Indian Journal of Fibre & Textile Research
Vol 43, December 2018, pp. 464-473

Turmeric dyeing and chitosan/titanium dioxide nanoparticle colloid finishing of cotton fabric

T M Al Sarhan & A A Salem[a]

Faculty of Arts and Design, Fashion Design Department, King Abdulaziz University, Jeddah, Saudi Arabia

Received 12 April 2017; revised received and accepted 30 August 2017

The possibility of combining the finishing and natural dyeing of cotton fabric has been studied using a single-stage, pad-dry-cure technique, by treating it with chitosan/titanium dioxide nanoparticle colloids and turmeric dye. Different parameters have been studied to optimise the process, such as the chitosan/TiO_2 nanoparticle colloid concentration, citric acid crosslinker concentration, sodium pyrophosphate catalyst concentration, dye concentration, *p*H, curing time, and temperature. To investigate the effects of combined treatment on the dyeing and functional properties of the treated cotton fabric, its ultraviolet protection factor, antibacterial activity, self-cleaning properties, rigidity, colour strength (*K*/*S*), fastness behaviour, nitrogen content, and wettability are determined. In addition, the cotton fabric surface is characterised using scanning electron microscopy. The samples treated with chitosan/TiO_2 in the presence of citric acid exhibit excellent protection against ultraviolet radiation as well as antibacterial activity. The optimum conditions are 0.75% TiO_2 (w/v), 10% dye (w/v), 2.5% chitosan (w/v), 30 g/L citric acid, 4 g/L sodium pyrophosphate, 70°C drying temp. and 5 min drying time, 180°C curing temp. and 2 min curing time. The results also indicate the efficiency of the treatment in improving the self-cleaning properties of the fabric. A significant improvement in the colour fastness is observed for the treated fabrics.

Keywords: Antibacterial activity, Chitosan, Cotton, Nanofinishing, Nano TiO_2, Self-cleaning property, Titanium dioxide, Turmeric dyeing, UV protection

1 Introduction

The production of high-value-added fabrics, such as protective or medical textiles, is important for improving the quality of human life[1,2]. The harmful effects of ultraviolet radiation necessitate a substantial need for photoprotection[3]. The most common methods to guard against ultraviolet radiation are protective creams and clothing. Currently, a variety of ultraviolet blockers are being manufactured to improve the ultraviolet-protection properties of textiles.

The application of nanotechnology has enabled rapid advances in textile production. Nanotechnology functional properties or to obtain multi-functional characteristics[4–8]. For example, nanoparticles (NPs) can provide high surface energies and large surface areas to improve the moisture affinity of the fabric and to increase textile durability[9].

Recently, TiO_2 has been used in the synthesis of a variety of nanomaterials[10]. Abundantly available, TiO_2 exhibits several beneficial properties such as its ease of handling, chemical stability, environmental benignity, low cost, and high photocatalytic activity[9–10]. Nano TiO_2 can impart useful properties to textiles, including self-cleaning[9,11–13], flame retardant[10], anti-wrinkling[12], antimicrobial[11], photocatalytic[1] and ultraviolet-protective[13] functionalities.

Antimicrobial products have been of recent interest owing to infectious disease outbreaks throughout the world[14]. Furthermore, consumers have become aware of the significant benefits of these substances[15]. Therefore, researchers have attempted to eliminate microbial attacks by using antimicrobial finishes to obtain aesthetic, hygienic and medical

Most of the current antimicrobial finishes are toxic and non-degradable. Hence, significant efforts have been made to develop non-toxic alternatives. Chitosan, an important and commercially available biopolymer, is easily produced by the *N*-deacetylation of chitin, which is the second most abundant polysaccharide (after cellulose). A number of studies have found that chitosan can be used in a variety of applications because of its significant antimicrobial activity, biocompatibility, biodegradability and low toxicity[15].

The combination of chitosan and titanium dioxide has attracted significant research interest because of

[a]Corresponding author.
E-mail: aasabdullah2@kau.edu.sa

its excellent photocatalytic performance, antimicrobial activity and stability in acidic and alkaline solvents.

Because synthetic dyes can cause inflammation and other conditions, the importance of using eco-friendly and non-toxic natural dyes on textiles has become increasing recognized. Synthetic dyes can be replaced by natural dyes that exhibit very good colour fastness and are available at reasonable prices[20]. Furthermore, the use of natural dyes and eco-friendly products for antimicrobial textile finishing has been widely reported[21,22-27].

In this investigation, a novel approach has been studied for the dyeing and finishing of cotton fabric in a single step. Chitosan/titanium dioxide nanoparticles (NP) colloids were used to impart multifunctional characteristics to cotton fabric, including ultraviolet protection, antibacterial activity and self-cleaning properties. In addition, turmeric dye was added to the treatment bath and citric acid was used as an eco-friendly crosslinker in order to increase the durability of the NP impregnated dyed fabric . The crosslinking was catalysed using sodium pyrophosphate as an inorganic catalyst. The colour fastness of the turmeric dye could be improved without using a mordant.

2 Materials and Methods

2.1 Substrate

Plain weave, mill-scoured and bleached cotton fabric (100%) was used as the substrate (warp count 60, weft count 36 and weight 114 g/m^2).

2.2 Dye

Natural turmeric[28] (*Curcuma tinctoria*) was used as the dye in this study. The coloured component of this substance is curcumin (diferuloye methane yellow), which has a colour index of Natural Yellow 3.

2.3 Chemicals and Auxiliaries

Following chemicals and auxiliaries were used:

- Sodium pyrophosphate (SPP, $Na_4P_2O_7$); supplied by Merck Chemical Co., Germany.
- Citric acid (commercial grade); supplied by Merck Chemical Co., Germany.
- Titanium dioxide nanopowder [21 nm particle size (TEM), 99.5% trace metal basis]; supplied by Sigma-Aldrich. Co., Germany.
- Chitosan, deacetylated chitin and poly(D-glucosamine); supplied by Sigma-Aldrich. Co., Germany.
- Tanaterge SD liquid (non-ionic detergent); supplied by Sybron-Tanatex Company.

