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Functionalization of cotton fabric with PVP/ZnO nanoparticles for improved reactive dyeability and antibacterial activity

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ABSTRACT

Poly-N-vinyl-2-pyrrolidone functionalization was done for improved the dyeability of dichlorotriazine dyes on cotton fabric. The synthesized ZnO nanoparticles were padded on functionalized cotton fabrics to improve antibacterial activity. The modification effects were characterized by FTIR, XRD, SEM and EDX studies. The antibacterial activity was done against *Staphylococcus aureus* and *Escherichia coli* bacterium. The dye exhaustion and fastness properties were analyzed for dyeing with sodium chloride, sodium sulfate and trisodium citrate bio-salt as exhausting agents. The functionalized cotton fabric showed improved dye uptake and good fastness properties. Poly-N-vinyl-2-pyrrolidone with ZnO nanoparticles padded fabrics showed very good antibacterial activity.

1. Introduction

Nowadays, reactive dyeing of cotton fabrics has been faced with many serious problems due to incomplete absorption of dyes during the exhaustion, incomplete reaction, and destruction of bond between fiber and dyes during the fixation (Houshyar & Amirshahi, 2002). The modification of cotton fabrics for improved dye uptake is considered as the best route to minimize the waste water pollution.

Several works have been reported on modification of cotton fabrics done for improved dye uptake with poly(sodium 4-styrenesulfonate), poly(diallyldimethylammonium chloride), (2,3-epoxypropyl) trimethylammonium chloride, carboxymethyl cellulose and sodium benzoylthioglycollate (Broadbent & Lewis, 2000; Lidija Fras, Per, Janne, & Karin, 2008; Wang & Peter Hauser, 2009). These modifications played only improvement of dye uptake function. But poly-N-vinyl-2-pyrrolidone (PVP) polymers play many roles such as film formers, detoxicants and bio-active compound. These can be crosslinked by heating, radiation and potassium persulfate. The mechanism of crosslinking of PVP chains by heating has been clearly explained. Recently the PVP with chitosan film was reported for improved antibacterial activity (Can, 2005; Fahmy, Abo Shoshaa, & Ibrahim, 2009; Lia, Zivanovica, Davidsona, & Kit, 2010; Minghong, Borong, Fumio, & Keizo, 2001).

Hsiao and Huang (2005) have been discussed the properties of hybrid materials formed by PVP/SiO_2. Hybrid nanomaterials coated fabrics have increased functionality such as antibacterial activity and UV-protection (Marini, Bondi, Iseppib, Toselli, & Pilati, 2007; Zimehl, Textor, Bahners, & Schollmever, 2004). Nanoparticles are more active than larger particles because of their higher surface area and they exhibit unique physical and chemical properties which make them suitable for preparing hygienic surfaces (Chen & Chiang, 2008). The microbial infectivity is a serious matter in healthcare and food industry, so that progress of antimicrobial agents and surface coatings has been attracting increasing awareness in recent years (Manjula Nair, Nirmala, Rekha, & Anukaliani, 2011). Therefore, the developments of nanoparticles with antimicrobial properties are of much interest in textile field. Hence the ZnO nanoparticles are selected as antibacterial agent in this work.

The ZnO nanoparticles have been measured to possess probable biological applications as efficient antimicrobial agents, drug carriers, bioimaging probes and possessing cytotoxic behavior for the treatment of cancer (Hanely et al., 2009; Ostrovsky, Kazimirsky, Gedanken, & Brodie, 2009). Being a semiconducting material, the band gap between conduction and valance electrons plays a vital role in the generation of reactive oxygen species (ROS), which bring about conformational changes/oxidant injury to the surface of the microorganism membrane (Sharma, Rajput, Kaith, Kaur, & Sharma, 2010). The ZnO nanoparticles, which have positive zeta potential, easily rupture the cell membrane of *Escherichia coli* (gram negative) on contact and release Zn^{2+} ions, which cause lysosomal and mitochondrial damages. Finally, it is leading to the death of

