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Dyeing of Cotton Fabric in Decamethylcyclopentasiloxane Using Alkyl Polyglucoside-based Reverse Micelle as Reactive Dye Carrier

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Abstract: The dyeing and color fixation properties of reactive dyes on cotton woven fabrics have been systematically studied using reverse micelle with biodegradable alkyl polyglucoside (APG)-based non-ionic surfactant as building blocks in cyclosiloxane-based solvent under one-bath one-step approach. Reactive dyes were solubilized in the interior region of the reverse micelle under optimized process conditions as indicated by the color strength. Assessment of the color strength and fastness properties of cotton fabrics in reverse micellar dyeing was conducted and compared with aqueous dyeing. It was found that fluoropyrimidine reactive group of Levafix CA Red dyes encapsulated in APG-based reverse micelle exhibited higher color yield on cotton fabric compared to vinylsulfone group of both Levafix CA yellow and blue dyes. The results also represent that reactivity of the functional group combination of heterofunctional dyes influences color fixation on cellulosic surface in terms of color strength (*K/S* sum).

Keywords: Cotton fabric, Solvent-assisted dyeing, Alkyl polyglucoside, Reverse micelle, Reactive dye

Introduction

Wet processing of textile fabrics has long been known for consuming significantly serious quantities of water and generation of wastewater [1-3]. However, in order to effectively improve dye-fiber interaction and minimization of contaminated dyes in textile effluents, various techniques have been introduced for improving dye affinity of different textile fibers, such as chemical grafting of disperse dyes with polyacrylonitrile fibers [4], nano-silica particles in disperse dyeing of poly(ethylene terephthalate)-based nanocomposites [5], direct dyeing of woven cotton fabric with nanoclay pretreatment [6] and removal of organic dyestuffs from textile effluents using chitin/graphene oxide hybrid composite [7], polyelectrolytes [8], ionizing radiation [9], immobilization of chitosan on the grafted jute fibers as an reactive dye adsorbent [10] and advanced oxidation technique via a combination of UV radiation and strong oxidizing agent (H_2O_2) [11]. In reactive dyeing of cotton in aqueous solution, large amounts of inorganic salts are required for reducing the repulsive force between dye molecules and the cellulosic fiber surface, and for enhancement of both dye affinity and dye absorption [12,13]. Consequently, the salts lead to high wastewater treatment cost and environmental pollution. Development of a way of using low-salt or salt-free approach is a significant issue in cotton dyeing process [14-20]. Dyeing methods using natural mordants [21-23], wastewater reutilization [24] and supercritical carbon dioxide as dispersion medium [25,26] have been explored in depth. With the increasing demand for greener process, energy saving and safety process environment, the use of nanocarrier to encapsulate reactive dyes has been effectively used in non-aqueous dyeing [27,28].

Among these salt-free dyeing processes, reverse micelles used as dye carriers have been shown to be promising as a salt-free non-aqueous dyeing process with minimal dye and water consumption. Reactive dye is capable of dispersing in a confined volume of water droplets and surrounded by the hydrophilic portion of amphiphilic surfactant. The hydrophobic segments of the surfactant tend to disperse in the non-aqueous phase or organic phase. Reverse micelles are thermodynamically stable self-assembled colloidal structures using amphiphilic surfactant molecules as a building block and are able to form water-in-oil (w/o) type emulsions containing stable "water-pool" micro-environment in organic solvent [29-31]. In order to uniformly disperse hydrophilic reactive dyes in the core of reverse micelles, anionic surfactants such as sodium (bis-2-ethyl-hexyl) sulfosuccinate (Aerosol-OT) have mainly been applied in textile dyeing [27]. Nevertheless, the use of anionic surfactants has a major drawback on the aquatic ecosystem [32,33]; water-pool polarity in the reverse micelle as it interacts with the charged groups of reactive dyes reveals a competitive dye adsorption between cotton fiber surface and ionic functional groups of the surfactants and eventually alters the conformational structure and function of the reactive dye. However, due to the physical and chemical properties of nonionic surfactants, for instance, good solubility in both aqueous and non-aqueous solvents, self-assembly of stable micellar structures in solvent, and inertness to electrolytes, nonionic surfactants are widely applicable in various fields such as drug encapsulation, cosmetics, and pretreatment for dyeing of textile fabric [34,35]. Hence, several approaches have been advanced for dyeing cotton fabric using nonionic surfactant as building block of reverse micelle for dye encapsulation including Triton X-100 reverse micelles [29,30] and Triton X-100/Span40 mixed reverse micelles [31], poly(ethylene

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glycol) (PEG)-based reverse micelles in reactive dyeing of cotton fabric in alkane-based solvent [36,37].

