophotometer. Crease recovery angle of treated samples were measured according to the AATCC-066 wrinkle recovery of woven fabrics method.

The chemical changes to cotton fabric treated with chitosan and AgCl–TiO_2 colloid were analyzed on FTIR spectroscopy (IR Prestige-21 by Shimadzu, Japan). SEM (S-3000N by Hitachi, Japan) was used to study morphology of fabric after treated with chitosan and AgCl–TiO_2 colloid. Energy dispersive X-ray (EDX) was used to analyze for elemental distribution over the surface of cotton fibers. The wide-angle X-ray diffraction (WAXD) experiments were performed at room temperature with hybrid nanofiber samples using a Rotaflex RTP300 (Rigaku Co., Japan) X-ray diffractometer operating at 50 kV and 200 mA Nickel-filtered Cu K_α radiation was used for the measurements, along with an angular range of $5 < 2\theta < 30^\circ$.

3. Results and discussion

3.1. Antibacterial activity against S. aureus and E. coli

The effect of chitosan/AgCl–TiO_2 colloid concentration on the antibacterial activity against *S. aureus* a gram-positive bacteria and *E. coli* a gram-negative bacteria is shown in Fig. 1a and b respectively. Fig. 1a shows that the antibacterial activity increased with increasing the concentration of AgCl–TiO_2 colloid without chitosan being added and the 100% BR against *S. aureus* obtained using concentration of 20 g/L of AgCl–TiO_2 colloid. The combination of chitosan with each concentration of AgCl–TiO_2 colloid significantly enhanced the %BR. The maximum of 100% BR could achieve at combination of chitosan/AgCl–TiO_2 colloid at 4 g/L and 10 g/L respectively. In general, combination of chitosan with AgCl–TiO_2 colloid showed even more antibacterial activity than the fabric treated without chitosan; this may be due to the availability of free amino groups present in chitosan to interact with the bacterial cell surface (Ali et al., 2011). Although any further increment in the concentration of chitosan was advantageous in terms of better

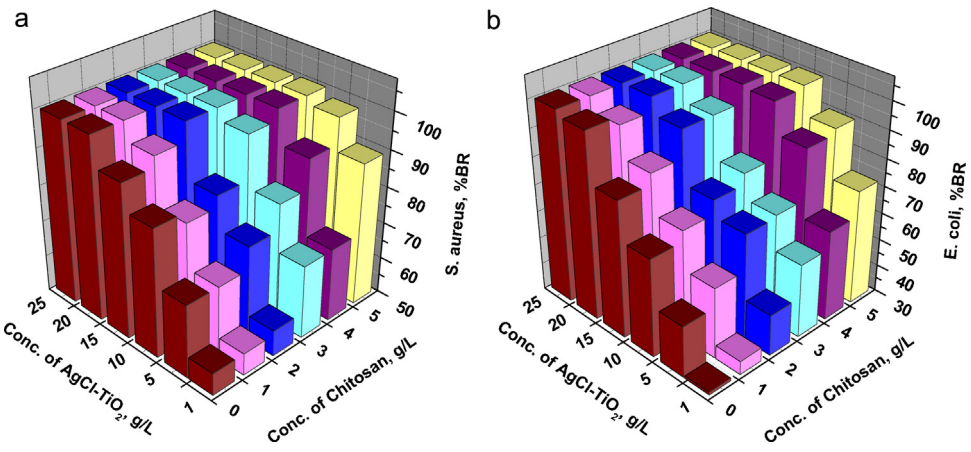

Fig. 1. Antibacterial activity against *S. aureus* (a) and *E. coli* (b).

antibacterial activity and reduction of AgCl–TiO_2 colloid concentration, but it thwarted by fabric stiffness imparted by the chitosan.