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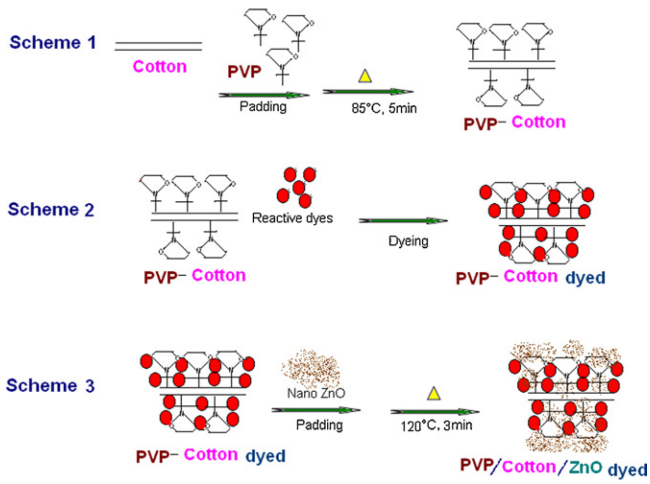

Fig. 1. Schematic diagram of PVP/ZnO functionalized cotton.

bacterial cells (Huang et al., 2008; Sharma, Sharma, Kaith, Rajput, & Kaur, 2011). The surface defects and morphological changes of ZnO nanoparticles do not play a significant role in the antibacterial activity (Tam et al., 2008; Xu & Xie, 2003). That the antibacterial activity depends on the particle size, with an increase in antibacterial activity observed for decreasing size of nanoparticles (Li et al., 2004). Recently the Krishna Raghupathi, Ranjit Koodali, and Adhar Manna (2011) also reported the properties of antibacterial activity against particles size. This report described the antibacterial activity of ZnO nanoparticles in the range from 212 nm to 12 nm particle size. The antibacterial activity of ZnO nanoparticles is inversely proportional to the size of the nanoparticles.

The ZnO nanoparticles coated fabrics have the antibacterial activity and UV-protection (Mao, Shi, Zhang, & Cao, 2009; Sivakumar et al., 2010). There are only a few methods such as the "pad-dry-cure" method, radiation and thermal treatments (Becheri, Durr, Lo Nostro & Baglioni, 2009; Kathirvelu, Souza, Durai, 2009; Yadav et al., 2006) that described the coating of ZnO nanoparticles on cotton fabrics. This was aimed in order to improve the dyeability of reactive dyes using PVP modification and to study the antibacterial activity of PVP and PVP/ZnO coated cotton fabrics.

2. Materials and methods

2.1. Materials

Knitted single Jersey bleached cotton fabric was used. Poly-N-vinyl-2-pyrrolidone (PVP), sodium carbonate, sodium hydroxide, acetic acid, starch, zinc nitrate, sodium chloride (SC), sodium sulfate (SS) and the bio-salt trisodium citrate (TSC) were purchased from Merck. The dichlorotriazine dyes Reactive Red M5B (RM5B), Yellow MXR (YMXR) and Blue MXR (BMXR) were supplied by DyStar, an Indian Company.

2.2. Functionalization of cotton fabric

Non-ionic wetting agent Lenetol was used to wet the fabric. 80–85% wet pickup of the fabric samples (15 cm × 15 cm) were padded twice in an aqueous solution of PVP (2%) using two bowel padding mangle. Treated samples were dried at 85 °C for 5 min (Fig. 1, Scheme 1) and then the samples were washed twice with hot water at 50 °C for 15 min. Finally the samples were dried at an ambient condition.

