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Cationic-cellulose nanofibers: Preparation and dyeability with anionic reactive dyes for apparel application

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ABSTRACT

Continuous effort in research and development of nanofibers for apparel usage has been focused within their functional properties only. We investigated esthetic properties by producing colored cationic-cellulose nanofibers for the very first time for the potential application of apparel use. The cellulose acetate nanofibers were electrospun followed by deacetylation and cationization to produce functional cationic-cellulose nanofibers and then dyed with anionic reactive dyes. The spectrophotometric measurement of dyed samples was carried out to determine color coordinates and color yield values. The cationic-cellulose nanofibers showed enhanced color yield and dye fixation without addition of an electrolyte in comparison to cellulose nanofibers. The cationization of cellulose nanofibers significantly enhanced the color yield values of around 76% at dye concentrations of 5%. Excellent color fastness results demonstrate that these new colored and breathable materials can potentially be considered as future apparel for casual or fashion.

1. Introduction

Cellulose-based fashion and casual apparel have been widely used by a consumer due to its outstanding properties of breathability, air permeability, hygroscopicity, no static electricity, and biodegradability (Schurz, 1999; Klemm, Heubletin, Fink, & Bohn, 2005; Klemm et al., 2011) and these apparels show interesting physical properties such as a low density together with high mechanical characteristics (Berlioz, Molina-Boisseau, Nishiyama, & Heux, 2009). These cellulosic apparels are marketed in the form of white, dyed or printed according to the end-user's requirement. Cellulose nanofibers have been reported to be used in several technical fields (Filpponen et al., 2012; Ifuku et al., 2007; Ishii, Saito, & Isogai, 2011; Iwamoto, Isogai, & Iwata, 2011). Nanofibers exhibit even better breathability than the conventional cellulosic apparel due to having a small pore size between nanofibers (Yoon & Lee, 2011) and high porosity (Maa, Kotakia, & Ramakrishna, 2005). Therefore, nanofibers have a great potential for use as apparel and have attracted a great deal of interest recently. Kim, Kimura, Kim, Watanabe, and Kim (2011) described garment breathability, thermal insulation, antibacterial and mold properties of nanofibers. Lee et al. (2009) and Lee, Kimura, Lee, Park, and Kim (2010) produced nanofiber on a mass scale for apparel use successfully. They demonstrated that nanofibers exhibit very good comfort properties and have excellent durability without loss of mechanical properties when subjected to laundering. Waterproof breathable nanofibers show the best combination of waterproofing and breathability as compared to the conventional fabric systems (Yoon & Lee, 2011). Another study showed very good performance by fabric laminated by polyurethane nanofibers (Kang, Park, Kim, & Kang, 2007).

The current research trend in nanofibers as apparel use is increasing gradually. The past research was mainly focused within the functional properties only and to the best of our knowledge esthetic properties of cellulose nanofibers are not investigated to date. We prepared colored cellulose and cationic-cellulose nanofibers via electrospinning and post-treatment, and dyed with anionic reactive dyes for potential use as apparel. There always been a choice for dye cellulose with reactive dyes, direct dyes, sulfur dyes and vat dyes, however, reactive dyes have become a prime choice for coloring cellulosic textiles, because they provide a wide range of inexpensive brilliant colors with excellent washing fastness (Wang & Lewis, 2002; Xie, Hou, & Wang, 2008). It

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Abbreviations: OMW, on mass of web; CT, cellulose triacetate; CO, cotton; PA, polyamide; PES, polyester; PAC, polyacrylic; CV, cellulose viscose; CMC, color measurement committee; CI, color index; CA, cellulose acetate; CA-DA, cellulose acetate deacetylated cellulose.

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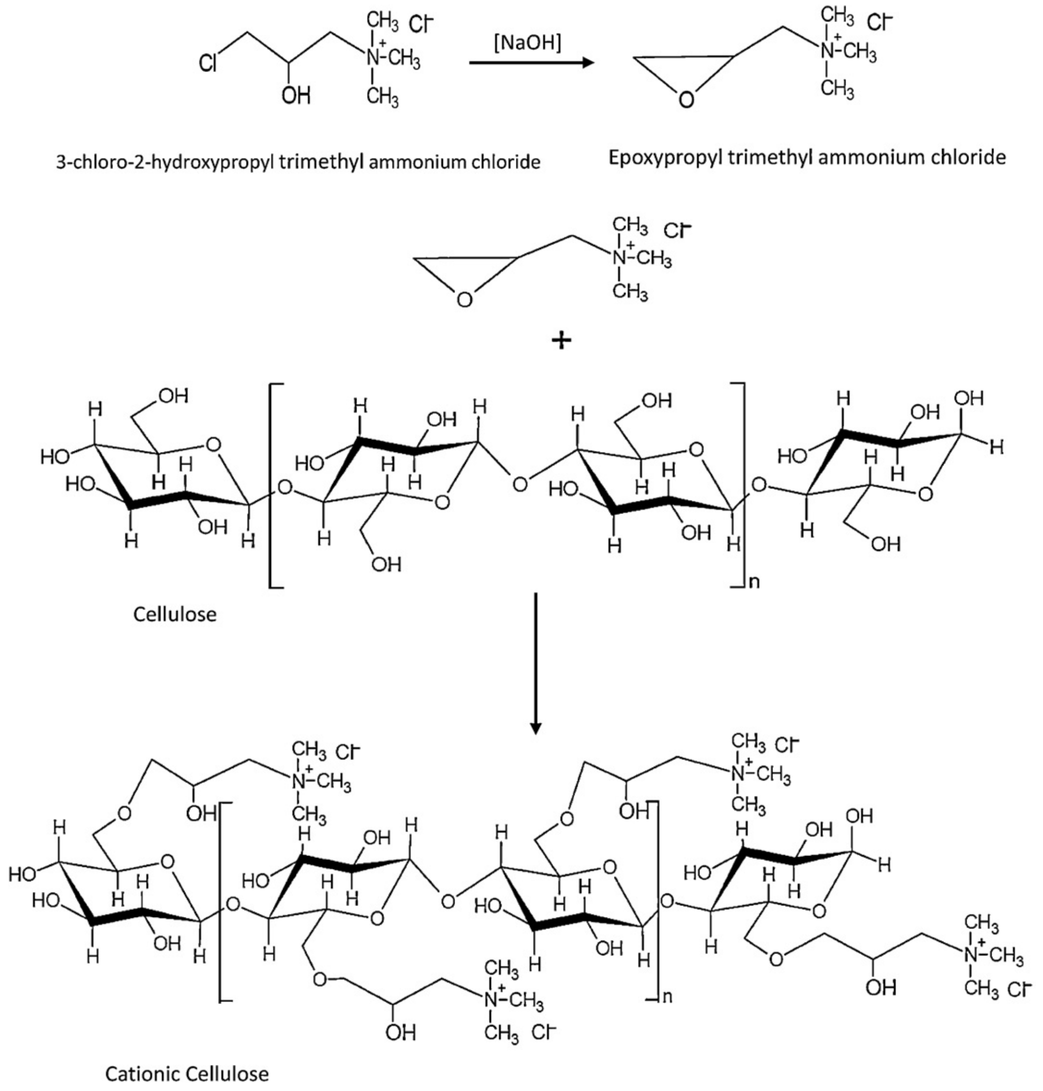