2.4 Chitosan Preparation

Chitosan (1 g) was dissolved in distilled water (100 mL), and then acetic acid (1 mL, 99.8%) was added under continuous stirring for 5 min. The resulting solution was left overnight at room temperature.

2.5 Dye Extraction

Dye was extracted from powdered turmeric root tissue (10 g) by mixing with water (100 mL), boiling for 1 h, and then filtering. After filtration, the extracted solution was stored in a cold location, and drops of alcohol were added to prevent the growth of bacteria prior to use.

2.6 Cotton Treatment with TiO_2/Chitosan

To functionalise the cotton fabric, it was subjected to a single-step pad-dry-cure process using TiO_2/chitosan colloid in the presence of the dye extract (10%, w/v). Citric acid (30 g/L) was added to the solution as a crosslinker, and pyrophosphate SPP (4 g/L) was added to the impregnating bath as a catalyst. Cotton fabric was impregnated with the finishing solution using 2-dip 2-nip technique with 80% pickup, followed by drying at 70 °C for 5 min and curing at 180 °C for 2 min. The treated samples were rinsed and washed using non-ionic detergent (2 g/L) at 60 °C for 10 min.

2.7 Determination of Colour Strength

Light reflectance measurements (UltraScan PRO Spectrophotometer; HunterLab) were used to evaluate the colour strength (K/S) of the dyed samples. Colour strength was calculated using the Kubelka-Munk equation[29].

2.8 SEM Study

To study the surface morphology of the treated cotton fabric, SEM was performed using an electron probe micro-analyser (JXA-840; JEOL).

2.9 Fastness Tests

The colour fastness of the dyed fabrics towards washing (61-1969), rubbing (8-1996) and perspiration (15-1997) were determined according to standard methods (AATCC). Light fastness was evaluated, according to BS Test No. 1006 (1978), to determine the colour resistance of the treated fabric to photodegradation.

2.10 Ultraviolet Protection Factor (UPF)

UPF values were calculated according to the Australian/New Zealand (AS/NZS 4366-1996) standard method.

2.11 Wettability

A water-drop test was applied according to AATCC test method 39-1980. The time required for a drop of water to be absorbed into the fabric was denoted as the absorbency value.

2.12 Durability to Washing

The durability of the functional properties of the treated fabric to washing was evaluated according to AATCC test method 124-1975. The UPF values were estimated after 5, 10 and 15 laundering cycles.

2.13 Stiffness

The stiffness of the treated and untreated samples was evaluated according to the ASTM D 1388 test method using a Toyosek apparatus (Technical Corporation, Japan).

2.14 Nitrogen Content

Nitrogen content was monitored according to the method detailed by Kjeldahl[30]. The following equation was used to calculate the nitrogen content:

$$N\% = (0.014 \times N \times V) \times 100/W$$

where N and V are the normality and volume (mL) of HCl; and W , the weight of the sample (g).

2.15 Antibacterial Activity

The antibacterial activities of the treated samples were evaluated according to the AATCC-100 method. Two bacterial strains were used as the test organisms:viz *Staphylococcus aureus* (*S. aureus*; Gram-positive) and *Escherichia coli* (*E. coli*; Gram-negative).

2.16 Self Cleaning

The efficiency of the self-cleaning behaviour of the treated cotton fabric was assessed by staining the fabric with methylene blue (0.01%). After drying, the stained samples were subjected to daylight radiation for different periods. A grey scale was used to evaluate the colour alteration of the stained samples.

3 Results and Discussion

3.1 Factors Affecting Finishing

3.1.1 Chitosan Concentration

The effect of chitosan concentration on the colour strength (K/S) and UPF of the dyed cotton fabric has been investigated [Fig. 1(a)]. The addition of chitosan to the treatment bath causes a significant increase in the K/S values of the treated samples as compared to the sample treated without chitosan. The maximum K/S (50.42%) is observed using 2.5% chitosan.

It has been reported that treating cotton fabric with chitosan prior to the dyeing process results in a proportional increase in the shade depth[31–33]. This phenomenon is attributed to the formation of a chitosan gel in excess water during exhaust dyeing[33]. This gel may attract more dye molecules than the untreated fabric, leading to deeper shades[31–32]. An alternative explanation for the increased K/S is that chitosan can produce positive charges on the cotton fibre, which would provide more dye sites than are present on the untreated fabric[34] and cause increase in the ionic interactions between the dye and the fibre.

In this study, chitosan is present within the same padding bath as the dye. Therefore, the competing affinities among cotton-chitosan, chitosan-dye, and dye-cotton pairs must be considered. At low chitosan concentrations, cotton has the same affinity for chitosan as the dye. Thus, the thin chitosan film efficiently absorbs the dye, resulting in increased shade depth. By using a higher concentration of chitosan in the pad liquor, a relatively decreased colour yield would be obtained. This may be attributed to the formation of a thicker chitosan film on cotton that cannot be penetrated by the dye molecules[35].

The UPF results show a similar trend. Increasing the amount of chitosan in the pad liquor leads to a proportional decrease in the UPF values, which may be attributed to the potential competition between the absorption of TiO_2 NPs and chitosan molecules onto the cotton fabric. Furthermore, the migration of TiO_2 NPs into the fabric would be slowed by down the thicker films formed at higher concentrations of chitosan.

The results in Fig. 1(b) indicate that the stiffness of the treated fabric increases with increasing chitosan concentration in the padding liquor. In the present study, 2.5% chitosan is used to obtain a desirable fabric stiffness.