Among all non-ionic surfactants, alkyl poly glucosides (APGs) are mainly derived from renewable natural resources. They are typical starch derivatives considered to have low health risk, are biodegradable and have reusable properties [38]. An APG-based surfactant has a biobased molecular structure and is categorized based on the carbon number in the alkyl chain molecular structure (C_{10}, C_{12}, and C_{14}). From these structural aspects, the hydrophobic hydrocarbon chain of surfactants can interact favorably with the surrounding apolar solvent phase whereas the glycosidic group can well interact with the hydrophilic reactive dyes via hydrogen bond.

In terms of economical production, safety, environmental, and technical properties, alkyl polyglucosides were evaluated as potential alternatives for non-ionic surfactant in the fabrication of reactive dye nanocarrier. Nevertheless, as far as we know, applications of reactive dyes encapsulated in reverse micelle using alkyl polyglycoside-based nonionic surfactants as reactive dye carriers in cotton dyeing do not appear to have been fully explored.

Reactive dyeing in non-aqueous “green” solvent has been successfully attempted as replacement of the conventional water-based dyeing, in the quest for a sustainable textile industry [39,40]. Water-soluble or hydrophilic reactive dyes are unlikely to be well dispersed in non-aqueous dyeing media due to limitations of materials and energy transport. A significant benefit of non-aqueous dyeing is that minimal amount of water is consumed to solubilize the dye and other chemical agents. Furthermore, a small amount of aqueous solution can be highly absorbed by the cotton fabric in order to swell the fiber without using any inorganic salts during the coloration process [41-43]. In the last decade, an environment-friendly non-aqueous dyeing system was effectively developed in textile industry using cyclosiloxane-based solvent as the dyeing medium [42,44-46]. Previous studies have demonstrated that siloxane-based solvent is both human health and environment friendly [45-47] and has been fully used in dry cleaning applications [48]. The preparation of non-ionic surfactant based reverse micelles and the assessment of dye solubilization in non-aqueous siloxane-based solvent have recently been investigated [49-51].

This study attempts to address for issues related to dyeing of cotton fabric: (a) Evaluation of dye and soda ash encapsulation in APG-based reverse micelle and the dispersion in cyclosiloxane-based solvent; (b) Optimization of dyeing and surfactant parameters in cyclosiloxane-assisted reverse micellar dyeing method; (c) Measurement of color yield from dyed samples; and (d) Comparison of color yield and color fastness for aqueous dyeing and cyclosiloxane-assisted dyeing.

Experimental

Materials and Reagents

Pure cotton (100 %) woven fabrics (50 warp per inch× 50 weft per inch, fabric weight of 138.8 g/m^2) were used in this study. Before dyeing, the fabrics were pre-cleaned with a detergent solution (2 g/*l*) in washing machine at 49 °C for about 45 min and then tumble-dried at ambient temperature. The dried fabrics were then conditioned (65±2 % relative humidity and 20±2 °C) for 24 h. Nonionic, natural and green surfactant, decyl-*β*-D-glucopyranoside (Triton™ CG-110) in reagent grade (Figure 1a) and D5 (decamethylcyclopentasiloxane) (Figure 1b) were used as building block for reverse micellar structure and dispersing medium, respectively. N-octanol (Reagent grade) was used as co-surfactant to reinforce the structure of reverse micelle. Reactive dyes (Levafix CA Red, Levafix CA Blue and Levafix CA Yellow) provided by Dystar, China were directly used without further purification.

Water-based Dyeing

Liquor-to-goods ratio was 50:1 for ensuring the levelness of the fabric in case of water-based dyeing. Table 1 lists the amount of salt corresponding to the concentration of dye in terms of percentage of weight of fiber (% owf) while Figure 2 shows the flow of the process of aqueous dyeing of cotton.

