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Cationic Starch (Q-TAC) Pre-Treatment of Cotton Fabric: Influence on dyeing with reactive dye

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ABSTRACT

Reactive dyes require high concentrations of an electrolyte to improve dye-fiber interaction, leading to the discharge of harmful effluent. One approach to reduce this unsafe release is treatment of the cotton fabric with cationic chemical reagents. This paper reports on the treatment of cotton fabric with cationic starch (Q-TAC), a commercial product, by batchwise method and pad batch method for the first time prior to reactive dyeing process. Furthermore, three commercial reactive dyes, based on *monochloro triazine, vinyl sulfone and monochlorotriazine + vinyl sulfone* chemistry, was applied on the cotton fabrics by continuous (pad-dry-cure) method. The treated cotton fabric by batchwise method produced 70% higher color yield (*K*/*S*) and 20% enhanced dye fixation (%*F*) than the untreated cotton fabric. X-ray photoelectron spectrometer (XPS) analysis revealed the presence of N1s peaks in the treated cotton fabrics. The crystallinity of treated cotton fabrics was reduced in comparison to untreated cotton fabric as revealed by wide angle X-ray diffraction (WAXD) measurements. Field Emission Scanning Electron Microscopy (FE-SEM) showed that the surface of treated cotton fabrics was rougher than untreated cotton fabric due to the deposition of cationic starch. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrum confirmed the existence of quaternary ammonium groups, $N^{+}(CH_3)_3$, in the treated cotton fabrics. The analysis of color fastness tests demonstrated good to excellent ratings for treated cotton fabrics. In this way, cationic starch treatment of cotton fabric before reactive dyeing process has been proven potentially a more environmentally sustainable method than conventional dyeing method.

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1. Introduction

Cotton is a dominant textile fiber over the years due to its unique properties including hydrophilicity, biodegradability, durability, good dyeability and relatively inexpensive (Fu, Hinks, Hauser, & Ankeny, 2013). For these reasons, the share of cotton in total fiber consumption is about 50% (Hashem, Ibrahim, El-Shafei, Refaie, & Hauser, 2009). Reactive dyes are vastly used in dyeing of cotton fiber owing to their wide gamut of hues and good wet fastness properties (Öner & Sahinbaskan, 2011). These dyes have a distinctive reactive nature due to active groups which form covalent bonds with hydroxyl groups of cotton (Khatri, Memon, Khatri, & Tanwari, 2011). However, considerable quantities of an inorganic electrolyte (e.g. sodium chloride or sulfate) and an inorganic alkali (e.g. sodium bicarbonate or carbonate or hydroxide) are required (Khatri, Padhye, & White, 2012). Under alkaline fixation condition (pH > 10.5), reactive dyes can react not only with the hydroxyl groups in cotton but also with water to form hydrolyzed dyes (Hao, Wang, Liu, & Liu, 2012b); resulting into a considerable amount of colored effluent arises during washing off. Furthermore, unfixed dyes in the effluent pose an environmental hazard (Xie, Liu, & Wang, 2009). Therefore, efforts have been made to enhance dye fixation (%*F* higher color yield during cotton dyeing with reactive dyes.

One method to overcome this problem is chemical modification of cotton with cationic agents, which can alter the surface charge of cotton enabling salt free dyeing with anionic dyes (Fu et al., 2013). The ionic attraction existed between the reactive dye and the cationized cotton brings about dye fixation (Hao, Wang, Liu, & Liu, 2012a). Numerous chemical reagents were studied to prepare cationic cotton including 3-chloro-2-hydroxypropyl

Abbreviations: o.w.f., on the weight of fabric; CT, cellulose triacetate; CO, cotton; PA, polyamide; PES, polyester; PAC, polyacrylonitrile; WO, wool.

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trimethylammonium chloride (CHPTAC) for enhancing color strength (*K*/*S*) of reactive dyes (Patiño et al., 2011) and natural dyes using ultrasonic technique (Kamel, El Zawahry, Ahmed, & Abdelghaffar, 2011). Similarly, poly-aminochlorohydrin quaternary ammonium polymer with epoxide functionality was successfully used as cationising agent for applying anionic pigments (Hao et al., 2012b) and natural dyes extracted from Cochineal insects (Kamel, El Zawahry, Ahmed, & Abdelghaffar, 2009) and plant waste (Oktav Bulut & Akar, 2012).

Cationic starch is the modified starch, produced by etherifying reaction of starch with the tertiary amino and quaternary ammonium cationising reagents (Käki et al., 2007); and are extensively used commercially due to their low cost and biodegradability (Zhang, 2001). It has a large molecular size and binds to cotton by means of ionic bonding, hydrogen bonding and van der Waals forces (Zhang et al., 2005). The presence of quaternary ammonium groups, $N^{+}(CH_3)_3$, in cationic starch enables anionic reactive dye molecules to attach rapidly forming ionic bonds.

Previous studies showed that cationic starch having higher degree of substitution (DS) = 0.8 was applied on cotton fabric only by pad-bake method; in which high quantity of surfactant was used to achieve leveling. Later on, the duration of reactive dyeing step employed was considerably high. For instance, it was carried out in 19 min using a continuous (Pad → Dry → Steam) method (Zhang et al., 2005); and in 70 min by batchwise method (Zhang, Ju, Zhang, Ma, & Yang, 2007) excluding washing off duration. To the best of our knowledge, no earlier attempts have been made for treatment of cotton fabric with cationic starch with low DS by batchwise method and pad batch method for enhancing *K*/*S* and increasing *%F* of reactive dyes. Moreover, keeping in view the significance of high production rate required by the dye houses, the duration of reactive dyeing step should be short.