The nitrogen content of the untreated sample is estimated against the concentration of chitosan used in the treatment bath [(Fig. 1(c)]. The nitrogen content ratio increases with increasing chitosan concentration, indicating that the number of amine groups present in the fibres increases with the amount of chitosan absorbed and fixed into the cotton fabric.

3.1.2 Effect of Citric Acid

A significant drawback of chitosan is its poor adhesion to cellulose fibres, resulting in its removal from the fibre surface with repeated washing. To strongly fix chitosan to the cellulose fibres, polycarboxylic acid crosslinking agents (citric acid),

has been used. In the presence of crosslinker, the hydroxyl groups of chitosan and cellulose can bond covalently with the carboxyl groups of the polycarboxylic acid via esterification, resulting in the formation of crosslinks between the chitosan and cellulose. Crosslinking significantly enhances the durability and washing fastness of treated fabrics[36-37]. In the present study, citric acid is also used to improve the binding of the TiO_2 NPs on the cotton fabric. $Na_4P_2O_7$ (SPP) has been used to catalyse the crosslinking reactions.

To investigate the influence of citric acid concentration on the ultraviolet protection and dyeing properties of the cotton fabric, samples are treated with different concentrations of citric acid (10, 20, 30, 40, and 50 g/L) in the presence of pyrophosphate SPP (4 g/L), TiO_2 NPs (0.75%, w/v), chitosan (2.5%, w/v) and turmeric dye (10%, w/v). After impregnation, the treated samples are squeezed for 80% pick up, and then cured at 180 °C for 2 min. The results of the *K/S* and UPF measurements of the dyed treated samples are shown in Fig. 2(a). The colour strength of the dyed samples is significantly increased, compared to that of untreated samples. This is attributed to the formation of crosslinks between the dye and the cotton via pyrophosphate SPP-catalysed esterification reactions with citric acid, as shown in Eqs (1)-(3).

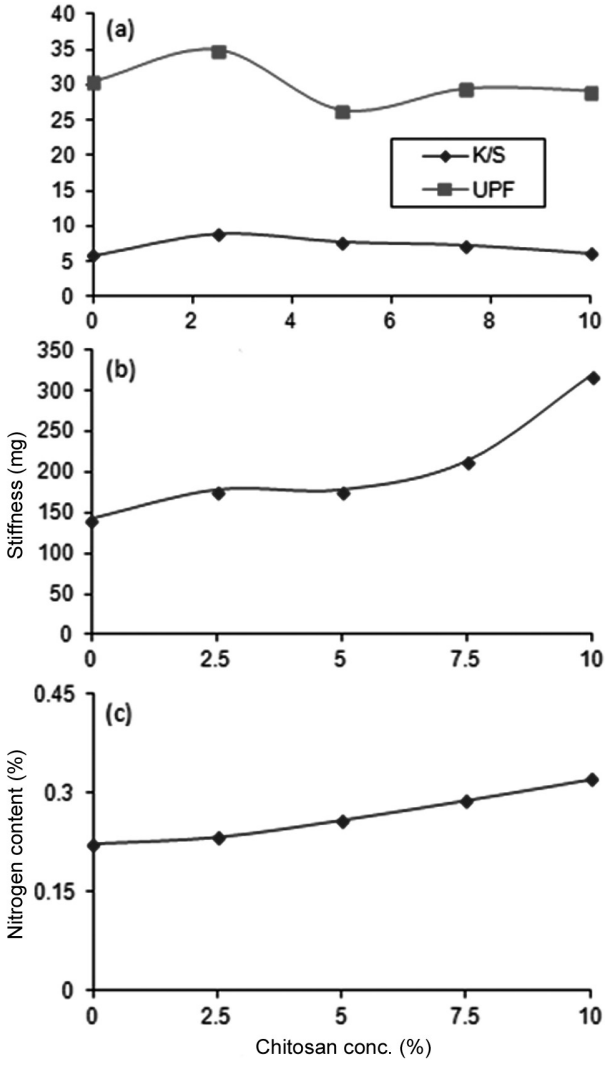
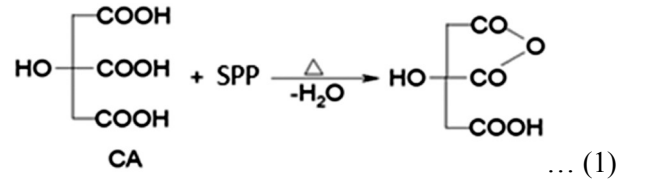


Fig. 1 — Effect of chitosan concentration on colour strength and ultraviolet protection factor (a), stiffness (b) and nitrogen content (c). [Conditions: 0.75% TiO_2 (w/v), 10% dye (w/v), 30 g/L citric acid, 4 g/L SPP, drying at 70°C for 5 min, and curing at 180°C for 2 min]

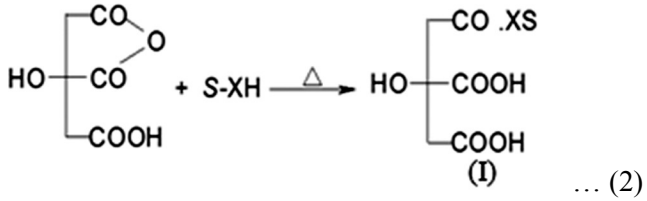
The UPF values of the cotton fabric also increases with increasing citric acid concentration in the treatment bath. The incorporation of the cross-linker's multiple functional groups [Eqs (1)–(3)] results in increasing UV protection, which may be attributed to the attraction of TiO_2 NPs by the hydroxyl groups of citric acid via cation-anion interactions[38-39], and the introduction of negative carboxylate groups that also increase the TiO_2 NP loading on the cotton surface[16].