2.3. Dyeing procedure

The modified and unmodified cotton fabrics were dyed (Fig. 1, Scheme 2) using open dye bath with the three dichlorotriazine dyes using optimized recipe. The following recipe was followed for dyeing, 3% of dye concentration, 60 gpl of exhausting agent, 10 gpl of Na_2CO_3 and 1:25 MLR at pH 11 with 120 min time duration. After completion of dyeing, the dyed samples were washed with water and neutralized with acetic acid. Again these fabrics were washed with cold water.

2.4. Synthesis of ZnO nanoparticles

The ZnO nanoparticles were synthesized by chemical method (Yadav et al., 2006) using soluble starch (2%) as stabilizing agent with zinc nitrate (7.43 g) dissolving by magnetic stirring. Sodium hydroxide (0.2 mol) was added drop by drop. After 2 h of stirring, the filtered nanoparticles were washed three times with distilled water. After the washed samples were dried at 80 °C for 12 h for complete conversion of Zn $(OH)_2$ into ZnO to take place.

2.5. Coating of cotton fabrics with ZnO nanoparticles

The ZnO nanoparticles were coated by pad-dry-cure method, which is represented in Fig. 1, Scheme 3. The modified and unmodified fabrics were immersed in the 2% of ZnO nanoparticles solution in the presence of 1–5% of non ionic wetting agent. The fabrics were padded with 100% wet pick-up. After padding, the samples were air dried and followed by curing at 120 °C for 3 min. Then the uncoated nanoparticles were removed by washing with sodium lauryl sulfate (2 gpl) for 5 min. The modified and unmodified cotton fabrics were completely rinsed 10 times with soap solutions. Then the samples were washed and air dried.

2.6. Testing and analysis

The dye uptake values of dyed samples were measured by taking the maximum absorbency value (λ_{max}) of the dye liquor samples (before and after dyeing) using UV-Visible spectrophotometer (Jasco-UV-530). The dye exhaustion value was calculated using Eq. (1):

$$\text{Exhaustion}\,(\%) = \frac{1 - A_2}{A_1} \times 100 \qquad (1)$$

where A_1 and A_2 are absorbencies of dye solution before and after dyeing respectively.

The color strength values were measured by a computer color matching system (Premier Colorscan SS 6200A spectrophotometer). The K/S values were calculated by Kubelka and Munk equation (2):

$$\frac{K}{S} = \frac{(1 - R)^2}{2R} \qquad (2)$$

where, R is the reflectance value of the dyed fabric, K is the absorption coefficient and S is the scattering coefficient. The spent dye liquor TDS and pH measurements were done by Merck made TDS and pH meter. The fastness properties of all dyed samples were measured by the ISO 105-C03, 1989, Geneva testing method.

2.7. Antibacterial activity test

The antibacterial activity of modified and unmodified fabrics were tested by the reduction of colony forming units (CFU) of *Staphylococcus aureus (S.aureus)* and *Escherichia coli* bacterium

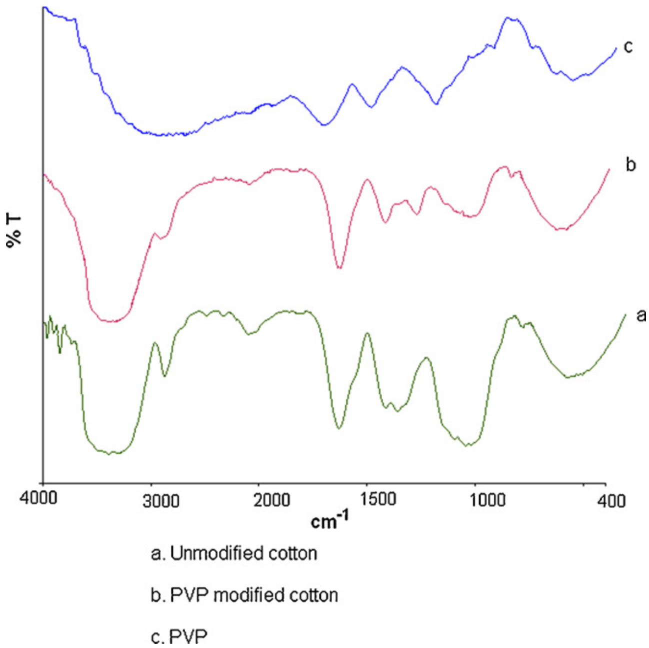

Fig. 2. FTIR spectra of PVP, unmodified and modified fabrics.