The aim of our study was to apply the cationic starch (Q-TAC) having low DS on cotton fabric by batchwise method and pad batch method. Furthermore, the treated fabrics were dyed with reactive dye by using a single-bath continuous (Pad → Dry → Cure) method. We performed the reactive dyeing step in just 4 min excluding washing-off duration.

2. Experimental

2.1. Materials

In this work, a commercially bleached and mercerized ready-to-dye cotton fabric (weight 120 g/m^2 produced from warp yarn count of Ne 30/1 and weft yarn count of Ne 30/1) was used. Three commercial reactive dyes were used for dyeing cotton fabrics, namely CI Reactive Red 120 (*Monochlorotriazine*), CI Reactive Blue 19 (*Vinylsulfone*) and CI Reactive Red 195 (*Monochlorotriazine + Vinylsulfone), supplied by DKC corporation Korea*. Sodium hydroxide (36°Be), acetic acid, urea, sodium carbonate and sodium chloride were of analytical grade. Q-TAC (Rafhan Maize Pakistan) having DS in the range of 0.036–0.042%, thermacol MIN (Migration Inhibitor based on solution of an acrylic copolymer, Hunstman Pakistan), Ladipur RSK (Anionic Detergent based on polycarboxylic acid, Clariant Pakistan), and Drimagen E2R (Anionic Leveling Agent based on aromatic polyether sulphonate, Clariant Pakistan) were of commercial grade. Deionized water was used for all the experiments done in this work.

2.2. Application of cationic starch

Q-TAC was applied on cotton fabric without using surfactant by batchwise method and pad batch method. In batchwise method, the cotton fabric was treated with 2–6% o.w.f. Q-TAC solution at 40 °C for 30 min in Rapid laboratory dyeing machine (Rapid Color C Type, Taiwan). Furthermore, the treated cotton fabric was washed with cold water and then with boil water for 5 min. The pH of the treated cotton fabric was neutralized in acetic acid solution followed by rinsing in cold water for 5 min. Treatment conditions were optimized by varying temperature (40–80 °C) and pH (8–12). 20:1 was the liquor-to-good ratio taken during experiments. In pad batch method, the cotton fabric was padded with 5–25 g/L Q-TAC solution at ambient temperature on Rapid horizontal padding mangle (Air-Pad P-B1, Taiwan). The pick-up% was set at 70. The padded fabric was immediately wrapped in a polyethylene bag to avoid any air exposure. Washing-off process was performed as stated previously. Dwell time (6–24 h) and pH (8–12) were optimized.

2.3. Reactive dyeing

The cotton fabrics were dyed by padding (single dip-single nip, 70% liquor pick-up) through a dye bath solution on Rapid laboratory horizontal padding mangle (Air-Pad P-B1, Taiwan). Dye bath solution contains 10 g/L reactive dye, 2 g/L drimagen E2R, 20 g/L thermacol MIN, 15 g/L sodium carbonate and 100 g/L urea. The padded fabric was immediately dried at 120 °C for 90 s followed by curing at 160 °C for 90 s on Rapid laboratory mini dryer (R-3, Taiwan). Furthermore, the washing-off process was carried out by batchwise method (cold wash → hot wash → soaping-off → hot wash → neutralization → cold wash). The soaping-off was done at boil for 15 min in the presence of 2 g/L Anionic detergent (Ladipur RSK, Clariant). The liquor-to-good ratio was taken as 50:1.

2.4. Color measurement and testing

K/*S* was assessed for each dyed sample with Gretag Macbeth CE-7000A spectrophotometer using the following instrument settings (8.4 mm sample aperture, illuminant D65, UV included and specular component included). Each specimen was measured from five different locations and the average value was reported. The relative color strength was assessed by using the Kubelka–Munk equation (Eq. (1)) as described in a previous report (Ali, Khatri, Khatri, & Tanwari, 2013).

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

where *R* is the decimal fraction of the reflectance of the dyed fabric, *K* is the absorption coefficient and *S* is the scattering coefficient.

The percentage of reactive dye fixed on cotton fabric was measured using the following equation.

$$\%F = \frac{(K/S)_a}{(K/S)_b} \quad (2)$$

where *F* is the dye fixation in percentage, $(K/S)_a$ is the color strength after wash and $(K/S)_b$ is the color strength before wash.

Color fastness to washing test was performed in Gyrowash (James H. Heal Co., UK) by following ISO-105-C10:2006; Color fastness to light test was carried out in Apollo (James H. Heal Co., UK) according to ISO-105-BO2:2013 (20 h) and Color fastness to rubbing was done on Crockmeter (James H. Heal Co., UK) by following ISO-105-X12:2001. The evaluation of color fastness properties of dyed fabrics were performed in accordance with ISO-105-AO2:1993 (Gray scale for assessing change in color) and ISO-105-AO3:1993 (Gray scale for assessing staining).