Dyeing was started with immersion of cotton fabric in dye liquor (containing dye and salt), followed by shaking at 30 °C for 5 min in water-bath, increasing the temperature to 70 °C (heating rate of 1 °C/min), dyeing at 70 °C for 40 min, adding the corresponding amount of soda ash (Table 1) and fixation at 70 °C for 60 min.

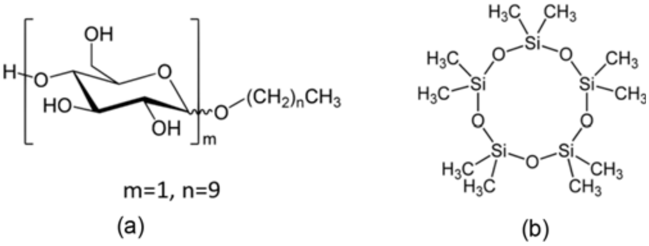

Figure 1. Chemical structure of (a) alkyl polyglucoside-based surfactant and (b) decamethylcyclopentasiloxane (D5).

Table 1. Various amounts of salt and soda ash for different concentrations of reactive dye

Liquor-to-goods ratio 50:1, 70 °C						
Dye	% owf	0.1	0.5	1.5	2.5	3.5
Salt (NaCl)	g/*l*	10	20	42.5	55	65
Soda ash (Na_2CO_3)	g/*l*	5	5	5	5	5

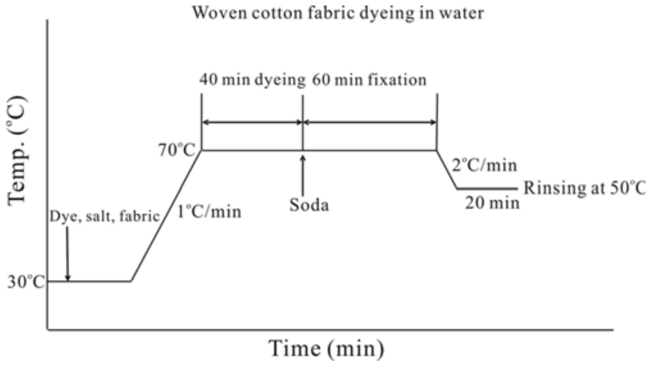

Figure 2. Working process of salt-included aqueous dyeing of cotton.

The dyed cotton fabric was subjected to a series of soaping and rinsing processes after dyeing and fixation processes. It was first immersed in 2 g/*l* soap solution (Tide original, P&G, USA) and soaped for 20 min at 50 ºC, followed by washing at 30 ºC for 10 min twice and drying for 24 h under relative humidity 65±2 % and controlled temperature at 20±2 ºC before measurement.

APG-based Reverse Micellar Coloration of Cotton in D5 Solvent

Preparation of APG-based Reverse Micelle

APG-based reverse micelles were formed by simple injection under ambient conditions. Non-ionic surfactant (decyl-*β*-D-glucopyranoside) and co-surfactant (n-octanol) were thoroughly mixed by manual stirring. Several surfactant to co-surfactant molar ratios, ranging from 0.05:1 to 0.025:1, were used for optimization. D5 solvent was then used as the dispersion medium to facilitate the self-assembling process of decyl-*β*-D-glucopyranoside surfactant molecules into well-defined reverse micelle.

Encapsulation of Dye and Soda Ash in APG Reverse Micelle

Different concentrations of dye in aqueous solutions and soda ash aqueous solutions were applied dropwise in the D5 solvent system with reverse micelles. The mixtures were then uniformly stirred until a well dispersed solution, with encapsulation of dye and soda ash in the water-pool of APG-based reverse micelle, was obtained (Figure 3).

Salt-free APG-based Reverse Micellar Coloration of Cotton

A one-step (all-in) dyeing method (Figure 4) involving a single bath was used in this study for reverse micellar coloration of cotton. Dyeing of cotton with APG-based reverse micelle system was started by immersing cotton fabric in reverse micelle encapsulated dye liquor at 30 ºC and shaking it for 5 min. The temperature of the bath was then increased to for different dyeing and fixation times (Figure 4).

After dyeing, the dyed cotton fabric was subjected to a series of soaping and washing processes. It was first immersed in 2 g/*l* soap solution (Tide original, P&G, USA) and soaped for 20 min at 50 ºC, followed by washing at 30 ºC for 10 min twice and drying at controlled relative humidity (65±2 %) and temperature (20±2 ºC) for 24 h before measurement.