Scheme 1. Reactions of CHPTAC showing cationization of cellulose nanofibers (Hauser, 2000).

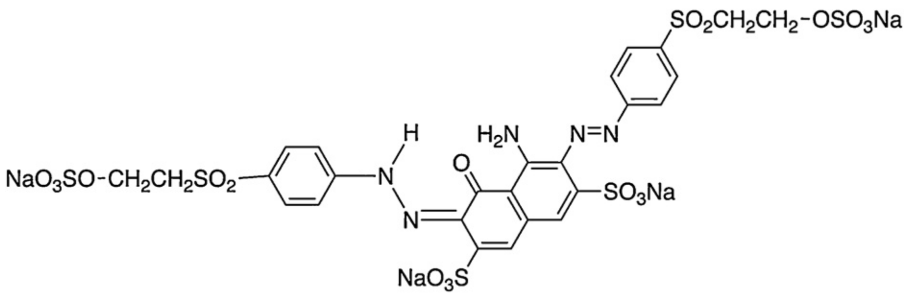
is well known that the dye fixation of the reactive dye obtained on the cellulosic materials is between 60% and 80%, the rest of the unfixed dye is drained into effluent during washing-off that may pose an environmental hazard (Xie, Liu, & Wang, 2009). The anionic character of reactive dyes is due to the presence of water solubilizing sulfonate groups ($SO_3{}^-$). In fact, cellulose also acquires a negative surface charge in water, which lowers the dye affinity to the cellulose fiber, so high concentration of sodium sulfate or sodium chloride (30–100 g/L) in the dyebath are desired to exhaust the dye onto cellulose surface; this leads to another serious environmental hazard as a large amount of electrolyte containing effluent is discharged (Wang, Ma, Zhang, Teng, & Yang, 2009). A good dyer puts his effort to prevent dye from being hydrolyzed and try to obtain dyed goods with minimum loss of dye. Therefore, dyer always attempts to improve color yield and higher dye fixation during cellulosic dyeing but this has remained a challenge. Over recent years, cationizing cellulose by the cationic agent has been increasing and shows significant advantages in terms of improved dyeing properties (Ma, Zhang, Tang, & Yang, 2005; Xie et al., 2009; Zhang, Chen, Lin, Wang, & Zhao, 2008; Zhang, Ju, Zhang, Ma, & Yang, 2007; Zhang et al., 2005). Among many cationizing agents, the 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) has attained much interest in cationization of cellulose because it is commercially available, is less toxic and has very good reactivity (Song, Sun, Zhang, Zhou, & Zhang, 2008; Song, Wang, et al., 2010; Song, Zhang, Gan, Zhou, & Zhang, 2010; You, Zhou, Li, & Zhang, 2012. Chemically cationized cellulose is usually produced by the etherifying reaction of cellulose with the quaternary ammonium cationizing reagents, such as 2,3-epoxypropyltrimehtylammonium chloride (Scheme 1) (Hauser, 2000; Montazer, Malek, & Rahimi, 2007; Wang et al., 2009). This compound is usually formed in situ from the reaction of CHPTAC with sodium hydroxide (see Scheme 1).

Here, we describe preparation of cationic-cellulose nanofibers for enhanced color yields and dye fixations, and provide comparison between dyed cellulose nanofibers and cationic-cellulose nanofibers. The dyed nanofibers were characterized by color yield (K/S), colorimetric properties by L^*, a^*, b^*, C^* and h° with $\Delta E^*_{\mathrm{CMC}}$, color fastness properties, FTIR and FE-SEM analysis.

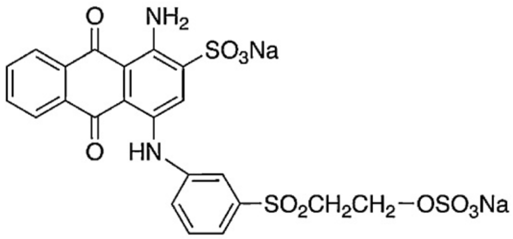
2. Experimental

2.1. Materials

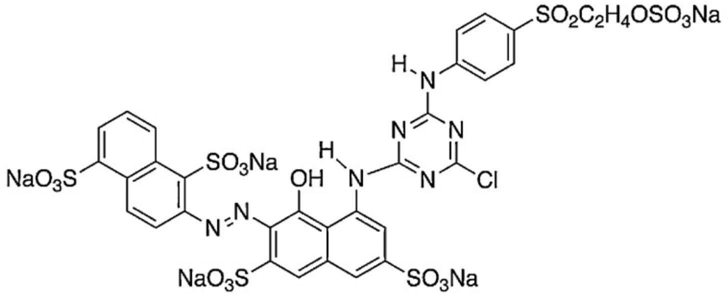
Cellulose acetate, CA (39.8% acetyl content having average Mw = 30 kDa), was obtained from Aldrich Chemical Company, and used without further purification. The cationizing agent, namely 3-chloro-2-hydroxypropyl trimethylammonium chloride solution,



CI Reactive Black 5



CI Reactive Blue 19



CI Reactive Red 195

Fig. 1. Dye structures of reactive dyes.