2.5. Characterization

Water absorbency of mercerized cotton fabric was monitored in accordance with AATCC Test Method 39 (Water Drop Disappearance). Degree of whiteness expressed as CIE Whiteness of cotton fabric was determined on reflectance spectrophotometer (Gretag

Macbeth CE-7000A). pH of cotton fabric was measured by following AATCC Test Method 81-2012. The chemical composition of the cotton fabric surfaces was examined by X-ray photoelectron spectrometry (XPS; Theta Probe Base System, Thermo Fisher Scientific Co.) with Al Kα radiation. Survey spectrum was recorded at a detector pass energy of 100 eV and the high resolution spectra for N 1s regions were also obtained at a pass energy of 50 eV. The crystallinity of cotton fabrics were measured using wide angle X-ray diffraction (WAXD; Rigaku Denki Co. Japan), with Cu K_α radiation ($\lambda = 1.5402$ Å) at a scanning speed of $2\theta = 2^\circ$/min. The data were taken in the range of 5–40° in steps of 0.02° at 40 kV and 60 mA. The morphology of untreated and treated cotton fabrics were examined under Field Emission Scanning Electron Microscopy (FE-SEM; JSM 6701F, JEOL Japan) at two magnifications, namely 1000× and 4000×, using 15 kV accelerating voltage. The fabrics were coated with Platinum under vacuum by sputtering method. The attenuated total reflectance-Fourier transform spectroscopy (ATR-FTIR) spectra of cotton fabrics were recorded on Nicolet 6700 FTIR spectrometer equipped with the ATR accessory (ThermoElectron Corporation, USA) in the range of 4000–800 cm^{-1}.

3. Results and discussion

3.1. Analysis of untreated cotton fabric

Before Q-TAC treatment, some important fabric properties were measured of the mercerized cotton fabric used in this study. The fabric had an absorbency of 1 s, CIE whiteness index of 60.44 and pH extract of 8.5. Furthermore, the untreated cotton fabric was dyed with three different commercial reactive dyes by continuous (Pad → Dry → Cure) method. The *K*/*S* value obtained was: CI Reactive Red 120 – 4.30, CI Reactive Blue 19 – 2.01 and CI Reactive Red 195 – 5.20.

3.2. Analysis of treated cotton fabric

3.2.1. Batchwise method

Table 1 summarizes the effect of different process parameters including temperature, pH and Q-TAC concentration on CIE whiteness and absorbency. It can be seen that by increasing process liquor temperature from 40 °C to 80 °C, CIE whiteness of treated cotton fabrics were enhanced. The optimum CIE whiteness was obtained at 80 °C. Comparing with the untreated cotton fabric, CIE whiteness of treated cotton fabrics remained inferior. It was earlier reported that treatment of cotton fabric with cationic agents reduced CIE whiteness (Kanik & Hauser, 2002). It was also revealed that fabric absorbency of treated cotton fabrics remained same at different process liquor temperatures. The observed water drop test rating of all specimens was 1 s. Hence, the amorphous content of cotton fiber polymer system was retained. Moreover, change of fiber surface polarity, from negative to positive, did not bring any adverse effect to moisture absorption characteristic of treated cotton fabrics. The optimized temperature considered for further experiments was 80 °C.

Additionally, the CIE whiteness of treated cotton fabrics was gradually enhanced as the alkalinity of Q-TAC solution increased. However, CIE whiteness was sharply declined at pH 12 possibly due to the yellowing effect of cotton fabric. The optimum CIE whiteness was achieved at pH 11. It was also observed that increasing alkaline pH of process liquor has not affected the fabric absorbency. The

Table 1
Summary of experimental results of treated cotton fabric by batchwise method.

S. no:	Temperature (°C)	pH	Concentration (%)	Liquor-to-good ratio	Time (min)	CIE whiteness	Absorbency (s)
1	40	10	2	20:1	30	40.43	1
2	50	10	2	20:1	30	42.16	1
3	60	10	2	20:1	30	44.01	1
4	70	10	2	20:1	30	46.52	1
5	80	10	2	20:1	30	50.87	1
6	80	8	2	20:1	30	48.20	1
7	80	9	2	20:1	30	49.02	1
8	80	10	2	20:1	30	50.87	1
9	80	11	2	20:1	30	53.02	1
10	80	12	2	20:1	30	50.04	1
11	80	11	2	20:1	30	53.02	1
12	80	11	3	20:1	30	53.91	1
13	80	11	4	20:1	30	54.31	1
14	80	11	5	20:1	30	55.10	1
15	80	11	6	20:1	30	56.30	1

Table 2
Summary of experimental results of treated cotton fabric by pad batch method.

S. no:	Batching time (h.)	pH	Concentration (g/L)	Pick-up (%)	Temperature (°C)	CIE whiteness	Absorbency (s)
1	06	10	5	70	25	43.51	1
2	12	10	5	70	25	41.50	1
3	18	10	5	70	25	40.17	1
4	24	10	5	70	25	39	1
5	06	8	5	70	25	41.69	1
6	06	9	5	70	25	42.60	1
7	06	10	5	70	25	43.51	1
8	06	11	5	70	25	44.76	1
9	06	12	5	70	25	47.37	1
10	06	12	5	70	25	47.37	1
11	06	12	10	70	25	44.80	1
12	06	12	15	70	25	43.90	1
13	06	12	20	70	25	43.04	1
14	06	12	25	70	25	42.10	1

Table 3
Atomic concentrations generated through XPS.

Cotton fabric	Binding energy (eV)			Atomic concentration (%)		
	C1s	O1s	N1s	C1s	O1s	N1s
Untreated	285	532	399	67.02	32.98	–
Treated with batchwise method				63.56	35.18	1.27
Treated with pad batch method				71.41	28.06	0.53

water droplet wet the surface of all specimens in 1 s. The optimized pH selected for further experiments was 11.