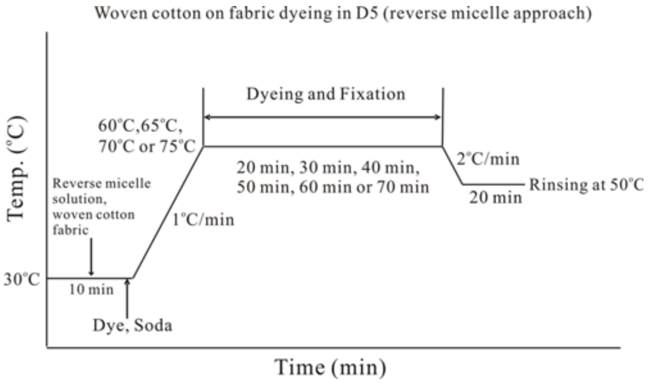

Figure 4. Working process of cotton dyeing and fixation process using salt-free reverse micelle approach in D5 solvent.

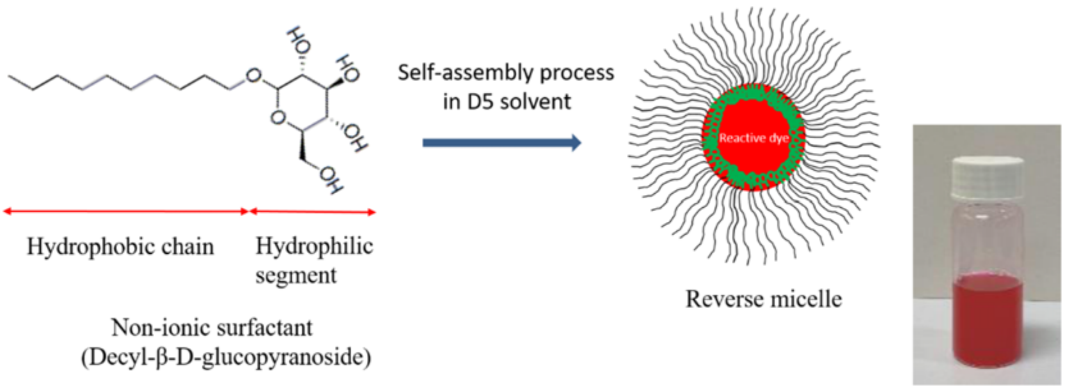

Figure 3. Molecular structure of nonionic surfactant (decyl-β-D-glucopyranoside) and reactive dye encapsulated APG-based reverse micelle solution.

Table 2. Soda ash (color fixation agent) to cotton weight ratio for APG reverse micellar dyeing system

Dye concentration (% owf)	Soda ash to cotton weight ratio (g/g)
0.1 %	0.020
	0.040
	0.060
0.5 %	0.020
	0.040
	0.060
1.5 %	0.060
	0.070
	0.080
2.5 %	0.080
	0.085
	0.090
3.5 %	0.090
	0.095
	0.100

Optimization of Dyeing Parameters for APG-based Reverse Micellar System

APG reverse micellar system for cotton reactive dyeing was optimized by using D5 solvent as dispersion medium and Levafix CA Red reactive dye as model dye. The optimization of dyeing parameters included: (i) solvent to cotton weight ratio (8:1, 10:1, 12:1, and 14:1); (ii) surfactant to water molar ratio (0.05:1, 0.04:1, 0.033:1, and 0.025:1); (iii) surfactant to co-surfactant molar ratio (1:7, 1:8, 1:9, 1:10, 1:11, and 1:12); (iv) volume of dye (0.3, 0.4, 0.5, 0.6, and 0.7 m*l*); (v) volume of soda ash (0.3, 0.4, 0.5, 0.6, and 0.7 m*l*); (vi) time required for dyeing and fixation (min) (20, 30, 40, 50, 60, and 70); (vii) dyeing and fixation temperature (ºC) (60, 65, 70, and 75); and (viii) soda ash concentration (soda ash to cotton weight ratio) (as shown in Table 2).

Color Measurement

Properties of dyed fabrics were measured by SF650 Spectrophotometer (Data Color International, USA). The cotton fabric was folded twice to ensure opacity and only face side was measured. Illuminant D_{65} and standard observer of 10 ^{o} were used under specular inclusion with large aperture. Four measurements were taken and average *K/S* value, obtained from 400 nm to 700 nm with 10 nm wavelength interval, was computed from equation (1). Higher *K/S* value represents better dye-uptake and color strength.