CHPTAC (60 wt% in H_2O, Mw = 188, Aldrich), was used to cationize cellulose nanofibers. Three dyes were used, namely CI reactive black 5 (*vinylsulfone*), CI reactive blue 19 (*vinylsulfone*), and CI reactive red 195 (*monoazo-monochlorotriazine + vinylsulfone*), supplied by the Sumitomo Chemical Company, Ltd., Japan. The corresponding dye structures for each class are given in Fig. 1. Sodium sulfate decahydrate (Glauber's salt, ACS reagent grade, Aldrich) and other Analar grade auxiliaries were used in this work and include sodium hydroxide, sodium carbonate and acetic acid.

2.2. Preparation of cationic-cellulose nanofibers

Cellulose is well known for its insolubility to most solvents; therefore, cellulose acetate nanofibers were produced via electrospinning and then deacetylated to convert into regenerated cellulose. The cellulose nanofibers were further treated with the cationic agent to form cationic-cellulose nanofibers. CA nanofibers were electrospun according to our previous work (Khatri, Wei, Kim, & Kim, 2012). Briefly, electrospinning was performed using a high-voltage power supply (Har-100*12, Matsusada Co., Tokyo, Japan). A CA solution of 17% by weight prepared in acetone/dimethyl formamide (DMF) with 2:1 by weight was supplied through a plastic syringe attached to a capillary tip with an inner diameter of 0.6 mm. A copper wire connected to a positive electrode was inserted into the CA solution and a negative electrode was connected to a metallic drum. The distance between the capillary tip and the collector was fixed at 15 cm and the supplied voltage was set at 12.5 kV. Electrospun nanofibers were collected onto a rotating drum and removed after the average thickness of the CA nanofibers web was obtained in the range 60–70 μm. The diameter of nanofibers was obtained in the range of 200–800 nm. The nanofiber webs were air dried for at least 48 h before deacetylation and cationization treatment. To convert cellulose acetate into cellulose, deacetylation was carried out in 0.05 M NaOH aqueous solution for 30 h at room temperature and rinsed-off thoroughly in distilled water until the pH of nanofiber webs reached to 7. Finally, all cellulose nanofiber samples were dried at 50 °C for 4 h (Khatri et al., 2012).

Cellulose nanofibers were cationized by a two-bath pad-bake process; the optimized parameters for cationization were followed (Wang et al., 2009). All samples were dipped through the CHPTAC/NaOH solutions, squeezed to a wet pick up of approximately 100% and baked in an oven (EYELA SLI-220) at 60 °C for 6 min, wherein, the molar ratio of CHPTAC to NaOH was 1:1. Finally, cationic-cellulose nanofibers were washed thoroughly to remove unfixed traces of CHPTAC and dried before a reactive dye application.

2.3. Dyeing of cellulose and cationic-cellulose nanofibers

All nanofiber web samples were dyed by batchwise method using a liquor-to-good ratio of 50:1 in glass tubes followed by heating in an oven with precise control of time and temperature. Dyeings were carried out to study the effect of temperature (10–80 °C), dyeing time (10–80 min) and dye concentrations (1, 3 and 5% omw). The dye and sodium sulfate were added in liquor as the dyeing started while sodium carbonate was added after 10 min. In case of cationic-cellulose nanofibers, the dyeing was carried out without an addition of salt. To remove unfixed dye from dyed nanofibers, soaping-off with 2 g/L nonionic detergent (Hostpal AE Liq., Clariant) was carried out at boil for 10 min using 50:1 liquor-to-good ratio.

2.4. Measurements

2.4.1. Color measurements

Color yield was determined by calculating corresponding K/S values from the reflectance values (%R) for each dyed cationic-cellulose nanofibers and cellulose nanofibers samples using a Konica-Minolta Spectrophotometer CM-3600d under illuminant D65, employing 10° standard observer with a UV component included and specular component excluded. The CIELAB colorimetric co-ordinates L^*, a^*, b^*, C^* and h°, and ΔE^*_{CMC} were also measured. The samples were folded so as to realize four thicknesses. The relative color strengths (the K/S values) were assessed using Eq. (1):

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

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

The extent of covalent bonding of the dye molecule with cellulose is generally determined by the extent of dye fixation, %F. Eq. (2) as described in our previous work was used to determine the absorbed dye fixation for each dyed sample (Khatri, Memon, Khatri, & Tanwari, 2011).

$$\%F = \frac{(K/S)_a}{(K/S)_b} \times 100 \quad (2)$$

where F is the dye fixation in percentage and $(K/S)_a$ and $(K/S)_b$ are after and before wash K/S of dyed samples.

2.4.2. FTIR spectroscopy

The chemical structure of cationic-cellulose and cellulose nanofibers before and after dyeing was analyzed on FTIR spectroscopy (IR Prestige-21 by Shimadzu, Japan).

2.4.3. FE-SEM

The morphology of nanofibers before and after dyeing was examined in FE-SEM (S-5000 by Hitachi, Japan) with the accelerating voltage of 20 kV.

2.4.4. Color fastness tests

Color fastness tests were performed for both dyed cellulose and cationic-cellulose nanofibers. Color fastness to washing was performed in Gyrowash (James H. Heal Co., UK) according to ISO 105–C10:2006 and color fastness to light was performed in Apollo (James H. Heal Co., UK) according to ISO 105–BO2.

3. Results and discussion

3.1. Effect of temperature on color yield and dye fixation

Before presenting dyeability and performance comparison between cationic-cellulose and cellulose nanofibers, the dyeing parameters such as temperature and time were optimized. The cellulose nanofibers were dyed with 1% of CI reactive black 5. Fig. 2a shows the effect of temperature on color yield and dye fixation for cellulose nanofibers. The color yield of CI reactive black 5 increased rapidly with increasing dyeing temperature from 30 °C to 50 °C and gradually until 60 °C but decreased slowly at 70 °C and 80 °C. Increasing dyeing temperature lowers the substantivity ratio which reduced the final color yield (Shore, 1995).

The substantivity ratio is the most influential factor governing fixation efficiency. Fig. 2a shows a gradual increment in dye fixation as the temperature was increased; a maximum of 85% dye fixation was achieved at 70 °C and 80 °C that reveals that the minimum dye hydrolysis of about 15% can be expected at this point. An increase of dyeing temperature lowers the substantivity ratio and may accelerate the rate of hydrolysis of the dye; both these effects reduce fixation efficiency (Shore, 1995). The rates of diffusion into and reaction with the nanofibers were also accelerated, however, these factors both favor fixation of the dye. It is worth considering the optimum dyeing temperature of 60 °C because of higher color yield. Although the dye fixation was lower than what obtained at higher temperatures but that can further be improved by optimizing dyeing time.