(E.coli) (AATC test method (100-1999)). The percentage reduction of CFU was calculated by Eq. (3):

$$\text{Reduction in CFU}\,(\%) = \frac{C - A}{C} \times 100 \tag{3}$$

where, C and A are the bacterial colonies of the untreated and the treated cotton fabrics respectively.

3. Results and discussion

3.1. FTIR analysis of unmodified and modified fabrics

The FTIR spectra of the PVP, unmodified and modified cotton fabrics were measured by transmission mode using PE IR SPECTRUM ASCII PEDS 1.60 instrument with KBr pellets. Fig. 2a and b shows a broad peak centered at 3400 cm^{-1} corresponding to –OH stretching and a peak at 3000–2980 cm^{-1} region for C–H stretching of cellulose. Although it has $-CH_2$ groups in their structure, the peaks are corresponding to the asymmetric stretching modes. The stretching vibration of C–O–C bond has been identified at 1110 cm^{-1} and 1049 cm^{-1}. Fig. 2c shows a peak at 1654 cm^{-1} that is assigned to the stretching vibration of the C=O in the PVP. The other important peaks at 1285 cm^{-1} and 1438 cm^{-1} are referring the C–N stretching vibration and the attachment of CH_2 groups in pyrrole ring of PVP. These stretching vibration spectra are evidence of the interaction between cellulose and PVP. Also the other functional groups of PVP and cotton fabrics are present in the range of 1000–1300 cm^{-1}. It is clear that the modified fabrics contain functional groups of both PVP and cellulose structure.

3.2. XRD pattern of ZnO nanoparticles

The crystalinity and average crystal size of synthesized ZnO nanoparticle were calculated from XRD pattern using XPERT PRO diffractometer. From Fig. 3, the peaks at $2\theta = 36^\circ$, 38°, 43°, 54° and 62° of ZnO nanoparticles are corresponding to (0 0 2), (1 0 0), (1 0 1), (1 0 2) and (1 0 3) in lattice (JCPDS No. 87-0713). Hexagonal structure of ZnO was confirmed by the 1 0 1 crystalline peak (Wu et al., 2010) and crystal size calculated using Debye–Scherer

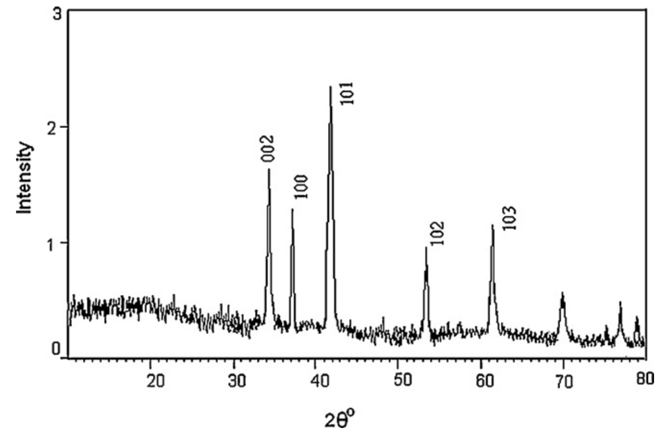

Fig. 3. XRD pattern of synthesized ZnO nanoparticles.

($D = 0.94\lambda/\beta\cos\theta$) formula. The average crystal size of synthesized ZnO nanoparticle is 37 nm.