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

where, K: absorption coefficient, depending on the colorant concentration

S: scattering coefficient

R: reflectance of the colored sample

Color Fastness to Laundering

Color fastness of dyed fabrics against laundering was assessed based on AATCC Test Method 61-2013 (Color Fastness to Laundering: Accelerated) with Test No. 2A.

Evaluation of Breaking Strength Property

Breaking strength and extension length at break values of undyed, water-dyed and D5-dyed woven cotton fabric samples were carried out by stripe method in accordance with ASTM D5034 standard (Breaking Strength and Elongation of Textile Fabrics). Both water-dyed and D5-dyed cotton fabrics are prepared at the dye concentration of 3.5 % for testing of tensile strength.

Results and Discussion

Solvent Ratio

Figure 5 illustrates the effect of solvent ratio (v/w) on APG reverse micellar dyeing of cotton with reactive red dye. The highest color yield was obtained at solvent ratio of 10:1. The color yield result indicates there were no significant effects of change in solvent volume. However, as the cotton fabric is completely immersed in solvent medium and that ensures the proper distribution of dye-encapsulated APG reverse micelles during the dyeing process, the color strength can be maintained due to stable dye uptake by cellulosic fiber. If the solvent volume to cotton fabric weight ratio is too high, hydrophilic reactive dyes may induce agglomeration under the fixed surfactant parameters, which results in the size of the reverse micelle becoming too bulky for effective dye diffusion into the fiber matrix [28], thus

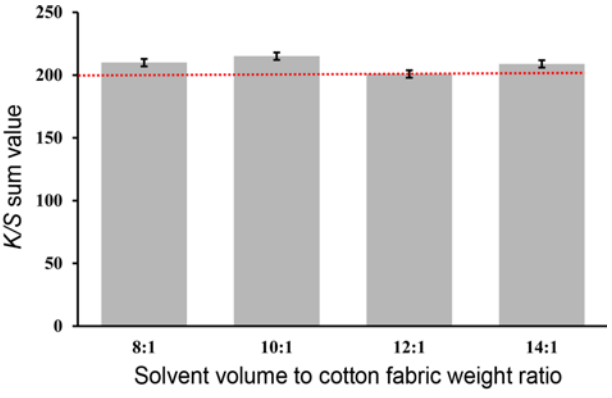

Figure 5. Color yield in different solvent ratio (Surfactant to co-surfactant mole ratio is 1:9; surfactant to water mole ratio is 0.05:1; dye volume is 0.5 m*l*; soda ash volume is 0.3 m*l*; dyeing and fixation time is 60 min; dyeing and fixation temperature is 70 ^{o}C; dye concentration is 3.5 %; alkali to cotton ratio is 0.095 g/g).

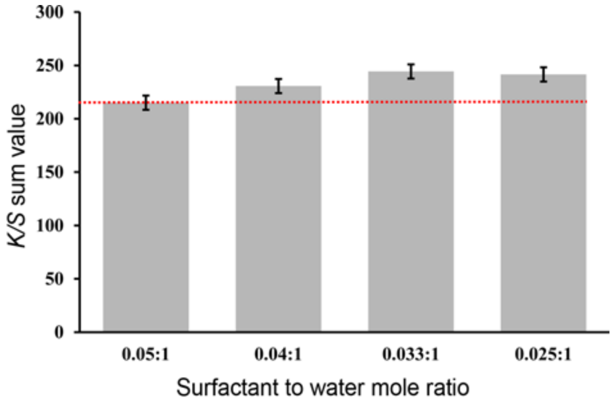

Figure 6. Color yield in different surfactant to water mole ratios (Solvent ratio is 10:1; surfactant to co-surfactant mole ratio is 1:9; dye volume is 0.5 m*l*; soda ash volume is 0.3 m*l*; dyeing time and fixation time is 60 min; dyeing and fixation temperature is 70 °C; dye concentration is 3.5 %; alkali to cotton ratio is 0.095 g/g).

leading to a relatively low dye uptake by the cotton fiber surface.