3.2. Effect of time on color yield and dye fixation

Fig. 2b shows the effect of dyeing time obtained at 60 °C (the optimized temperature) on the color yield of the cellulose nanofibers. Color yield increased sharply until 60 min dyeing time but decreased slightly when dyeing lasted for 80 min. The reason for this may be the dye hydrolyzes at prolonged dyeing time. The %F profile as depicted in Fig. 2b, increased as the dyeing time was increased, and these results commensurate with the color yield values obtained. Like the temperature, dyeing time is one of the most influencing parameters for assessing dyeability of nanofibers. Color yield obtained at the dyeing time of 60 min was higher than 80 min, whereas %F showed no further increase at 80 min dyeing time; dye hydrolyses could be a contributing factor to this. Therefore, 60 min dyeing time was selected for further study.

3.3. Comparison of build-up property and dye fixation between cationic-cellulose and cellulose nanofibers

As discussed earlier, the anionic reactive dye has poor substantivity toward cellulose as cellulose adopts anionic charges when immersed in water (Xie et al., 2009). The repulsive charges between cellulose surface and the reactive dye can be overcome by either electrolyte addition into dyebath or surface modification of cellulose. Therefore, a substantial quantity of electrolyte (sodium sulfate) was added to cellulose nanofibers and no electrolyte was added to cationic-cellulose nanofibers.

Fig. 3 shows a build-up property and %F of cationic-cellulose nanofibers and directly compared with cellulose nanofibers each dyed with three different dyes such as CI reactive black 5, CI reactive blue 19 and CI reactive red 195. Irrespective of the type of dye, higher color yield and %F were obtained for cationic-cellulose nanofibers than the cellulose nanofibers. A build-up characteristic of each dye was investigated measuring K/S values at each dye concentrations (1%, 3% and 5%) used. The black 5 is amongst the most successful of all reactive dyes having four solubilizing groups in the precursor form of CI reactive black 5 (Fig. 1) confer high solubility but unusually low substantivity. This dye is almost symmetrical in structure and when the sulfate ester groups are lost by 1,2 elimination, the substantivity for cellulose is enhanced and the bis(vinylsulfone) structure formed shows highly efficient fixation under alkaline conditions (Shore, 1995). Build-up of CI reactive black 5 for cationic-cellulose and cellulose nanofibers revealed that there was a significant increase in K/S when dye concentration was increased from 1% to 3%, and no enhancement in K/S was obtained at higher dye concentration of 5%. This indicates that the dyeing at 3% dye concentration reached near to fiber saturation. Comparing the build-up results for cationic-cellulose nanofibers with cellulose nanofibers, it could be observed that at all dye concentrations,

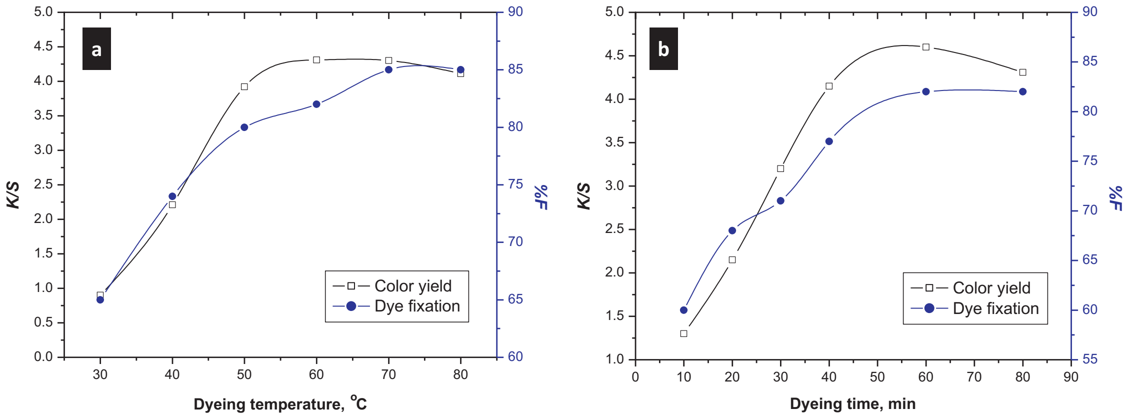


Fig. 2. Effect of temperature (a) and effect of time (b) on color strength (*K*/*S*) and dye fixation (%*F*) of CI reactive black 5 (dyeing time 80 min, dye concentration 1% omw).

K/*S* of the former was higher than the latter. This may be due to a higher ionic attraction between dye anion and cationic-nanofibers leading to higher dye absorption. The extremely attractive bright blue hue combined with an excellent light fastness of CI reactive blue 19 (Fig. 1) remained unchallenged by competing blue reactive dyes for many years. The aqueous solubility of this structure is inherently low; depending only on the 2-sulfonate group after 1,2-elimination of the sulfate ester has taken place. This has led to poor reproducibility and leveling problems, but nevertheless this dye has remained second only to CI reactive black 5 in terms of market share amongst reactive dyes (Shore, 2002). The CI reactive blue 19 demonstrated a very poor build-up on cellulose nanofibers whereas the built-up on cationic-cellulose nanofibers was linear. The results showed that the cationization of cellulose nanofibers significantly enhanced the *K*/*S* of around 4.9%, 27% and 76% for dye concentrations of 1%, 3% and 5% respectively. CI reactive red 195 is a unique class of reactive containing two dissimilar reacting groups. The reaction of a dichlorotriazine dye with an arylamine containing a 2-sulfatoethylsulfone grouping is the preferred route to mixed bifunctional reactive dyes capable of reacting with cellulose either via a monochlorotriazine moiety or a vinylsulfone group (Fig. 1). Both reactive systems can contribute to the fixation process but the relatively greater reactivity of the vinylsulfone group ensures that most of the fixation arises via this function. The build-up of CI reactive red 195 was higher on cationic-cellulose nanofibers than on cellulose nanofibers. There was no further increase in *K*/*S* of cationic-cellulose and cellulose nanofibers when dye concentration was increased from 3% to 5%, however, the cationic-cellulose yielded higher *K*/*S* than the cellulose nanofibers, for instance, about 21%,