3.3. Surface morphology of the unmodified and modified fabrics

The surface morphology of fabrics was examined by SEM images of JEOL USA JSM-6390 Scanning Electron Microscope. The images show that unmodified cotton fibers have ribbon and rod-like structure with plain surface in Fig. 4a and b. The corresponding EDX spectrum showed the presents of no newer elements. The PVP polymer present on the fiber surface improved swelling nature of this fiber (Fig. 4c and d). The EDX spectrum of PVP modified fabric showed that the nitrogen element is present. It is clear that the PVP was crosslinked with cotton. The coated ZnO nanoparticles and PVP molecules are present on the modified cotton fiber surface (Fig. 4e and f). The size of synthesized ZnO nanoparticles shows in the nanoscale range (Fig. 4f) and the EDX spectrum presents the nitrogen and zinc elements. It is the evidence for the coating of PVP and ZnO nanoparticles on cotton fabric.

3.4. Effect of dyeability and fastness for modified and unmodified fabrics

The RM5B dye showed better dye uptake than other BMXR and YMXR reactive dyes with the three exhausting agents at modified condition. From Fig. 5a, the maximum 86% of dye uptake was obtained for TSC with RM5B dyed cotton fabric. In the case of RM5B with SC and YMXR with TSC produced 83% of dye uptake. In modified fabric produced better dye uptake than unmodified fabrics in all systems because the PVP is thermally fixed on the fabric in curing and the PVP is played as an adhesive agent (Zhang et al., 2003) between dye and fiber. Hence the amount of unfixed dye molecules may be minimized and large number of dye molecules may react with cotton fabric.

In color strength (K/S) measurement of modified system, the dyed fabric resulted higher K/S value for RM5B with three exhausting agents (Fig. 5b). The other two dyes also showed improved K/S values in modified fabrics. It may be due to the activity of PVP. The fastness properties of the all dyed samples produced better results in modified fabrics than in unmodified fabrics. Also the light fastness of these fabrics has good results for modified fabrics (Fig. 6a and b).

The TDS measurements were done before and after dyeing process. All the dye effluents with TSC exhausting agent showed lower TDS values than the other two exhausting agents (Table 1). PVP modified fabrics also showed lower TDS values than unmodified fabrics. It is the evidence for the functionalized polymer which