Antibacterial activity for *E. coli*, gram-negative bacteria, is demonstrated in Fig. 1b. The %BR increased with the increase of AgCl–TiO_2 colloid concentration. Fig. 1b depicts that he concentration of at least 25 g/L of AgCl–TiO_2 colloid could completely inhibit the growth of *E. coli* as the %BR was 100%. The bacterial reduction was fairly obvious for chitosan/AgCl–TiO_2 colloid blend. A significant %BR obtained as the chitosan concentrations was increased with each AgCl–TiO_2 colloid concentration used. The %BR of 98% (if not 100%) achieved at 4 g/L and 10 g/L of chitosan/AgCl–TiO_2 colloid concentrations respectively. As discussed earlier that the chitosan concentration of more than 5 g/L imparted a considerable stiffness to the fabric and therefore not selected as optimum sample. It was inferred that the chitosan enhanced %BR of around two fold to the antibacterial property obtained using AgCl–TiO_2 colloid without chitosan. This is mainly due to polycationic nature of chitosan, which is caused by protonation of the amino groups at the C-2 atoms of the glucosamine units. Positively charged amino groups have ability to bind to the negatively charged bacterial surface, resulting in the disruption of the cell membrane and an increase in its permeability (Simoncic & Tomsic, 2010).

3.2. Fabric tensile strength and bending length

It is well known that the chitosan significantly imparts stiffness in fabric and affect tensile strength of fabric; therefore, we studied the effect of chitosan concentration on fabric tensile and bending length, keeping AgCl–TiO_2 colloid concentration of 10 g/L as optimized. Fig. 2 shows the results of tensile strength and bending length of fabric treated with various concentrations of chitosan. The tensile strength of fabric increased gradually with increasing the concentration of the chitosan. This increase in strength is probably due to binding of chitosan between fibers and yarn. The fabric bending length is also demonstrated in Fig. 2. The increasing bending length of the treated fabric demonstrates the extent of stiffness in the fabric. As expected, the fabric bending increased with increasing concentration of chitosan; our results are in agreement with the work by Gupta and Haile (2007).

3.3. Whiteness Index and wrinkle recovery angle

The effects of chitosan concentration on Whiteness Index (WI) and wrinkle recovery angle (WRA) were evaluated on optimized sample treated with 10 g/L of AgCl–TiO_2. The results in Fig. 3 revealed that the sample treated with AgCl–TiO_2 containing no chitosan produced WI of 66 which is considered to be a natural

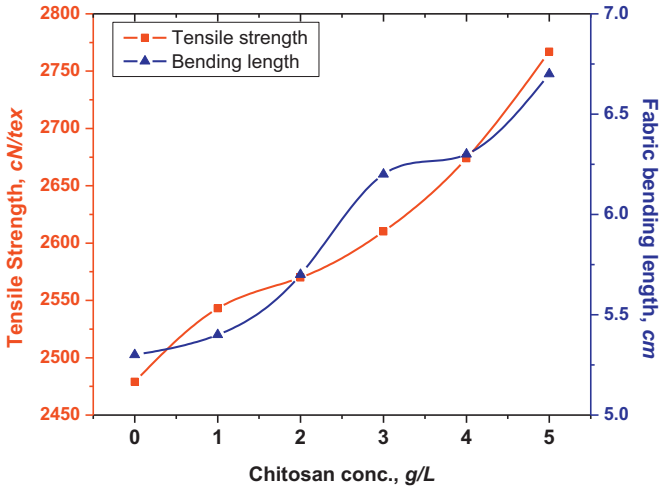

Fig. 2. Effect of chitosan concentration on fabric tensile strength and fabric bending length. (The concentration of AgCl–TiO_2 colloid in each blend of chitosan/AgCl–TiO_2 was 10 g/L.)

white under daylight conditions. Addition of chitosan cause decreament in WI with increasing concentration from 1 to 5 g/L, for instance, cotton fabric treated with 5 g/L of chitosan showed around 6 degrees less than the cotton fabric treated with 1 g/L of

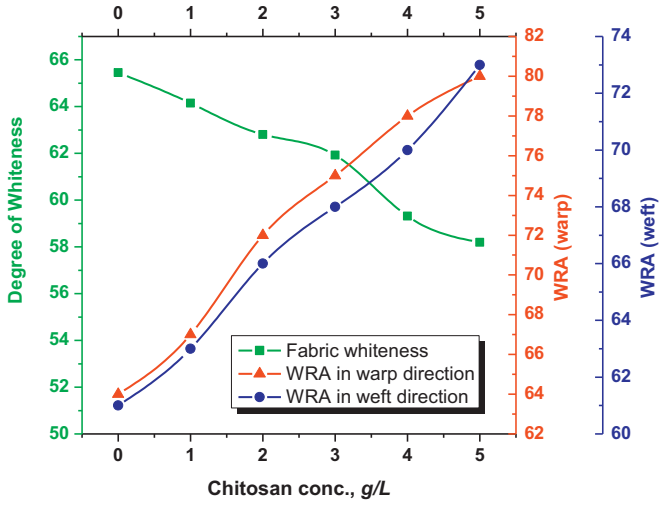

Fig. 3. Effect of chitosan concentration on Whiteness Index and WRA. (The concentration of AgCl–TiO_2 colloid in each blend of chitosan/AgCl–TiO_2 was 10 g/L.)