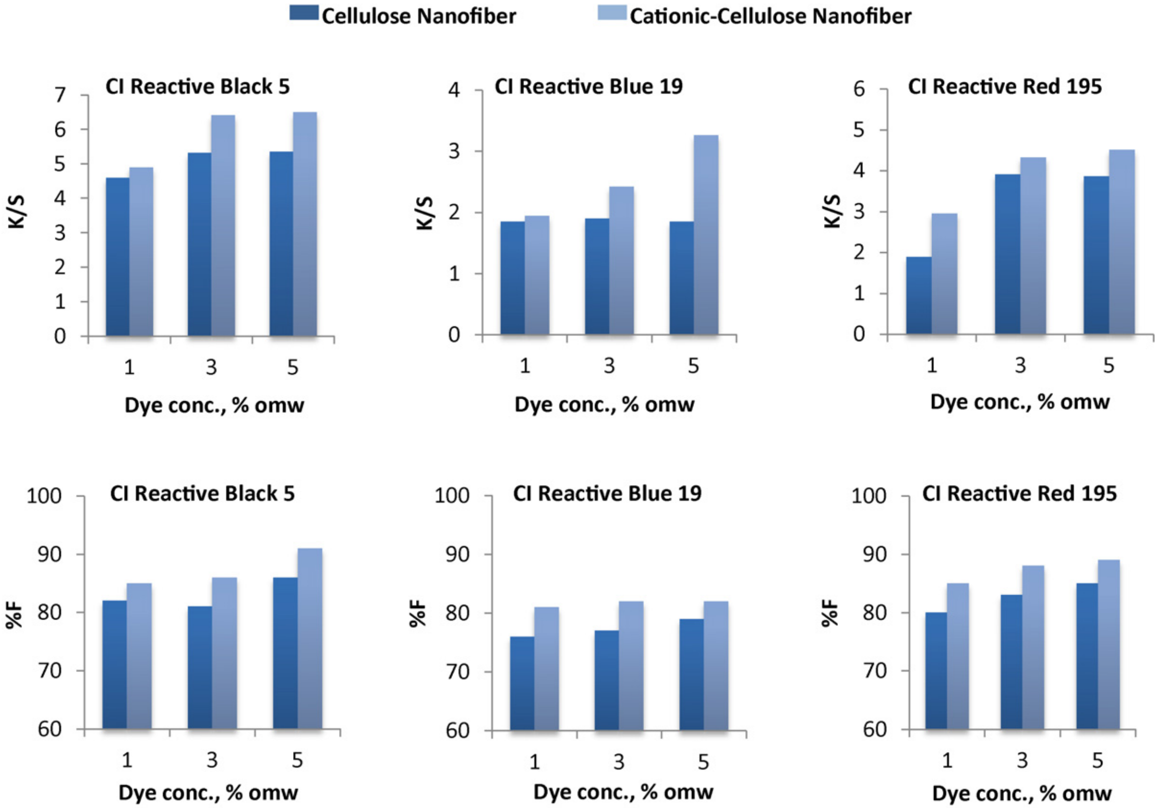


Fig. 3. Build-up and dye fixation (%*F*) of three dyes each at (1%; 3%; 5% omw) dye concentrations obtained for cellulose and cationic-cellulose nanofibers (dyeing temperature 60 °C and dyeing time 60 min).