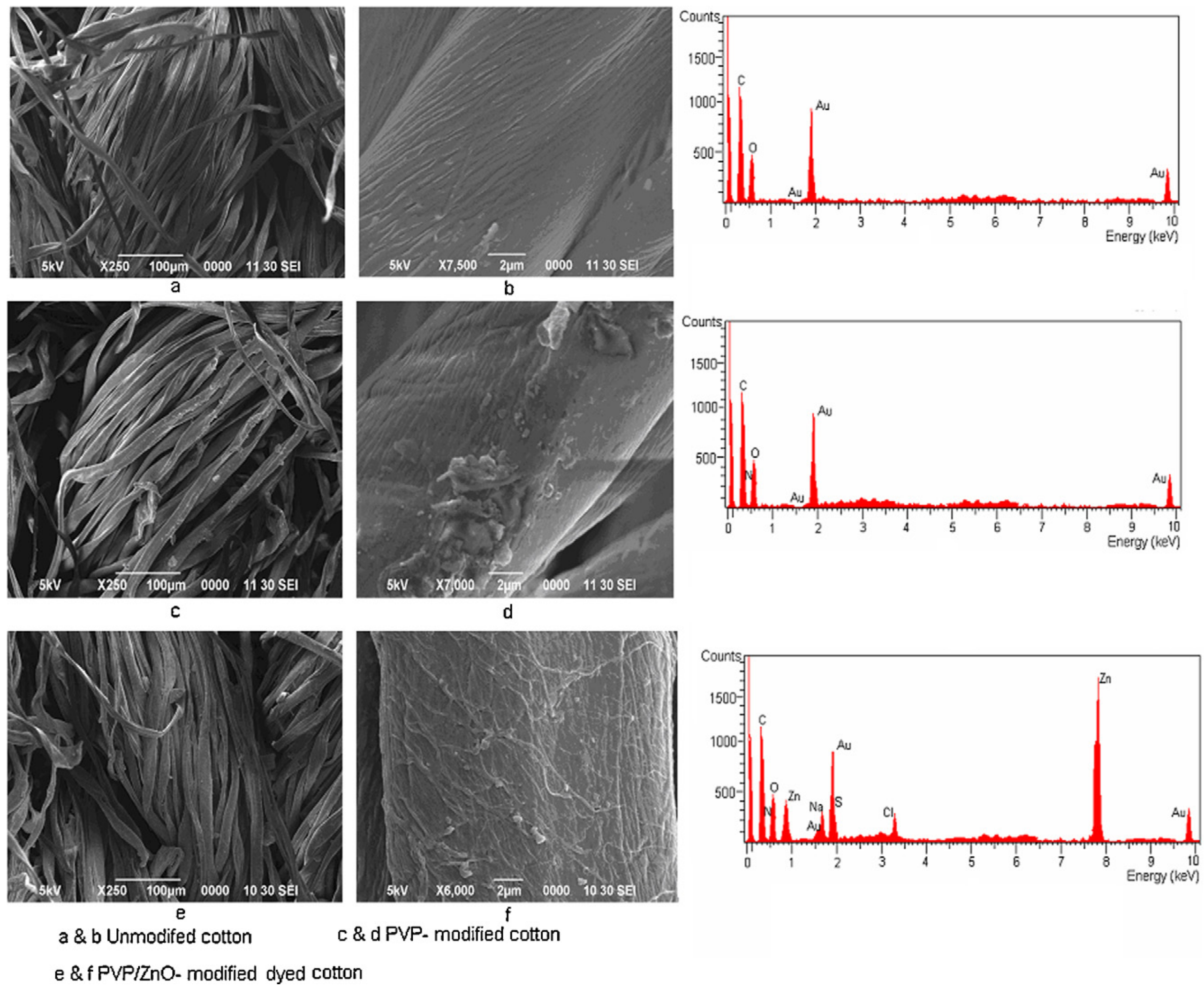

Fig. 4. SEM/EDX images of unmodified, PVP modified and PVP/ZnO modified fabrics.

minimized the unfixed dye molecules for the improvement of dyeability. In trisodium citrate, having three Na^+ ions and that ion are ionized in the dye bath. These Na^+ ions are minimizing the repulsion behavior of fabric and dye (Ahmed & El-Shishtawy, 2010). The numbers of Na^+ ions are increased in TSC. The reactive dye molecules easily formed a covalent bond with cellulose. The minimum amount of unfixed dye molecules are present in the spent dye bath and good dye uptake with low TDS values was obtained. It is the reason for the TSC, which produced lower TDS values than other exhausting agents.

3.5. Antibacterial activity of unmodified and modified fabrics

The antibacterial activity of unmodified, PVP modified and PVP/ZnO modified fabrics were tested using the Gram-positive bacterium *S. aureus* and the Gram-negative bacterium *E. coli*. The antibacterial growth was tested at 30, 60 and 120 min for modified and unmodified cotton. Modified cotton fabrics leading to the inhibition behavior of *S. aureus* and *E. coli* are shown in Table 2. There is no antibacterial activity observed for unmodified fabric. The 20 mg/L concentration of ZnO nanoparticles with PVP

Table 1
TDS values for unmodified and modified cotton with three reactive dyes.

Reactive dyes	Unmodified cotton						Modified cotton					
	Before dyeing TDS 1×10^2 ppm			After dyeing TDS 1×10^2 ppm			Before dyeing TDS 1×10^2 ppm			After dyeing TDS 1×10^2 ppm		
	SC	SS	TSC	SC	SS	TSC	SC	SS	TSC	SC	SS	TSC
RM5B	420	450	220	310	320	160	300	380	140	320	220	120
BMXR	310	340	210	200	220	120	220	270	100	270	140	75[a]
YMXR	340	370	270	310	240	190	310	320	150	210	190	100

SC: sodium chloride; SS: sodium sulfate; TSC: trisodium citrate.
[a] Good TDS reduction.