3.1.3 Effect of Pyrophosphate SPP

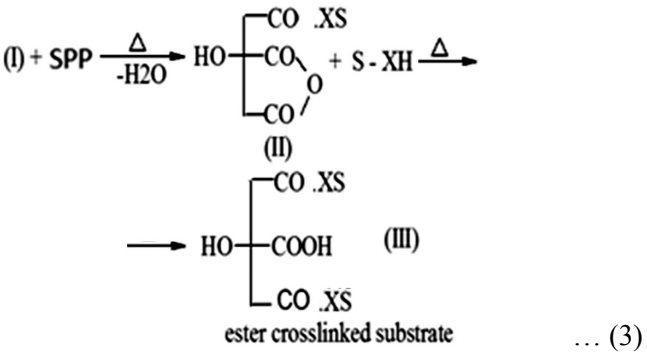
It has been reported that, for the effective crosslinking of fibres, the *p*H of the solution



… (1)



… (2)



… (3)

containing the polycarboxylic acid should be in the range of 1.5–4.5. However, high acidities are unsuitable because of their detrimental effects on the fibres. Therefore, optimal conditions of *p*H 3.7–4.5 have been reported in the presence of a suitable catalyst[40]. The effects of pyrophosphate SPP concentration on crosslinking at a constant citric acid concentration are also studied. The results presented in Fig. 2(b) show a significant increase in *K*/*S* with increasing pyrophosphate SPP concentration. The maximum colour strength is observed using a SPP pyrophosphate concentration of 4 g/L. At higher concentrations, a decrease in colour strength is observed. Moreover, the UPF values increase with increasing SPP pyrophosphate concentration. This is attributed to the increased anhydride production via catalyst action, which increases the rate of esterification and produces carboxylic active sites. These active sites increase the absorption and fixation of the TiO_2 NPs or dye molecules within the modified substrate, resulting in the improved ultraviolet protection and *K/S* of the coated cotton fabric[36]. The decrease in UPF and *K/S* at pyrophosphate SPP concentrations greater than 4 g/L is attributed to the neutralization of free carboxyl groups, thereby restricting the citric acid crosslinker from binding the TiO_2 NPs or dye[41].

3.1.4 TiO_2 NP Concentration

Cotton fabrics are dyed with turmeric extract using the single-step pad-dry-cure technique in the presence of chitosan/TiO_2 NP colloids, using different concentrations of TiO_2 NPs in the padding liquor [Fig. 2(c)]. The presence of TiO_2 NPs in the padding liquor improves the UPF values of the treated fabrics, reaching a maximum of 37 at 1.5 g/L TiO_2 NPs. The increased UPF is attributed to the high refractive index of the TiO_2 NPs, which results in the scattering and/or reflection of most of the ultraviolet radiation[42]It has been suggested that TiO_2 NPs absorb ultraviolet photons because of their semi-conductive properties[43].

The results shown in Fig. 2(c) also indicate that the *K/S* gradually increases with increasing TiO_2 NP concentration in the pad liquor, until reaching a maximum at 0.5%. This may be attributed to the high wettability of TiO_2 particles[44]. A further increase in the TiO_2 NP concentration results in decreased *K/S*, because TiO_2 acts as a white pigment in the pad liquor dispersion and reduces the dyeing depth[44]. The optimal concentration of TiO_2 is determined as 0.75%, at which an acceptable UPF and a satisfactory colour strength are observed.

The wetting properties of the TiO_2-NP-treated cotton fabric are determined using the water drop method. The wettability value of the treated fabrics is 0 s, in contrast to > 60 s for the untreated sample. This is attributed to the hydrophilicity of TiO_2, which can absorb water and transfer it to other hydrophilic particles, resulting in rapid wetting[44].

3.1.5 Curing Time and Temperature

Figure 2(d) shows the effects of curing temperature on the UPF and *K/S* values. The UPF

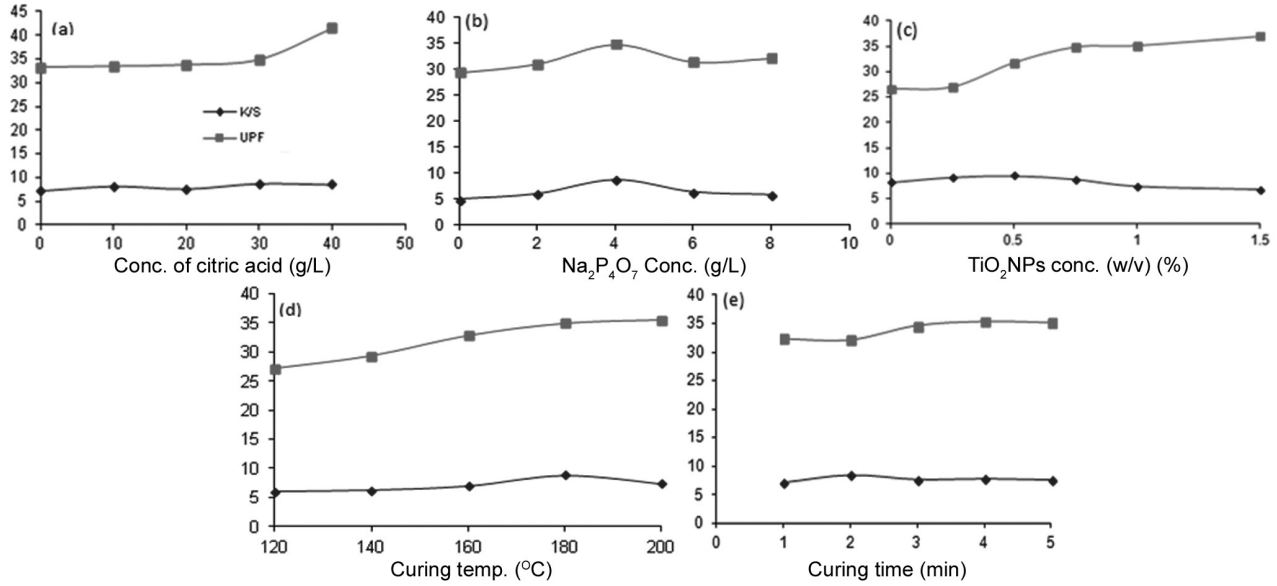


Fig. 2 — Effects of different treatment factors on color strength (*K/S*) and ultra violet protection factor: (a) citric acid conc., (b) $Na_2P_4O_7$ conc., (c) TiO_2 NPs conc., (d) curing temp., and (e) curing time [For (a)-(c), samples were dried for 5 min at 70°C and cured for 2 min at 180°C.

values of treated cotton samples increase with increasing curing temperature, due to increased catalyst efficiency and anhydride production. These factors increase the rate of fabric esterification, which forms –COOH active sites within the modified fabric and increases the degree of TiO_2 NP fixation[39]. The maximum *K/S* (8.38) is obtained by curing the treated sample at 180°C, above which a gradual decrease in the *K/S* is observed.