It was also revealed that increasing Q-TAC concentration enhanced CIE whiteness of treated cotton fabrics. At 6% Q-TAC concentration, optimum CIE whiteness of treated cotton fabric was achieved. Hence, it can be assumed that Q-TAC has been deposited well on the cotton fiber surface at optimized conditions. Fabric absorbency remained unchanged at different Q-TAC concentrations suggesting that amorphous region of treated cotton fabrics is retained which contributes toward wettability. Also, the duration of Q-TAC treatment by batchwise method before reactive dyeing step was found higher than the previous reports (Zhang et al., 2005, 2007).

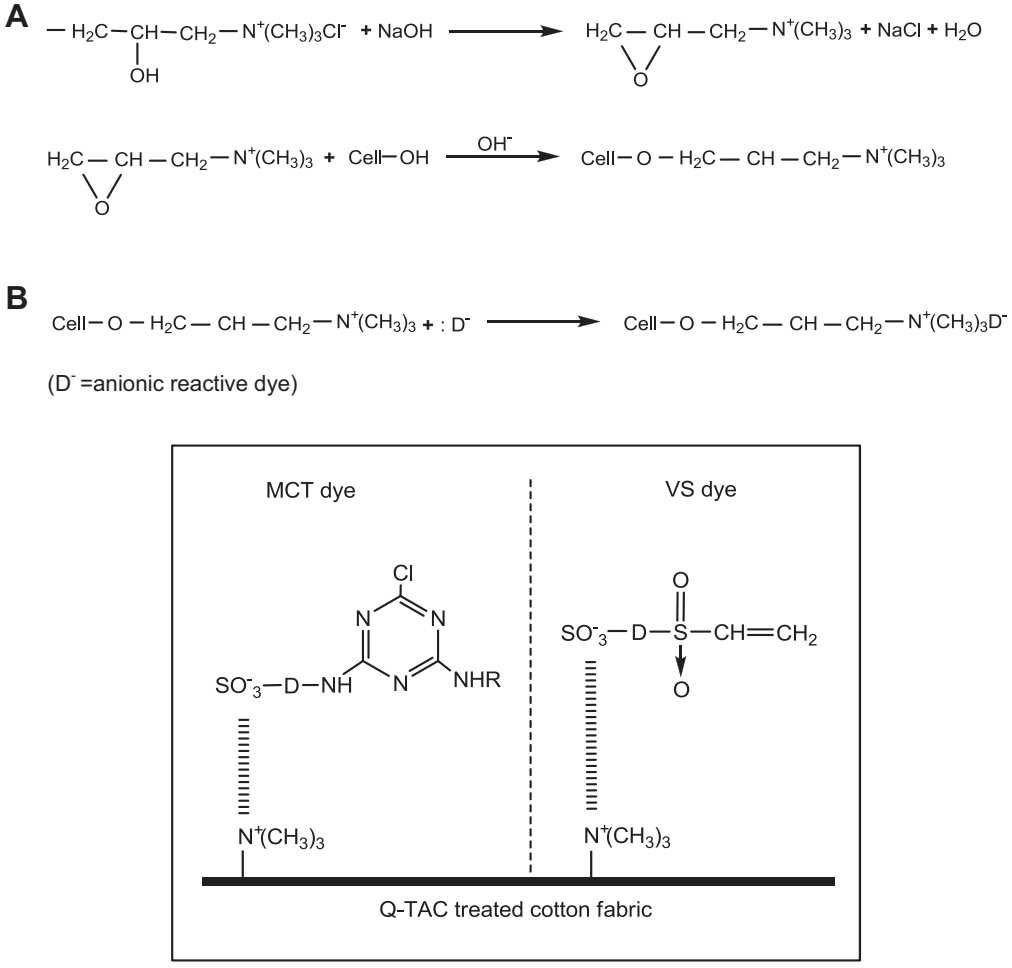
3.2.2. Pad batch method

Table 2 demonstrates the effect of different process parameters including batching time, pH and Q-TAC concentration on CIE whiteness and absorbency. It is evident that a gradual decline in CIE whiteness, that is, dullness was observed with increasing batching time possibly due to the yellowing effect on cotton fabrics. Fabric absorbency remained identical, that is, water droplet wet the treated cotton fabric surface in 1 s. The optimized batching time considered for further experiments was 6 h.

Referring Table 2, a steady enhancement in CIE whiteness was achieved with increasing alkalinity of process liquor. Water droplet wet the treated cotton fabric surface in 1 s for all the samples. The optimized pH chosen for further experiments was 12.

Furthermore, a gradual decrease in CIE whiteness was achieved with a simultaneous increase in the Q-TAC concentration. Similar results were also reported previously (Kanik & Hauser, 2002). At 5 g/L Q-TAC concentration, optimum CIE whiteness of treated cotton fabric was obtained. The treated cotton fabrics showed identical absorbency which suggest that their amorphous content is retained. Additionally, the duration of Q-TAC treatment by pad batch method before reactive dyeing step was found higher than the previous reports (Zhang et al., 2005, 2007).