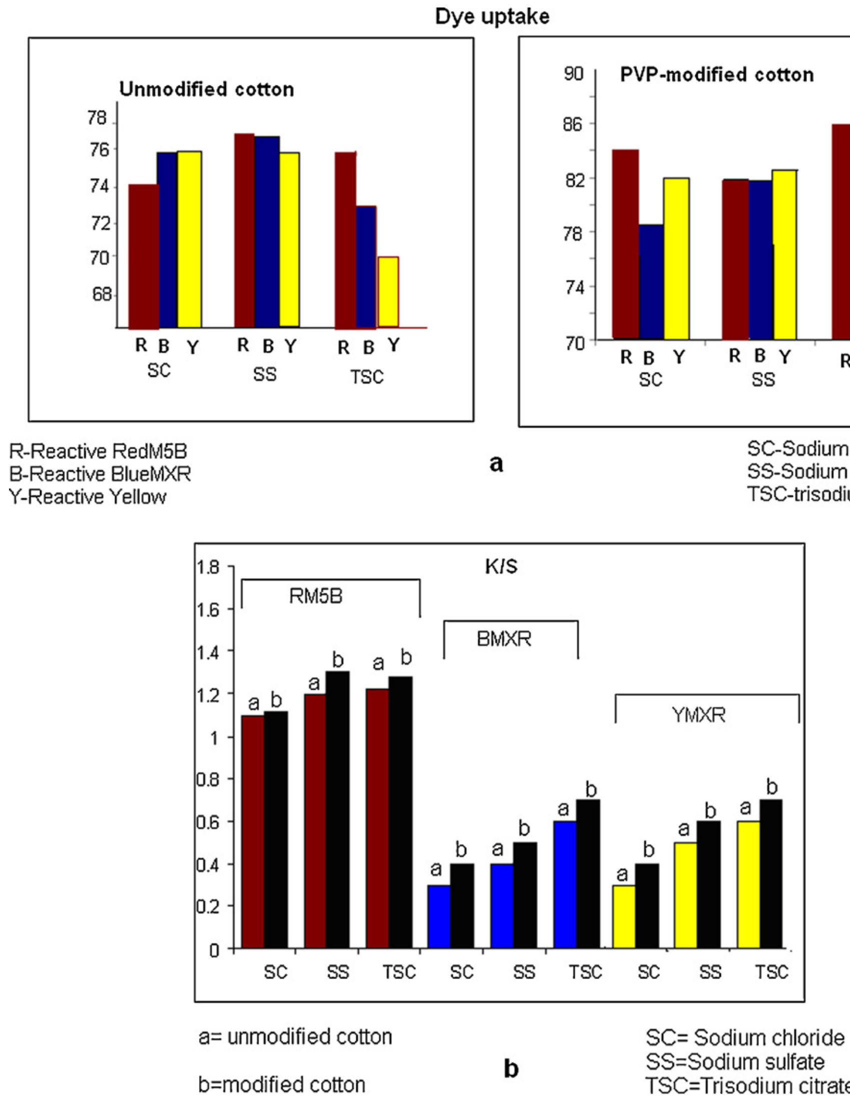

Fig. 5. Dye uptake and *K*/*S* values for unmodified and modified cotton fabrics.

functionalized cotton fabric exhibits 100% of bacterial reduction within short time intervals. The PVP/ZnO nanoparticles coated fabric results better antibacterial activity than PVP modified fabric due to the combination of both ZnO and PVP, which are having inhibition property of bacteria. In increased concentration of ZnO nanoparticles produced increases antibacterial activity. The Zn element is also an important micronutrient at super physiological levels. It is clear that the PVP inhibits the growth of bacterium in