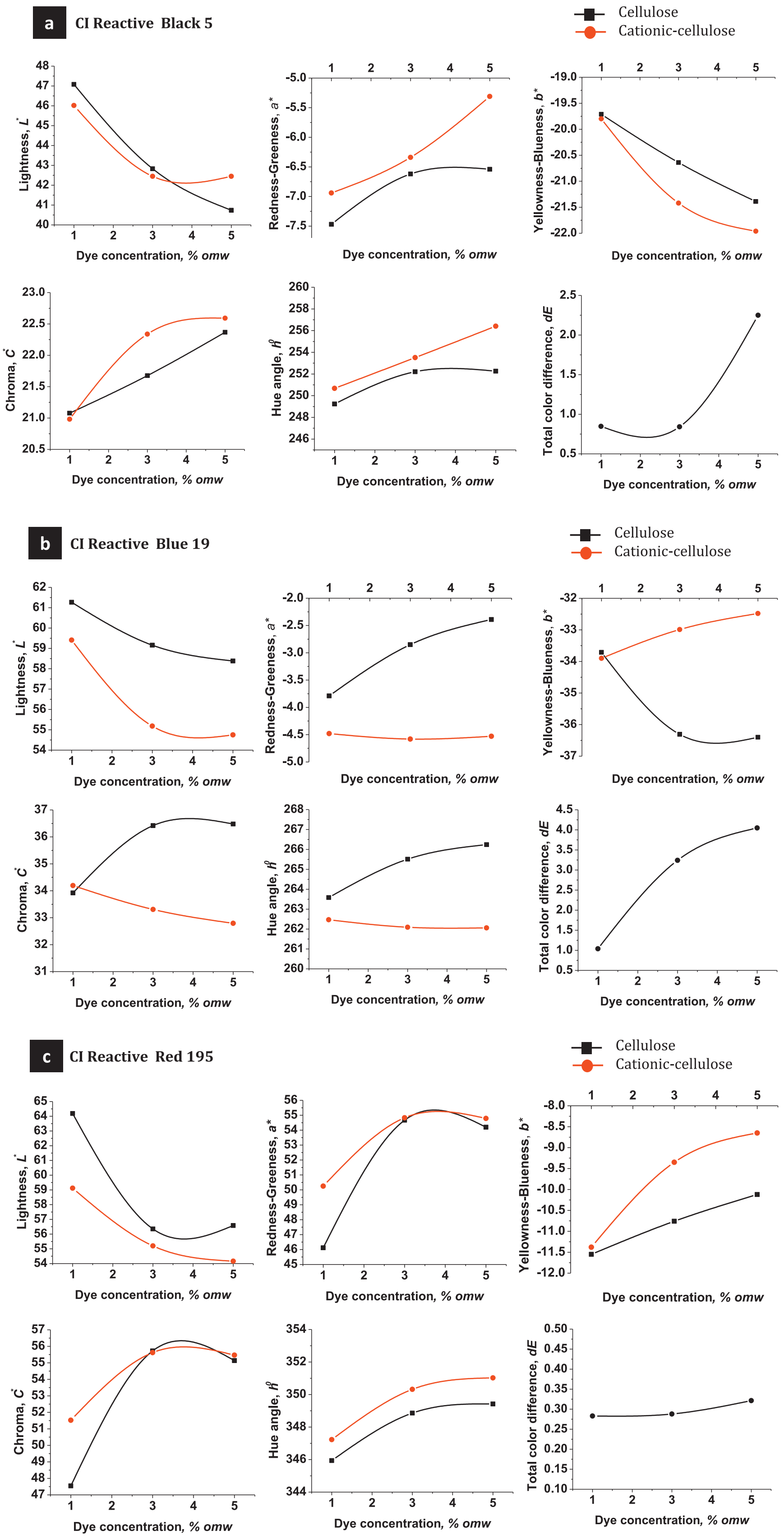


Fig. 4. (a) Color difference for CI reactive black 5. (b) Color difference for CI reactive blue 19. (c) Color difference for CI reactive red 195.

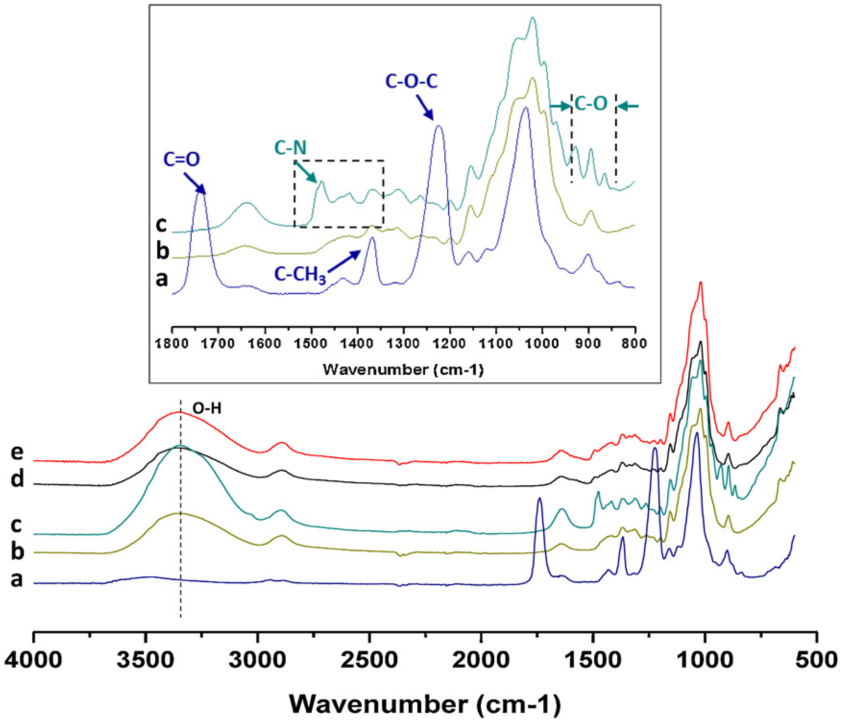


Fig. 5. FTIR spectra: (a) CA, (b) CA-DA, (c) cationic cellulose, (d) cellulose dyed with CI reactive black 5, (e) cationic-cellulose dyed with CI reactive black 5.

10% and 16% K/S enhancement at 1%, 3% and 5% dye concentrations respectively.

The dye fixation $\%F$ was investigated for each dye that corresponds to the degree of dye fixation to cellulose structure. Fig. 3 depicts $\%F$ for each CI reactive black 5, CI reactive blue 19 and CI reactive red 195. Irrespective of dye concentrations used, the $\%F$ of all three dyes obtained for the cationic-cellulose was higher than the cellulose nanofibers. For instance, CI reactive black 5 and CI reactive red 195 on cationic-cellulose nanofibers achieved dye fixation values of 85–91% and 85–89% respectively. A relatively lower dye fixation of 81–82% was achieved for CI reactive blue 19 compared to CI reactive black 5 and CI reactive red 195 in case of cationic-cellulose nanofibers. In general, the higher color yields obtained for cationic-cellulose nanofibers without electrolyte addition may be due to the ionic attraction between the quaternary ammonium groups of CHPTAC and anionic sites of the dyes.

3.4. Colorimetric data of dyed nanofibers

When the shade of the dyed cationic-cellulose nanofibers was compared visually, it showed a noticeable shade difference compared to cellulose nanofibers samples. To compare the shade difference between cationic-cellulose nanofibers and cellulose nanofibers, the color difference ($\Delta E^*_{\mathrm{CMC}}$) was calculated using the measured values of CIELAB L^*, a^*, b^*, C^* and h°. Color differences between cationic-cellulose nanofibers and cellulose nanofibers by Colorimetric data obtained for each dye are shown in Fig. 4a–c.

3.4.1. CI reactive black 5

Referring Fig. 4a, cationic-cellulose nanofibers became darker until the dye concentration of 3% was reached and remained consistent at 5% dye concentration while cellulose nanofibers showed linear decrement of lightness value demonstrating that samples became darker as the dye concentration was increased. The tonal differences that were studied by Cartesian coordinates a^* and b^* showed that the tone of cationic-cellulose nanofibers shifted toward a redder region in coordinate a^* and toward a bluer region in coordinate b^* as the dye concentration was increased. In addition, the tonal differences were also investigated using Polar coordinates C^* and h°. Higher C^* value suggested that the cationic-cellulose nanofibers were brighter than the cellulose nanofibers at higher dye concentrations. The total color difference was calculated using ΔE_{CMC} formulae (Khatri et al., 2011) that quantify total color deviations from reference. ΔE_{CMC} for cationic-cellulose nanofibers was calculated against reference cellulose nanofibers and as expected, data demonstrated that the cationic-cellulose nanofibers went beyond commercial factor set at 1.0 and significantly increased at dye concentrations of 5%. The major contributing factor to this difference was a significant difference between cationic-cellulose nanofibers and cellulose nanofibers samples in a^* value at 5% dye concentration.