We have successfully applied Q-TAC as a cationic agent on the cotton fabric by batchwise method and pad batch method for the



Scheme 1. (A) Reaction of cationic starch with cotton fabric. (B) Reactive dye fixation on Q-TAC treated cotton fabric by ionic bonding.

first time. However, it was accompanied with some loss of CIE whiteness. In general, cotton fabrics treated with Q-TAC by batchwise method exhibited higher CIE whiteness in comparison to pad batch method. The probable reason could be the combined effect of temperature and agitation given in the earlier method.

3.3. Surface chemical composition of cotton fabrics

Table 3 shows the atomic composition of cotton fiber surface at a 10 nm depth and the binding energy of electrons associated with those atoms. The measurements were recorded on XPS. The cotton fabrics showed C1s and O1s peaks at 285 eV and 532 eV respectively. However, the untreated cotton fabric has no N1s peak at 399 eV, which is consistent with its chemical structure and reported previously (Patiño et al., 2011). The treated cotton fabrics showed N1s peak indicating the presence of Q-TAC on the surface of cotton fiber (Scheme 1a). The treated cotton fabric by batchwise method produced higher nitrogen content (1.27%) in comparison to the treated cotton fabric by pad batch method (0.53%) suggesting greater attachment of Q-TAC by earlier method. Comparing with untreated cotton fabric, the application of Q-TAC by batchwise method was resulted into a decrease in the carbon content by 3.46% as well as an increase in the oxygen content by 2.2% (Patiño et al., 2011). On contrary, Q-TAC treatment by pad batch method increased the carbon content by 4.39% and decreased the oxygen content by 4.92% in comparison to the untreated cotton fabric. This may possibly be due to the lack of temperature and agitation present in pad batch method resulting into an inadequate deposition of Q-TAC on the cotton surface.

3.4. Crystallinity of cotton fabrics

Cationic agent treatment of cotton fabrics can change the crystal form and crystallinity of fibers (Wang, Ma, Zhang, Teng, & Yang, 2009). In addition to this, WAXD patterns of undyed cotton fabrics were measured and presented in Fig. 1a–c. The cotton fabrics showed a sharp peak at $2\theta = 22.9^\circ$ along with other small peaks at $2\theta = 15^\circ$, 16.7° and 34.7°, corresponding to (3.94 Å), (6.01 Å), (5.35 Å), and (2.58 Å) *d*-spacing, which is the characteristic of cellulose I structure (Ford, Mendon, Thames, & Rawlins, 2010). The results revealed that Q-TAC treatment does not change the crystalline form of treated cotton fabrics. However, the peak intensities of the treated cotton fabrics were reduced compared to untreated cotton fabric (Shateri Khalil-Abad, Yazdanshenas, & Nateghi, 2009), possibly due to the hydroxyl groups being substituted by grafting of the Q-TAC (Scheme 1a). Furthermore, the crystallinity of treated cotton fabrics were reduced as the density of hydrogen bonds lowered because of the hydroxyl group substitution. The cotton fabric treated by pad batch method showed the least crystalline form (Fig. 1c). This may possibly be attributed to the prolonged reaction time (6 h) given to the cotton fabric at high alkaline pH.

3.5. Morphology of cotton fabrics

Fig. 2a–f shows the surface morphology of undyed cotton fabrics using FE-SEM. It can be observed that the untreated cotton fibers are relatively parallel with smooth surface. But they are bent due to the two reasons; firstly the effect of twist in the yarn and secondly is the interlacing of the yarns in the fabric structure (Fig. 2a–b). In contrast, the treated cotton fibers showed rough surface (Fig. 2c–f); which is in agreement with earlier reports (Shateri Khalil-Abad et al., 2009; Wang et al., 2009). This is due to the attachment of cationic agent on the cotton fiber surface (Ristić & Ristić, 2012). The deposition of Q-TAC by batchwise method (Fig. 2c–d) is higher than pad batch method (Fig. 2e–f) probably due to the combined effect