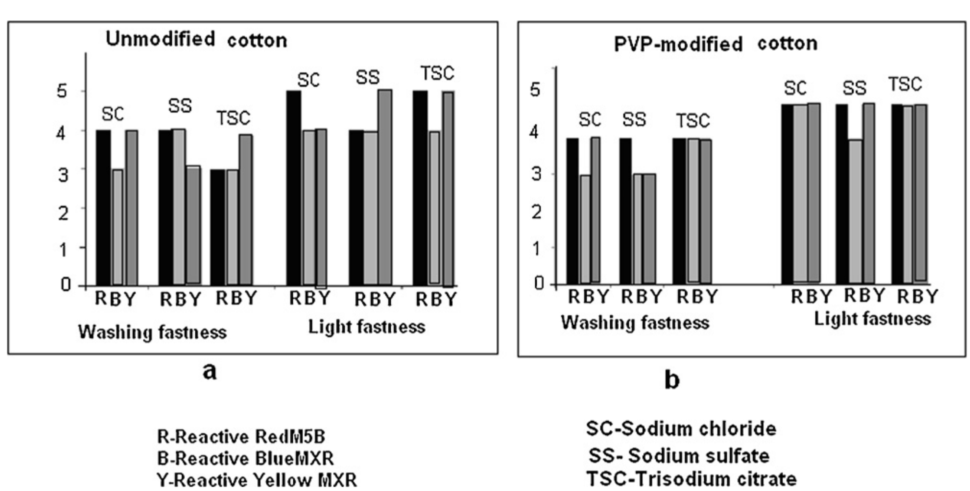

Fig. 6. Washing fastness, light fastness for unmodified and modified cotton fabrics.

Table 2
Antibacterial activity test of the unmodified, PVP modified, PVP/ZnO modified fabrics against *S. aureus* and *E. coli*.

Sample	*S. aureus* Treatment duration				*E. coli* Treatment duration			
	30 min % R	60 min % R	90 min % R	120 min % R	30 min % R	60 min % R	90 min % R	120 min % R
Control	0	0	0	0	0	0	0	0
Clean cotton	0	0	0	0	0	0	0	0
PVP-cotton	47	55	76	81	58	63	81	87
(5 mg/L)ZnO-cotton	23	28	39	57	47	61	78	81
(5 mg/L)ZnO/PVP-cotton	40	53	58	71	38	59	73	80
(10 mg/L)ZnO/PVP-cotton	38	63	83	88	47	65	67	77
(15 mg/L)ZnO/PVP-cotton	46	71	96	98	65	87	100	100
(20 mg/L)ZnO/PVP-cotton	64	87	100*	100	73	100[a]	100	100

R: reduction viability.
[a] Very good antibacterial reduction.

its medium (Soderberg, Agren, Tengrup, Hallmans, & Banck, 2001). In ZnO nanoparticles coating is the release of the active ingredient (ROS) into the surrounding of the bacterial medium. The ZnO, release of H_2O_2 has been proposed as a mechanism responsible for antibacterial activity. It has also been shown that the ZnO nanoparticles cause membrane damage of bacteria (Furno et al., 2004).

4. Conclusion

The functionality of poly-N-vinyl-2-pyrrolidone and cellulose linkage is confirmed by FTIR, and the SEM–EDX analysis clearly showed that the PVP and ZnO nanoparticles are present on cotton fiber surfaces. The PVP modified cotton fabrics have good dye uptake, color strength and fastness properties for the three dichlorotriazine reactive dyes. In antibacterial test, PVP and PVP/ZnO modified fabrics had very good bacterial reduction. From these results, concluded that the PVP could play dual role to improve reactive dyeing and antibacterial activity. These types of fabrics may be used as wound cloths, surgical cloths, sports wears and kids wears.

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