3.4.2. CI reactive blue 19

Referring Fig. 4b, the L^* of cationic-cellulose nanofibers obtained was relatively darker than the cellulose nanofibers as the dye concentration was increased. The Cartesian coordinates a^* and b^* showed a significant difference between cationic-cellulose nanofibers and cellulose nanofibers; the results demonstrated that the tone of cationic-cellulose nanofibers samples shifted toward a redder region in coordinate a^* and a yellower region in coordinate b^* as the dye concentration was increased. In contrast to cationic-cellulose nanofibers, the cellulose nanofibers showed no significant change in coordinate a^* but significantly shifted toward a bluer region in coordinate b^* as the dye concentration was increased. The tonal differences using Polar coordinates C^* and h° demonstrated that the Chroma, C^* of cationic-cellulose nanofibers resulted in lower values than the cellulose nanofibers signifying dullness of cationic-cellulose nanofibers samples as the dye concentration was increased. On the other hand, cellulose nanofibers became brighter as the dye concentration was increased. This suggests that the increasing dye concentration of CI reactive blue 19 produced dullness in cationic-cellulose nanofibers. Since the differences between cationic-cellulose nanofibers and cellulose nanofibers were big in all coordinates (L^*, a^*, b^*, C^* and h°) at 3% and 5% dye concentrations,

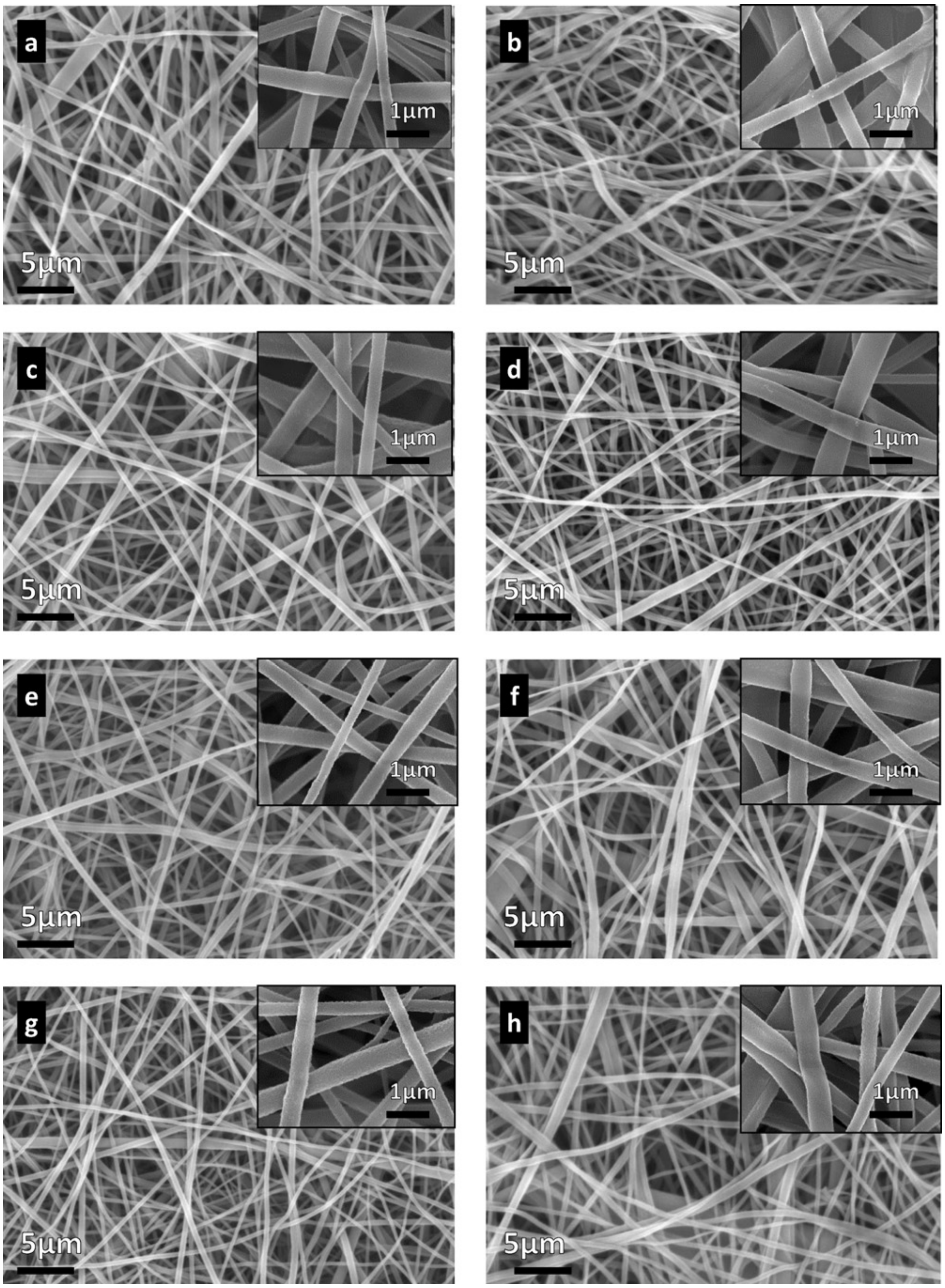


Fig. 6. SEM images (a, c, e and g) cellulose and (b, d, f and h) cationic-cellulose nanofibers; inset are FE-SEM images; (a and b) undyed, (c and d) dyed with CI reactive black 5, (e and f) dyed with CI reactive blue 19 and (g and h) dyed with CI reactive red 195.

Table 1
Color fastness to washing test ISO 105-C10:2006 and color fastness to light test ISO 105-BO2.

Sample	Dye class	Light fastness	Change of shade	Staining on multifiber					
				CT	CO	PA	PES	PAC	CV
Cationic-cellulose nanofibers[a]	CI reactive black 5	3–4	4–5	5	5	5	5	5	5
	CI reactive blue 19	5–6	4–5	5	5	5	5	5	5
	CI reactive red 195	3–4	4–5	5	5	5	5	5	5
Cellulose nanofibers[a]	CI reactive black 5	3–4	4–5	5	4–5	4–5	5	5	4–5
	CI reactive blue 19	5–6	4–5	5	4–5	4–5	5	5	4–5
	CI reactive red 195	3–4	4–5	5	4–5	4–5	5	5	4–5

[a] *Dyeing conditions*: Dye concentration 3%, temperature 60 °C and time 60 min.

therefore, $\Delta E^*_{\mathrm{CMC}}$ of cationic-cellulose nanofibers was expectedly high at higher dye concentrations.