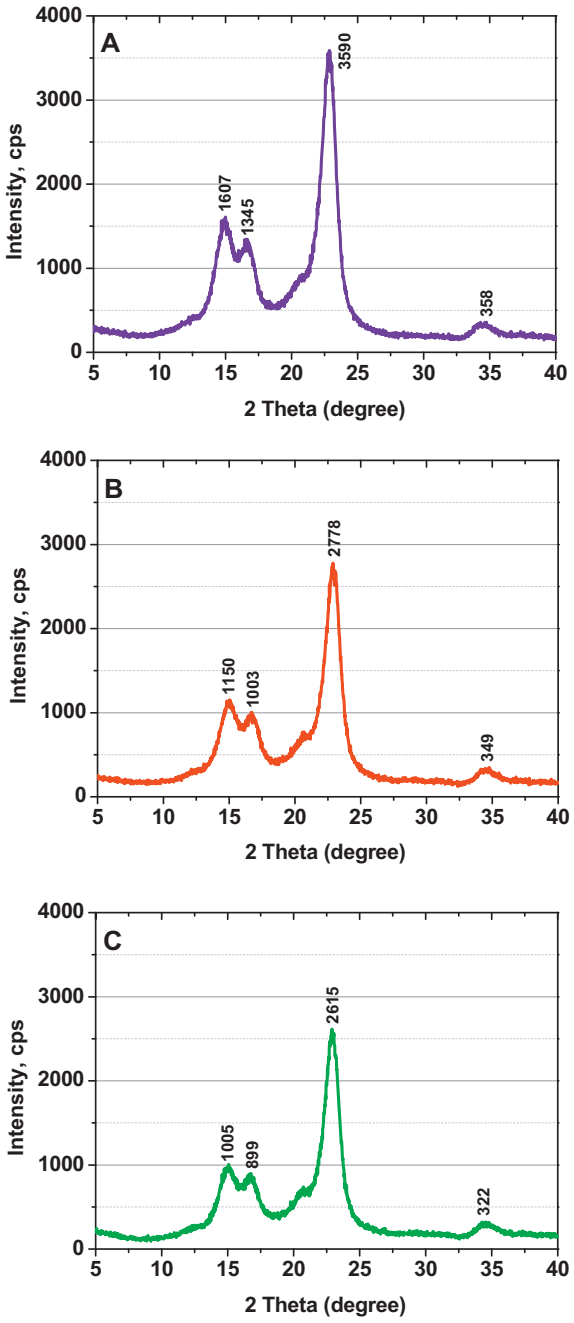


Fig. 1. XRD patterns of cotton fabric (A) untreated, (B) treated with Q-TAC by batchwise method, and (C) treated with Q-TAC by pad batch method.

of temperature and agitation used in the latter method. This result also supports the XPS findings in which the cotton fabric treated by batchwise method exhibited higher nitrogen content than the cotton fabric treated by pad batch method.

3.6. Analysis of color strength (*K*/*S*) and dye fixation (%*F*)

Fig. 3 shows the effect of processing method employed for Q-TAC treatment on *K*/*S* and %*F* of cotton fabrics with three different reactive dyes. In general, the results revealed that higher *K*/*S* and %*F* values were obtained for treated cotton fabrics than the untreated cotton fabric. This may possibly be due to the two reasons. Firstly, higher ionic attraction existed between the dye anion and the quaternary ammonium groups of Q-TAC leading to

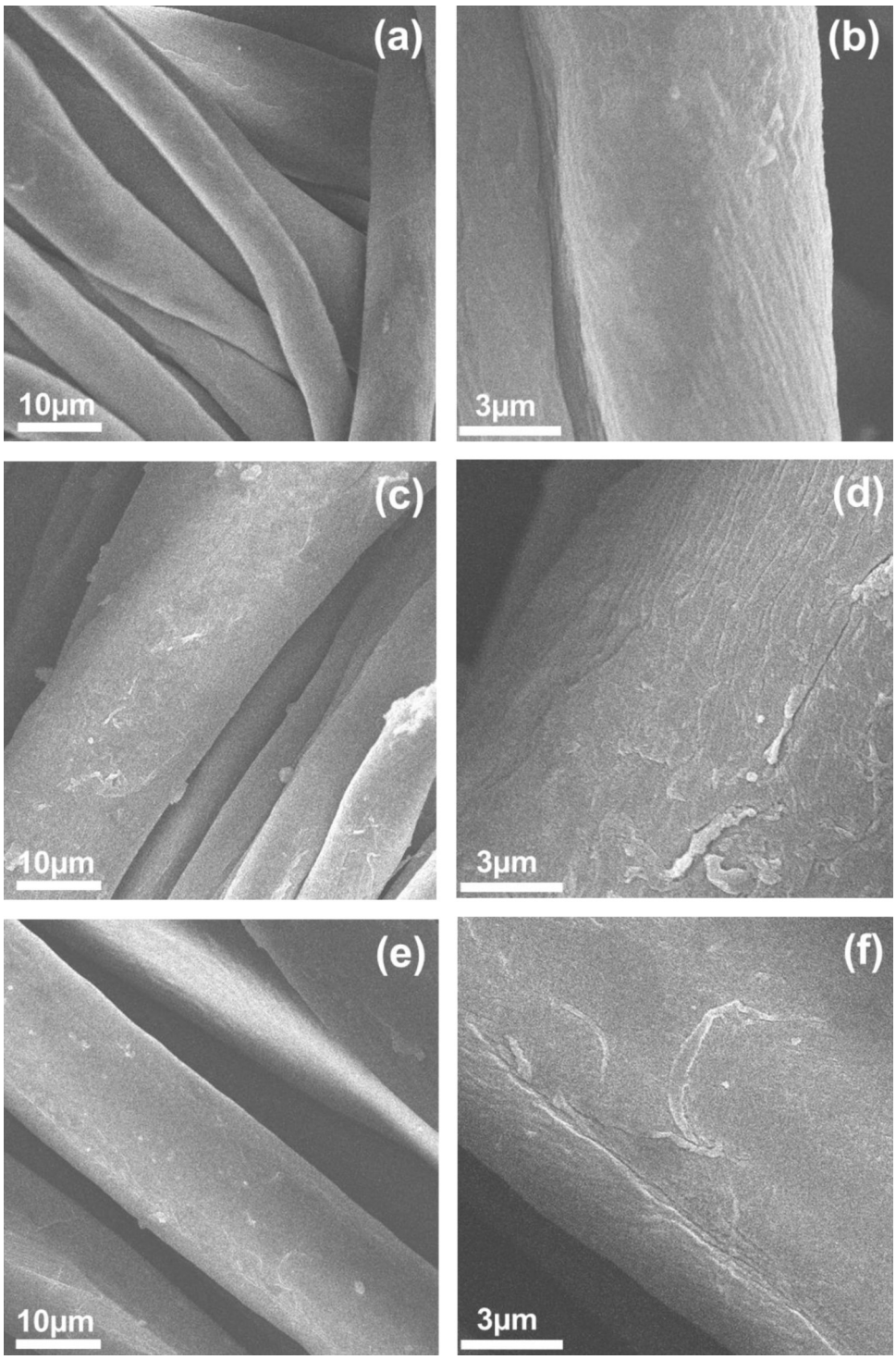


Fig. 2. FE-SEM images of cotton fabric (a and b) untreated, (c and d) treated with Q-TAC by batchwise method, and (e and f) treated with Q-TAC by pad batch method.