As shown in Fig. 2(e), 2 min is sufficient for the catalytic formation of the anhydride, the maximum modification of the cotton fabric, and to attain the maximum *K/S* of the dyed samples. Curing time longer than 2 min results in decreased colour strength.

3.2 Factors Affecting Dyeing Process

3.2.1 Dye Concentration

To determine the optimal concentration of dye in the treatment bath, different concentrations of turmeric extract (10, 20, 30, 40 and 50%, w/v) are investigated. The corresponding *K/S* and UPF results [Fig. 3(a)], indicate that increasing dye concentration increases both the colour strength and UPF.

The increase in *K/S* value is attributed to the larger quantity of coloured particles in the bath, and the corresponding increase in the migration of the dye component from the bath to the fabric surface. The maximum *K/S* is observed at a turmeric extract concentration of 30%; above this concentration, a slight decrease in *K/S* is observed. This decrease in *K/S* may be attributed to the aggregation of the dye molecules at high concentrations. Therefore, 10% extract is chosen for the following experiments to avoid heterogeneous dyeing.

The UPF factor increases with increased dye concentration. Hence, turmeric dye is effective in increasing the ultraviolet protection of cotton fabric. In the absence of the finishing materials, the UPF of the dyed sample is 25.5, which elevates the UPF value of the fabric from 'poor' to 'good'.

3.2.2 Effect of pH

Natural dyes are very sensitive to the *p*H of the dyeing bath. Therefore, it is important to study the effect of *p*H on the colour strength of the dyed fabric. Figure 3(b) shows that the *p*H of dye bath has a significant effect on the dyeability of the cotton fabric with turmeric extract. Increasing the *p*H of the dyeing bath decreases the dyeability of the treated samples, which may be attributed to the relationship between the fabric structure and the dye. Because turmeric dye is water soluble and contains carbonyl and hydroxyl groups, it can interact with the modified cotton fabric via hydrogen bonding at acidic *p*H. As the *p*H increases, the affinity for the dye decreases and the rate of dyeing is reduced because of the repulsion between the ionized fabric and the dye. Moreover, increasing the *p*H of the dyeing bath may also solidify the chitosan/TiO_2 composite in the dyeing bath, agglomerating the dye and preventing coloration and the dispersal of TiO_2 NPs in the treatment bath, which would reduce the UPF of the treated cotton fabric.

3.3 Durability to Washing

After treatment under the optimum conditions [0.75% TiO_2 (w/v), 10% dye (w/v), 2.5% chitosan (w/v), 30 g/L citric acid, and 4 g/L pyrophosphate SPP; drying at 70 °C & 5 min; and curing at 180 °C & 2 min], samples are subjected to durability washing tests. The UPF values of the treated and dyed fabrics after 5, 10 and 15 laundering cycles are presented in Table 1. A negligible reduction (7.92% after 15 cycles) in the UPF values is observed after repeated laundering.

In the present study, citric acid is used as a crosslinker and pyrophosphate SPP as a catalyst to increase the durability and binding efficiency of TiO_2 NPs on cotton fibre surfaces. The durability of the UPF indicates that strong bonds are formed between the TiO_2 NPs and the cotton fabric. The decrease in the UPF values after repeated laundering cycles can be attributed to the removal of unfixed and physically attached TiO_2 NPs[39].

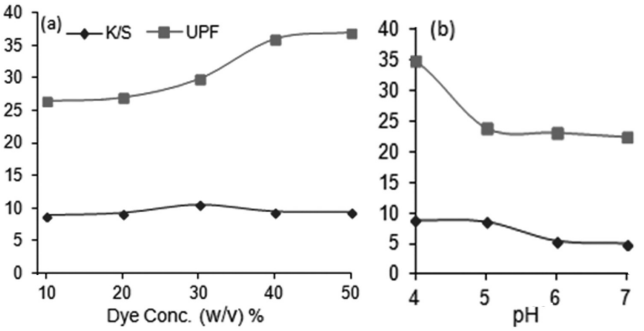


Fig. 3 — Effect of dye concentration and bath *p*H on colour strength and ultraviolet protection factor[Allsamples were dried for 5 min at 70°C and for cured for 2 min at 180°C]

Table 1—Effect of washing on UPF values for TiO_2 NPs–treated cotton fabric

Washing cycles	UPF	UV-B transmittance (290–315 nm)	UV-A transmittance (315–400 nm)
5	30.44	2.29	13.22
10	29.87	2.43	13.49
15	28.03	2.50	14.60

3.4 Antibacterial Properties

The effects of chitosan/TiO_2 NPs colloid treatment on the antibacterial activity of cotton against *S. aureus* and *E. coli* are shown in Table 2. Increasing the concentration of chitosan in the bath liquor significantly enhances the antibacterial properties of the cotton fabric. The antimicrobial properties of chitosan result from its polycationic nature. Positively charged amino groups can bind to the negatively charged bacterial surface, resulting in the disruption of the cell membrane and an increase in its permeability. Furthermore, chitosan can interact with the DNA of microorganisms to prevent protein synthesis. The antimicrobial efficiency of chitosan depends on its average molecular weight, its degree of deacetylation and the ratio between protonated and unprotonated amino groups in its structure[36].