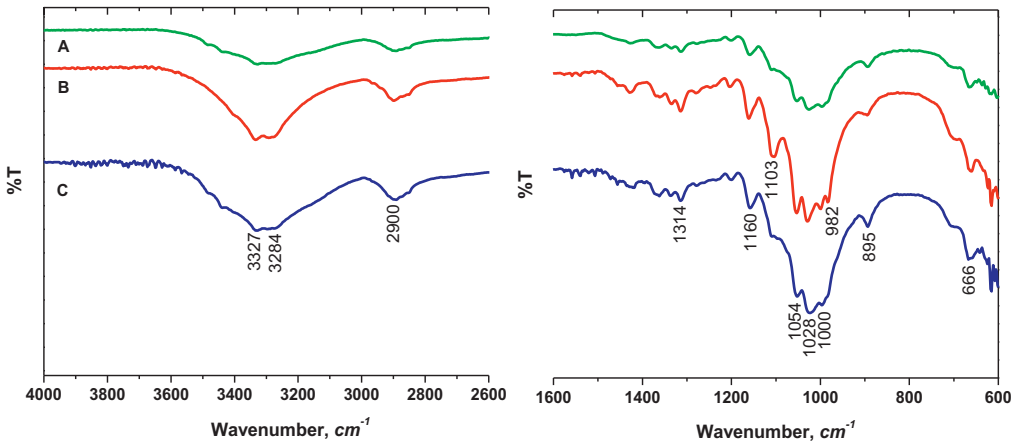

Fig. 4. FT-IR spectra untreated cotton (A) treated cotton with 10 g/L AgCl–TiO_2 colloid (B) and treated cotton with chitosan/AgCl–TiO_2 colloid (C). (The concentrations of chitosan and AgCl–TiO_2 colloid in the blend were 4 g/L and 10 g/L respectively.)

chitosan. The obvious reason for this is the increased concentration of chitosan which imparts yellowness in the fabric. Our results are in agreement with the work by Gupta and Haile (2007).

The results of WRA in warp and weft directions of the treated fabrics are also shown in Fig. 3. Irrespective to the warp or weft directions, WRA of treated cotton is better than the untreated one. Moreover, WRA increased with increasing concentration of chitosan. It may be due to the stiffness imparted in the fabric, as discussed in Section 3.2 (Fig. 2). Results show that the use of chitosan is advatangeous in terms WRA improvement and has less significant effect on WI.

3.4. FTIR analysis

The FTIR spectra of untreated and treated cotton fibers have been shown in Fig. 4. The characteristic adsorption peaks of cellulose at around 1000–1200 cm^{-1}, hydrogen-bonded OH stretching at 3550–3100 cm^{-1}, the CH stretching at 2900 cm^{-1}, and the CH wagging at 1314 cm^{-1} (Khatri, Mayakrishnan, Hirata, Wei, & Kim, 2013). The C—H banding and —CH_2 stretching at 895 cm^{-1} indicate amorphous structure of cellulose. The treated cotton (Fig. 4B) show distinctive peaks at 1103 cm^{-1} correspond to TiO_2 stretching (Wang et al., 2012), band of Ti—O vibrations at around 982 cm^{-1} (Fakin, Veronovski, Ojstrsek, & Bozic, 2012) and symmetric O—Ti—O stretch bands at around 666 cm^{-1} (Fakin et al., 2012). The cotton treated with chitosan/AgCl–TiO_2 colloid (Fig. 4C) exhibits broadening of peaks at 3327 cm^{-1} and 3284 cm^{-1} correspond to O—H and N—H stretchings respectively, which are the characteristic bands of chitosan (Wang, Zhang, Liu, & Lin, 2006). In comparison to cotton fabric treated with AgCl–TiO_2 colloid (b), the peak intensities at around 982 cm^{-1} and 1103 cm^{-1} in cotton fabric treated with chitosan/AgCl–TiO_2 (c) are reduced significantly, this may be due to the complexation of chitosan with AgCl–TiO_2 (Ali et al., 2011; Arain, Khatri, & Memon, 2012). Owing to a very lower concentration of silver salt in AgCl–TiO_2 colloid used in commercial product Sanitized T 27-25, the silver salt could not be detected in FTIR spectra. Our results are in well agreement with (Tomšič et al., 2009). The SEM-EDX revealed that the TiO_2 concentration is dominated in the AgCl–TiO_2 colloid.