3.4.3. CI reactive red 195

Referring Fig. 4c, the cellulose nanofibers did not show any further decrement in L^* value at an extent the cationic-cellulose nanofibers showed at the dye concentration of 5%. This suggests that color darkness was enhanced in cationic-cellulose nanofibers as the dye concentration was increased from 3% to 5%. The Cartesian coordinate a^* showed a relatively no significant difference between cationic-cellulose nanofibers and cellulose nanofibers at dye concentrations of 3% and 5%; the results for both cationic-cellulose nanofibers and cellulose nanofibers demonstrated that the tone shifted toward a redder region. It has less effect on sample appearance due to the fact that the samples were dyed with red hue dyes. The results of cationic-cellulose nanofibers in coordinate b^* showed a tone shifting toward a yellower region as the dye concentration was increased. In fact, the yellowness imparted a brightness in both cationic-cellulose nanofibers and cellulose nanofibers. The increment of C^* value at higher dye concentrations indicate samples become brighter. The results of C^* and b^* are well in agreement. Except for the coordinate b^*, all coordinates (L^*, a^*, C^* and h°) were found to have small color differences between cationic-cellulose nanofibers and cellulose nanofibers; this is the reason why $\Delta E^*_{\mathrm{CMC}}$ of cationic-cellulose nanofibers was achieved within commercial factor 1.0 and was consistent at all dye concentrations.

3.5. Structural feature of nanofibers

The change in chemical structure of dyed and undyed nanofibers is described in Fig. 5. The characteristic adsorption peaks of cellulose acetate attributed to the vibrations of the acetate group C=O at 1745, C—CH_3 at 1375 and C—O—C at 1235 cm^{-1} disappeared and an absorption peak O—H at 3500 cm^{-1} increased, as shown in Fig. 5a. This substantiates a complete conversion of cellulose acetate nanofibers into cellulose nanofibers. FT-IR spectra of all samples showed characteristic cellulose peaks around 1000–1200 cm^{-1}. Other characteristic bands related to the chemical structure of cellulose were the hydrogen-bonded O—H stretching at 3550–3100 cm^{-1}, the C—H stretching at 2917 cm^{-1}, and the C—H wagging at 1316 cm^{-1}. Cationic-cellulose nanofibers (Fig. 5c) has an obvious new peak at 1491 cm^{-1} (C—N) compared to cellulose nanofibers (Fig. 5b), which attributed to quaternary ammonium groups (Zhang et al., 2007). These results indicated that the reaction has successfully converted cellulose into cationic-cellulose. Two additional bands appeared at 875 cm^{-1} and 925 cm^{-1} which attributed to an asymmetrical ring stretching of the epoxy ring of un-reacted CHPTAC (Robert, Francis, & David, 2005). It is difficult to identify the dye interaction with nanofibers due to small ratio of dye concentration to nanofiber mass; however, the spectra of cationic-cellulose nanofibers retained the cellulosic form after being dyed with CI reactive black 5 (Fig. 5d and e). The FTIR spectra of CI reactive blue 19 and CI reactive red 195 were similar to that of CI reactive black and therefore, omitted. This suggests that the cationization was an interim product before dye was applied and we may expect structural properties of dyed cationized-nanofiber as that of the dyed cellulose nanofibers.

3.6. Surface morphology of nanofibers

Fig. 6a–g shows SEM images of cationic-cellulose nanofibers and cellulose nanofibers each undyed and dyed nanofibers and the inset images are FE-SEM images. Referring Fig. 6, the cationic-cellulose nanofibers (b) became irregular slightly than the cellulose nanofibers (a) after cationization treatment but again retained their regularity after dyeing with each dye class; refer images (c)–(h). The SEM images show a very good stability and regularity of nanofibers even after dyeing in aqueous solution. Therefore, it is inferred that the dyeing process does not affect morphology of cationic-cellulose nanofibers and cellulose nanofibers. Besides, surface smoothness of nanofibers (see inset FE-SEM images) is unaffected throughout various wet treatments such as deacetylation, cationization, dyeing and washing-off process.

3.7. Color fastness performance of nanofibers

Table 1 outlines the color fastness to washing test according to ISO 105–C10:2006. Irrespective of the class of dye used, the dyed cationic-cellulose nanofibers qualifies well along with the dyed cellulose nanofibers and showed superior staining ratings on each component of a multifiber strip. The reason for this may be due to the ionic interaction that took part in addition to covalent bonding between dye and the cationic-cellulose nanofibers and thus reduced the removal of dyes from the nanofibers during the washing. The shade change rating of 4–5 obtained in both cases, cationic-cellulose nanofibers and cellulose nanofibers, are good to excellent. The results obtained from wash fastness test confirm that the dye fixation was very good on cationic-cellulose nanofibers as well as on cellulose nanofibers. It could be safely concluded that the cationic-cellulose nanofibers can significantly be preferred over cellulose nanofibers for dyeing based on the advantages discussed earlier.

The color fastness to light was performed according to ISO 105–BO2 and the results are summarized in Table 1. The Light fastness ratings in all cases were found reasonably good keeping dark shades in consideration. There was no difference obtained between cationic-cellulose nanofibers and cellulose nanofibers in the case of all three dyes used. Interestingly, the color fastness to light for CI reactive blue 19 was found to have very good ratings for both cationic-cellulose nanofibers and cellulose nanofibers samples due to having anthraquinone chromogen.

4. Conclusion

The cationic-cellulose and cellulose nanofibers can effectively be dyed with commercially available reactive dyes by batchwise method. The cationic-cellulose nanofibers demonstrated potential advantages over cellulose nanofibers due to enhanced color yield and higher dye fixation without addition of electrolyte. Built-up property of each dye showed improvement at all dye concentrations in case of cationic-cellulose nanofibers. Except CI reactive blue 19, it was observed that there was no significant improvement in color yield and dye fixation at the dye concentration of 5%. Excellent color fastness to washing results were achieved for both dyed cellulose and cationic-cellulose nanofibers. Despite the number of wet treatments, the morphology of nanofibers remains structurally stable, smooth and regular. The cellulose-based colored and breathable nanofibers paved the way toward novel apparel applications and can potentially be considered as future apparel for surgical gowns, institutional articles, casual and fashion.

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