A similar trend is observed with increasing TiO_2 NP concentrations in the padding liquor. TiO_2 NPs can inhibit the formation of bacteria on the treated fabric. However, the stiffness of the fabric increases because of chitosan treatment, for a chitosan concentration in the treatment bath of 10%.

A blend of chitosan and TiO_2 NP colloids increases the cotton's resistance against Gram-positive and Gram-negative bacteria more effectively than treatment with TiO_2 NPs or chitosan alone. The optimal antibacterial activity is observed with treated and dyed fabric, indicating that turmeric dye also exhibits antibacterial effects. The results confirm the efficiency of the combined treatment in enhancing the antibacterial activity over the individual treatments.

Table 2—Effect of chitosan/TiO_2 treatment on the antibacterial properties of the cotton fabric

Treatment	Antibacterial activity %	
	E.coli	*S. aureus*
Control	0	0
2.5% chitosan	66	63
10% chitosan	76	74
0.75% TiO_2 NPs	70	69
1.5% TiO_2 NPs	75	72
2.5 % chitosan + 0.75% TiO_2 NPs	85	82
2.5 % chitosan + 0.75% TiO_2 NPs + turmeric	87	84

3.5 Surface and Self –cleaning Characteristics

SEM images (Fig. 4) show the distribution and adhesion of the TiO_2 NPs on the surface of the cotton fibres [Fig. 4(c)]. The addition of chitosan results in the formation of a homogeneous film covering the fibre surface [Figs 4(b) and (d)].

Untreated samples and samples treated with TiO_2 NPs are stained with an aqueous solution of

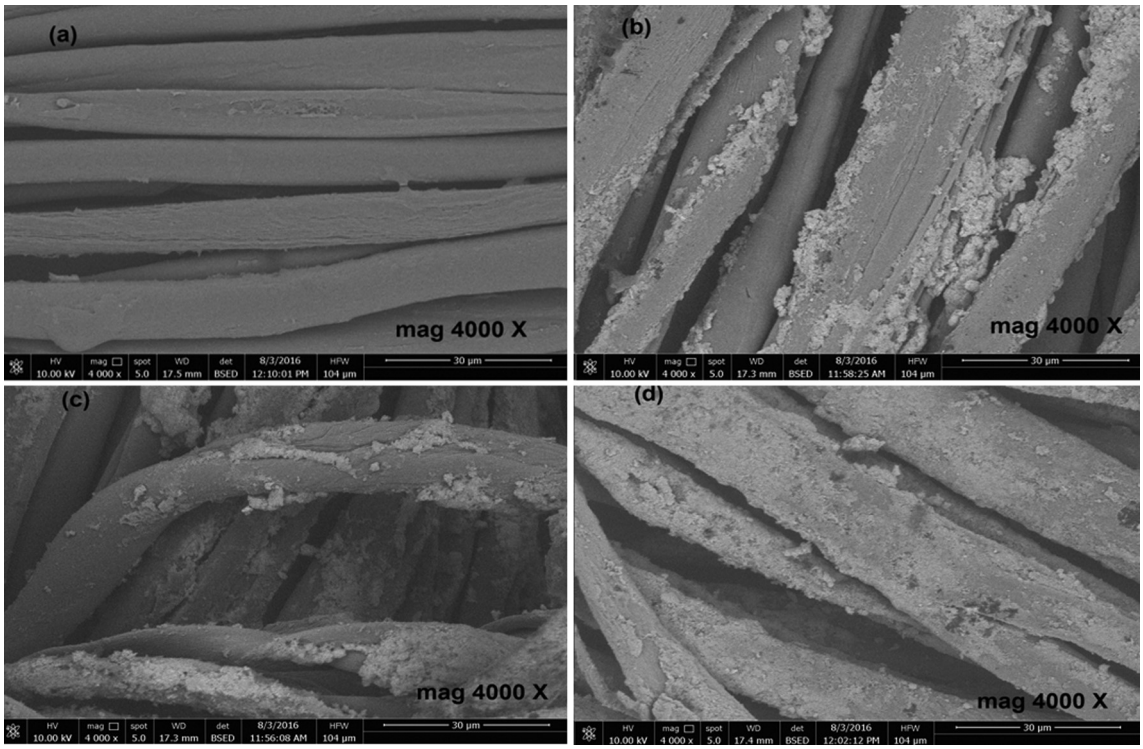


Fig. 4 — SEM images of (a) untreated cotton, and cotton treated with (b) chitosan, (c) TiO_2 NPs and (d) TiO_2 NPs + chitosan + turmeric

Table 3 — Discolouration of cotton samples treated with TiO_2 stained by methylene blue