3.5. Wide angle X-ray diffraction

The XRD patterns of treated and untreated cotton have been given in Fig. 5. Both treated and untreated cotton demonstrated peaks at $2\theta = 14.9^\circ$, 16.7°, 20.3° and 22.7°, which correspond to (1 0 1), (1 0 $\bar{1}$), (0 2 1) and (0 0 2) crystal planes of cellulose I (Khatri, Arain, et al., 2013; Nithya et al., 2011; Segal, Creely, Martin, & Conrad, 1959). The TiO_2 peaks appeared at $2\theta = 37.9^\circ$, 42.4° and 47° correspond to (0 0 4), (0 0 2) and (1 1 1) crystal planes (JCPDS File Card No. 21-1272) (Chang & Liu, 2007; Yamamoto et al., 2009; Yin et al., 2011; Zhu et al., 2012). XRD measurement suggests that the crystalline phase of the cotton treated with chitosan/AgCl–TiO_2 colloid has changed slightly, which may owing to the interactions between AgCl–TiO_2 colloid with the oxygen atoms on either cellulose or chitosan chains and (Yan, Wang, Huang, Xin, & Tong, 2007), which may also be due to the interactions between cellulose and chitosan. Moreover, the peak intensities of treated cotton were observed to be higher than the untreated cotton and therefore, exhibit better crystalline phase. We believe, this may be the reason why tensile strength of treated cotton increased with increasing chitosan concentration as discussed earlier in Section 3.2.

3.6. Surface morphology and energy dispersive X-ray analysis

The SEM images of untreated and treated cotton fabric with AgCl–TiO_2 and chitosan/AgCl–TiO_2 colloid are shown in Fig. 6a–c respectively. A layer of chitosan can be seen over the surfece cotton fibers Fig. 6c. Moreover, the binding of chitosan between the cotton

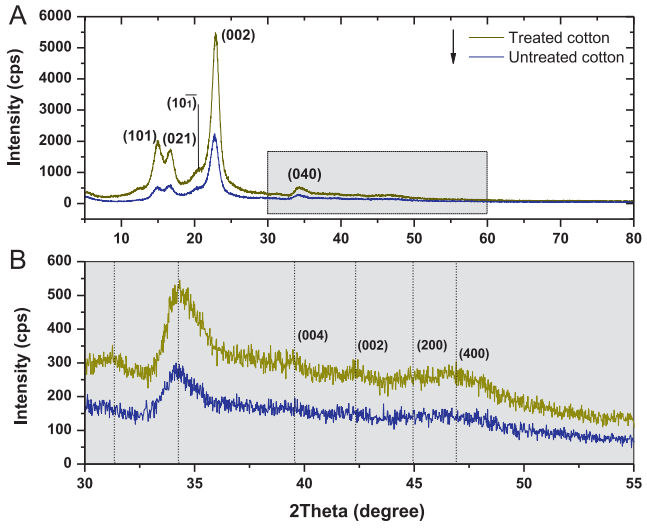

Fig. 5. X-ray pattern of untreated cotton and treated cotton with chitosan/AgCl–TiO_2 colloid (a) and zoom between 30and 55 2θ degrees (b). (The concentrations of chitosan and AgCl–TiO_2 colloid in the blend were 4 g/L and 10 g/L respectively.)