Table 4
Color fastness to washing test ISO 105 C10:2006, Color fastness to rubbing test ISO 105 X12:2001 and color fastness to light test ISO 105 BO2:2013 of cotton fabric dyed with Procion Dark Blue HEXL.

Dyed fabric	Rubbing fastness		Light fastness	Washing fastness						
	Dry	Wet	Blue wool reference	Change in color	Staining on multifiber					
					CT	CO	PA	PES	PAC	WO
Untreated	3.5	3.5	6	4	4.5	4	4	4	4.5	4.5
Cationic starch treated	3.5	3.5	6	4	4.5	4	4	4	4.5	4.5

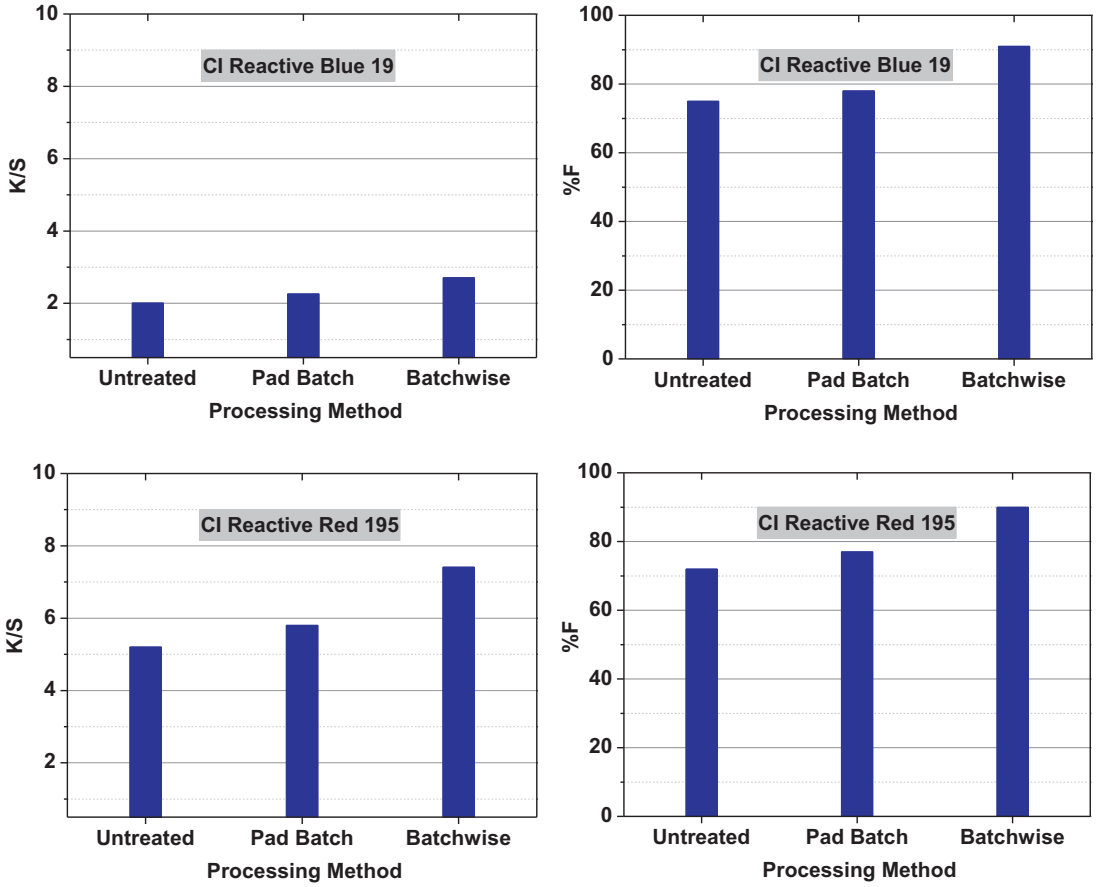


Fig. 3. Effect of processing method on *K*/*S* and *%F* of dyed cotton fabrics with three dyes. (Dyeing conditions: dye – 10 g/L, sodium carbonate – 15 g/L, urea – 100 g/L, pick-up 70%.)

higher dye absorption (Scheme 1b). Secondly, the crystallinity of cotton fabrics was reduced after Q-TAC treatment resulting into the greater diffusion of dye molecules into the treated cotton fabrics. It was also found that the cotton fabric treated by batchwise method exhibited maximum *K*/*S* and *%F* (Fig. 3) possibly due to the greater deposition of Q-TAC on its surface as shown in Fig. 2c–d. For CI Reactive Red 120,the results indicated that the Q-TAC treatment of cotton fabrics significantly enhanced the *K*/*S* to 10% and 70% for pad batch method and batchwise method respectively, and the treated cotton fabric yielded higher *%F* than the untreated cotton fabric showing an increase of 6% and 20% for pad batch method and batchwise method respectively.