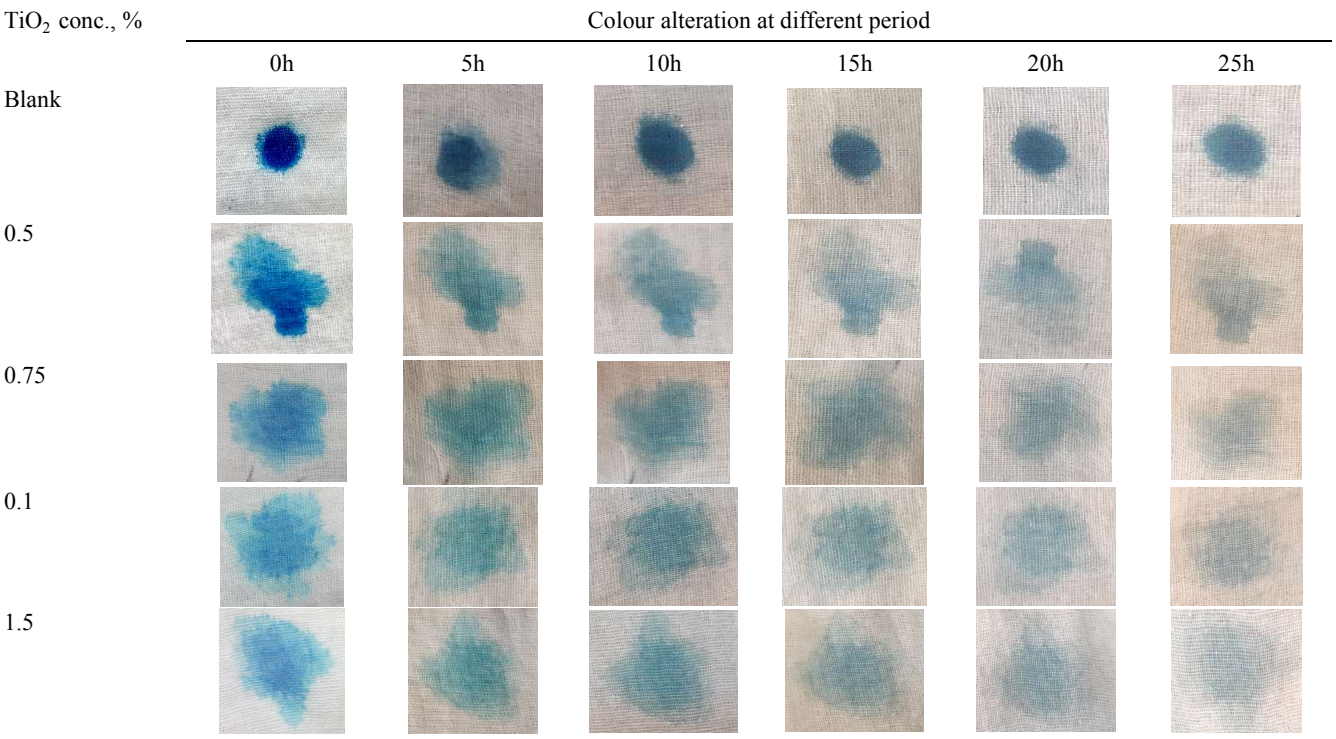


Table 4 — Colour fastness properties of treated cotton fabrics

Treatment condition	UPF	*K/S*	Wash		Rub		Light
			Alt.	St.	Dry	Wet	
Untreated sample	25.5	6.5	2	4	4–5	3–4	2–3
0% chitosan	30.5	5.87	3	3	4–5	4–5	3–4
0% TiO_2 NPs	26.6	8.18	2–3	4–5	4–5	3–4	2–3
0 g/L citric acid	33.3	7.22	2–3	4	4–5	3–4	3
40 g/L citric acid	41.5	8.58	3–4	4	4–5	3–4	3–4
Optimum conditions	34.9	8.83	3–4	4–5	4–5	4–5	3–4

methylene blue (0.01%). The decomposition rates of the methylene blue in daylight are used to determine the self-cleaning properties of the fabrics. The colours of the stained cotton samples before and after different periods of daylight exposure are evaluated using a grey scale.

The colour variations are shown in Table 3. The self-cleaning properties improve with increasing TiO_2 NP concentration in the treatment bath. This can be attributed to the absorption of a greater amount of TiO_2 NPs on the cotton fabric, resulting in the increased production of active radicals, and greater photocatalytic activity and decolouration of methylene blue[45]. In addition, increasing the daylight exposure time increases the rate of dye decomposition.

The colour fastness properties of the untreated and treated cotton fabrics are evaluated (Table 4). A significant improvement in the colour fastness is observed for the treated fabrics. For example, the colour alteration after washing is enhanced from 2 to 3–4 using 40 g/L citric acid. This result confirms the role of citric acid in forming ester linkages between the cotton fabric and the dye molecules, and binding the dye molecules onto the cotton fibres. The crosslinked dye molecules exhibit excellent resistance to washing, resulting in enhanced colour fastness.

Additionally, treating the cotton fabric with TiO_2 NPs/chitosan results in improved light fastness. This is attributed to the scattering and/or reflection of ultraviolet radiation by the TiO_2 NPs.

4 Conclusion

A novel approach for the dyeing and finishing of cotton fabric in a single step was developed. This approach consisted of the application of TiO_2

NPs/chitosan colloids in the presence of turmeric dye using a pad-dry-cure technique. The optimum conditions were determined to be as follows: 10% dye extract, 0.75% TiO_2 NPs (w/v), 4 g/L SPP, 2.5% chitosan (w/v), 30 g/L citric acid, drying at 70 °C for 5 min and curing at 180 °C for 2 min.

Treating the cotton fabric with TiO_2 NPs/chitosan colloids improves the UPF of the cotton fabric. Citric acid is successfully used to increase the binding of TiO_2 NPs onto cotton fabric via crosslinking. However, high concentrations of chitosan are found to increase fabric stiffness. Moreover, we demonstrated the antimicrobial properties of chitosan/TiO_2 NPs treatment against Gram-positive and Gram-negative bacteria. The results show that the combined treatment of chitosan/TiO_2 NP/turmeric enhance the antimicrobial activity over the individual treatments. The results of the nitrogen content studies demonstrate that the chemical modification of the cotton fibre occurs during chitosan/TiO_2 NP treatment. SEM images exhibit the formation of a homogeneous film coating on the surface of the cotton fibres. The results also indicate the efficiency of the treatment in improving the self-cleaning properties of the fabric. The wash fastness of the fabric is found to be improved because of increased fixation of the natural dye inside the cotton fibre. The light fastness is improved by treatment with TiO_2 NPs.

The present investigation shows the possibility of combining dyeing and finishing into a single step to produce multifunctional textiles. However, further studies are necessary to determine the effects of different crosslinking agents on the colour fastness properties of dyed fabrics.