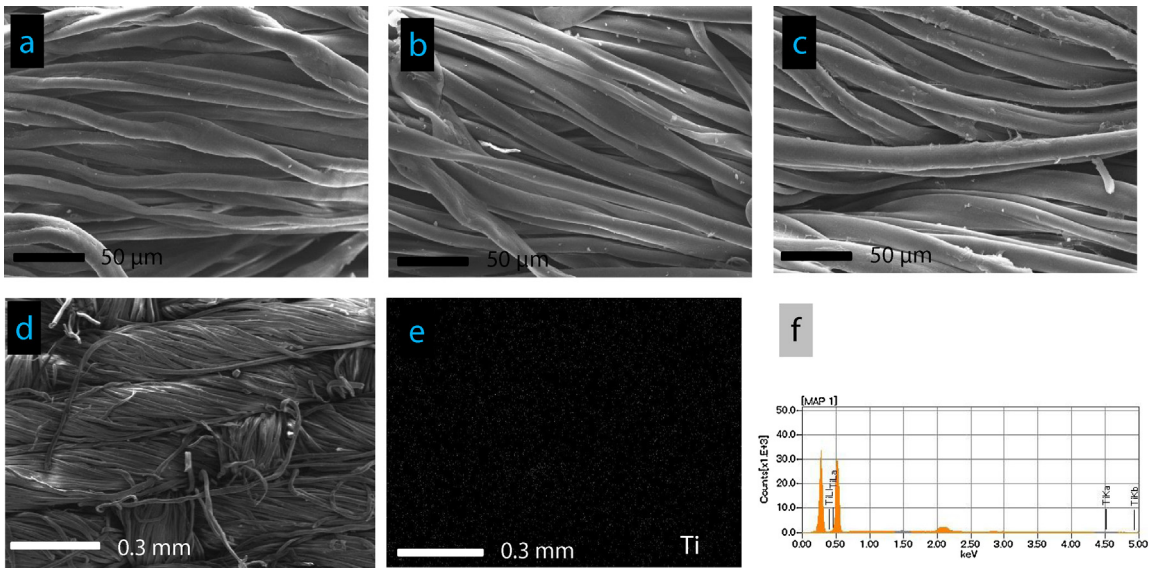

Fig. 6. SEM images of (a) untreated cotton, (b) cotton fabric treated with AgCl–TiO_2 and (c) cotton fabric treated with chitosan/AgCl–TiO_2; SEM-EDX of treated cotton, (d and e) selected area for mapping and (f) its corresponding elemntal mapping of Ti. (The concentrations of chitosan and AgCl–TiO_2 colloid in the blend were 4 g/L and 10 g/L respectively.)

fibers may be a contributing factor of increased bending length and enhanced tensile strength. The particles of Ag-TiO_2 are also visible in Fig. 6b and c.

The presence of Ti particles on the surface of cotton fabrics was substantiated by SEM analysis performed in EDX mode. EDX spectra of the fabrics treated with AgCl–TiO_2 and chitosan/AgCl–TiO_2 are shown in Fig. 6d–e. EDX measurements revealed that the Ti was around 7% and its distribution was uniform over the surface of cotton fibers, whereas, the silver could not be detected by EDX due to even lower concentration than the Ti in the colloid.

4. Conclusion

In general, combination of chitosan with AgCl–TiO_2 colloid showed better antibacterial activity than the fabric treated without chitosan. The concentrations optimized were 4 g/L for chitosan and 10 g/L for AgCl–TiO_2 colloid; and the bacterial reduction of 100% and 98% achieved against *S. aureus* and *E. coli* respectively. The concentration of chitosan greater than 4 g/L was advantageous in terms of better antibacterial activity and reduction of AgCl–TiO_2 colloid concentration, but it thwarted by fabric stiffness imparted by the chitosan. The effects of increasing concentration of chitosan on physical properties of cotton fabric showed an increase in tensile strength and improvement in WRA, while the fabric bending length increased that demonstrates the fabric stiffness. The results for degree of whiteness demonstrated that AgCl–TiO_2 colloid has no negative effect on fabric whiteness; however, a slight decrease at higher concentration of chitosan was observed. Owing to a lower concentration of chitosan/AgCl–TiO_2 colloid, the SEM images revealed a very clean and uniform surface morphology of treated cotton. The characterization of treated cotton by FTIR revealed a better absorption of AgCl–TiO_2 by chitosan and SEM-EDX showed a dominating TiO_2 with uniform distribution over cotton fiber surface. We conclude that the proposed work provides a rationale for direct industrial application due to the following reasons; first, the antibacterial agents used are commercially available from number of suppliers at competitive price; second, no special treatment is required after blending and mixing chitosan and AgCl–TiO_2 colloids; and the third is the ease of application by virtue of a single pad-dry-cure process.

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