We have achieved *%F* of 90, which is 18% higher than a previous study (Zhang et al., 2005) for Monochlorotriazine (MCT) dye. Furthermore, 17% and 15% higher *%F* were obtained for Monochlorotriazine + Vinylsulfone (MCT/VS) dye and Vinylsulfone (VS) dye respectively (Zhang et al., 2007). More significantly, the duration of reactive dyeing step used was considerably shorter than the previous reports (Zhang et al., 2005, 2007). Additionally, the combined duration of Q-TAC treatment by batchwise method and reactive dyeing steps was shorter by 65 min (Wang et al., 2009), 39 min (Zhang et al., 2007) and higher by 17 min (Zhang et al., 2005).

3.7. Analysis of color fastness tests

Table 4 outlines the results of color fastness to washing, rubbing and light. By comparing with untreated dyed fabric, the color fastness properties of the treated dyed fabric were similar demonstrating that the dye fixation was equally good on them. In the color fastness to rubbing test, the dry and wet rubbing fastness was found good with no significant color change for all the samples. The light fastness rating was good to excellent for both samples. The results for color fastness to washing (change in color) was good, and the color fastness to washing (staining on multifiber) ratings were good to excellent except CO, PA and PES which were good probably due to the greater affinity of reactive dyes toward these three types of fibers. The better results for the color fastness to washing (staining on multifiber) for CT, PAC and WO was ascribed to their anionic nature resulting into the repulsion of reactive dyes under the testing condition (Hao et al., 2012b). We have successfully applied reactive dye using a continuous (Pad → Dry → Cure) method in just 4 min without compromising color yield as well as fastness properties.

3.8. Chemical structure of cotton fabrics

Fig. 4a–b shows the ATR-FTIR spectra of undyed and dyed cotton fabrics previously treated with Q-TAC. The treated cotton fabrics showed characteristic cellulose peaks at around 1000–1200 cm^{-1} (Khatri, Arain, et al., 2013) in which the peaks present at 1160 cm^{-1} and 1028 cm^{-1} are ascribed for C—N stretching vibration and primary C—O—H stretching deformation respectively (Kamel et al., 2009; Oktav Bulut & Akar, 2012). Other characteristic bands related to the chemical structure of cellulose were the hydrogen-bonded O—H stretching around 3500–3200 cm^{-1}, the C—H stretching at 2900 cm^{-1}, and the C—H wagging at 1316 cm^{-1} (Chung, Lee, & Choe, 2004; Jonoobi et al., 2011). ATR-FTIR spectra of dyed fabrics (Fig. 4b) have retained their chemical structure after being

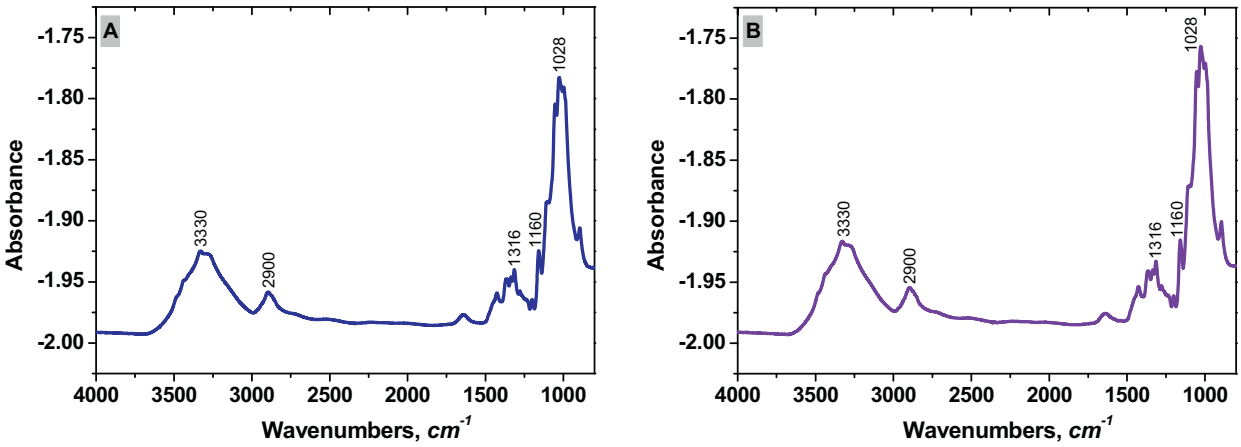


Fig. 4. ATR-FTIR spectra of cotton fabric (A) Untreated, (B) treated with Q-TAC/reactive dyed.

dyed with Procion Dark Blue HEXL. The interaction in between the reactive dye molecule and the treated cotton fabrics is difficult to identify probably due to the small amount of dyestuff used in the experiments (Khatri, Mayakrishnan, Hirata, Wei, & Kim, 2013).

4. Conclusion

We investigated that after Q-TAC treatment by batchwise method; *K*/*S* and *%F* have increased to 70% and 20% respectively in comparison to the conventional method. Excellent color fastness properties were achieved for both untreated dyed cotton and treated dyed cotton fabrics. The existence of N1s peaks was found by XPS measurements showing the presence of Q-TAC on the surface of treated cotton fabrics. The crystallinity of treated cotton fabrics was reduced in comparison to untreated cotton fabric as demonstrated by WAXD analysis. The existence of Q-TAC deposits on the cotton fiber surface was revealed by FE-SEM micrographs. The cotton fabrics showed characteristic cellulose peaks, and they retained their chemical structure after being dyed as demonstrated by ATR-FTIR analysis.

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