Acknowledgement

The authors acknowledge the financial and technical support by the Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah (Grant No. G-40-364-38)

References

1 Mihailović D, Šaponjić Z, Radoičić M, Radetić T, Jovančić P, Nedeljković J & Radetić M, *Carbohydr Polym*, 79 (2010) 526.
2 Petrulyte S, *Dan Med Bull*, 55 (2008) 72.
3 Rai R & Srinivas C R, *Indian J Dermatol Venereol Leprol*, 73 (2007) 73.
4 Dastjerdi R & Montazer M, *Colloids Surf B*, 79 (2010) 5.
5 Montazer M & Pakdel E, *Photochem Photobiol*, 86 (2010) 255.
6 Dastjerdi R, Montazer M & Shahsavan S, *Colloids Surf B*, 81 (2010) 32.
7 Nazari A, Montazer M, Rashidi A, Yazdanshenas M & Moghadam M B, *J Appl Polym Sci*, 117 (2010) 2740.
8 Nazari A, Montazer M, Moghadam M B & Anary-Abbasinejad M, *Carbohydr Polym*, 83 (2011) 1119.
9 Norranatrakul P, Siralertmukul K & Nuisin R, *Mater Miner*, 23 (2013) 9.
10 Haldorai Y, *Plast Res Online* (2013). 10.2417/spepro. 005202.
11 Tung W S & Daoud W A, *J Appl Polym Sci*, 112 (2009) 235.
12 Lessan F, Montazer M & Moghadam M B, *Thermochim Acta*, 520 (2011) 48.
13 Pavasupree S, Jitputti J, Ngamsinlapasathian S & Yoshikawa S, *Mater Res Bull*, 43 (2008) 149.
14 Nazari A, Montazer M, Rashidi A, Yazdanshenas M E & Ansari-Abasinejad M, *Appl Catal A*, 371 (2009) 10.
15 Peng L, Wenli D, Qisui W & Xi L, *Photochem Photobiol*, 86 (2010) 633.
16 Montazer M & Morshedi S, *J Ind Eng Chem*, 20 (2014) 83.
17 Zhang H, Millington K R & Wang X, *Polym Degrad Stab*, 94 (2009) 278.
18 Sun G & Hong K H, *Text Res J*, 83 (2013) 532.
19 Elshafei A & Elzanfaly H T, *Asian J Appl Sci*, 4 (2011) 585.
20 Goh C H, Heng P W & Chan L W, *Carbohydr Polym*, 87 (2012) 1796.
21 Zemljic LF, Volmajer J, Ristic T, Bracic M, Sauperl O,& Kreze T, *Text Res J*, 84 (2014) 819-830
22 http://www.mdidea.com/products/herbextract/marigold/data. html (downloded on 30/3/2010).
23 Ke G, Yu W & Xu W, *J Appl Polym Sci*, 101 (2012) 3376.
24 Chen C & Chang W, *Indian J Fibre Text Res*, 32 (2007) 122.
25 Perumal K, Stalin V, Chandrasekarenthiran S, Sumathi E & Saravanakuma A, *Text Res J*, 79 (2009) 1178.
26 Dev V R G, Venugopal J, Deepika G & Ramakrishna S, *Carbohydr Polym*, 75 (2009) 646.
27 Joshi M, Ali S W & Purwas R, *Indian J Fibre Text Res*, 34 (2009) 295.
28 Deo H T & Paul R, *Int Dyer*, 188 (2003) 49.
29 Judd D B & Wyszecki G, *Color in Business Science and Industry*, 3rd edn (John Wiley Sons, Cleveland, USA), 1975.
30 Vogel, A. *Textbook of Quantitative Inorganic Analysis*, 3rd edn (Longman, London), 1961.
31 Erdawati & Fithriyah N H, *J Basic Appl Sci Res*, 3 (2013) 5.
32 Saravanan P, Chandramohan G, Maria Jancy Rani J & Shanmuga Sundaram P, *Int J Recent Trends Sci Technol*, 9 (2013) 72.
33 Chenite A, Chaput C, Wang D, Combes C, Buschmann M D, Hoemann C D, Leroux, J C, Atkinson B L, Binette, F & Selmani, A, *Biomaterials*, 21 (2000) 2155.
34 Campeerapappun P, Phattararittigul, Jittrong S,& Kullachod D, *Chiang Mai J Sci,* 38 (2010) 95-104.
35 Ratnapandian S, *Application of Natural Dyes by Padding Technique on Textiles*, Ph.D. thesis, School of Fashion and Textiles, Design and Social Context Portfolio, RMIT University, Melbourne, 2013.
36 Ibrahim N A, El-Zairy W M, El-Zairy M R, Eid B M & Ghazal H A, *Carbohydr Polym*, 83 (2011) 1068.

37 Ibrahim N A, El-Zairy W M, El-Zairy M R, Eid B M & Ghazal H A, *J Text Inst*, 102 (2011) 863.
38 Ali S W, Rajendran S & Joshi M, *Carbohydr Polym*, 83 (2011) 438.
39 Simoncic B & Tomsic B, *Text Res J*, 80 (2010) 1721.
40 Mossotti R, Innocenti R, Dimechelis R & Pozzo P D, *Proceedings, 10th International Wool Textile Research Conference* (DWI, Aachen, Germany), 2000, F1–P15, 245.
41 Bohringer B, *Proceedings, 37th International Man-Made Fibers Congress* (Wien Osterr, Chemiefaser-Inst, Dornbirn, Austria), 1998, 1031.
42 Gupta K K, Tripathi V S, Ram H & Raj H, *Colorage*, 49 (2002) 35.
43 Ibrahim N A, Eid B M, Hashem M M, Refai R & El-Hossamy M, *J Ind Text*, 39 (2010) 233.
44 Hari T & Montazer M, *Dye Pigm*, 97 (2013) 440.
45 Montazer M & Pakdel E, *J Text Inst*, 102 (2011) 343.