Surfactant to Water Mole Ratio

Figure 6 illustrates color yield data (*K/S* sum value) of fabrics dyed in different surfactant to water mole ratios. In contrast to PEG-based surfactant, these color yields show an increasing trend when the amount of surfactant is reduced. The optimum color yield is obtained when surfactant to water mole ratio is 0.033:1 while the color yield declines when there is further reduction in the amount of surfactant used in the dyeing process. This indicates that reverse micelle with stable dye encapsulation can be formed with relatively less amount of natural APG surfactant. This in turn makes the APG-based reverse micellar dyeing system more surfactant-saving than the PEG-based system. However, when the amount of APG surfactant is too small, it may adversely distort the encapsulated structure (morphology) and stability of reverse micelles, leading to dye aggregation and phase separation.

Surfactant to Co-surfactant Mole Ratio

Surfactant and co-surfactant are both located at the interfacial region of the reverse micelle which separates the small water pool region and the surrounding medium (D5 solvent), stabilizing the mutual dispersion throughout the dyeing process. The inter-chelation of co-surfactant within the reverse micelle interface forms a well-defined partition in order to effectively reduce the interfacial free energy. With hydrophilic-lipophilic balance (HLB) (HLB value=11) of decyl-β-D-glucopyranoside and the curvature of the micellar interface [52], water-pool partition that favors the non-aqueous dyeing process can be achieved.

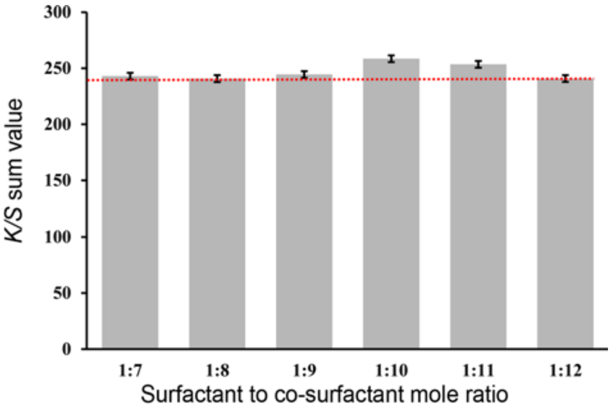

Figure 7. Color yield in different surfactant to co-surfactant mole ratios. (Solvent ratio is 10:1; surfactant to water mole ratio is 0.033:1; dye volume is 0.5 m*l*; soda ash volume is 0.3 m*l*; dyeing time and fixation time is 60 min; dyeing and fixation temperature is 70 °C; dye concentration is 3.5 %; alkali to cotton ratio is 0.095 g/g).

Figure 7 presents the color yield of samples dyed in different surfactant to co-surfactant mole ratios. The color yield shows an increasing trend when the amount of co-surfactant is increased, and it reaches the optimum value when the ratio is 1:10.

Further addition of co-surfactant only results in a reduction of color yield of the dyed samples (ratio of 1:11 and 1:12). This indicates that optimal amount of n-octanol relative to the fixed surfactant amount can relieve the stress of the micelle interfacial layers and enhance the interfacial stabilities, contributing to good dispersion of reverse micelles in the non-aqueous media and stable encapsulation of reactive dye molecules.

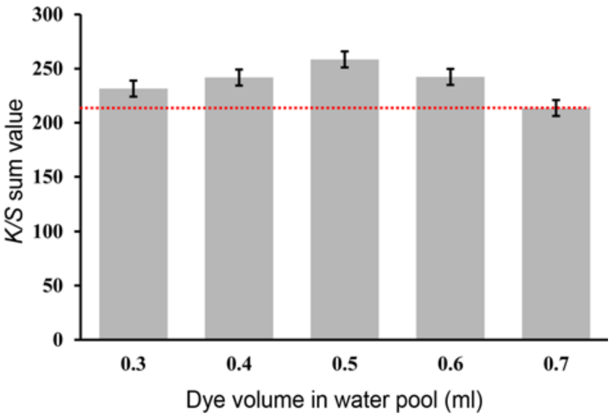

Figure 8. Color yield in different dye volumes (Solvent ratio is 10:1; surfactant to co-surfactant mole ratio is 1:10; surfactant to water mole ratio is 0.033:1; soda ash volume is 0.3 m*l*; dyeing time and fixation time is 60 min; dyeing and fixation temperature is 70 °C; dye concentration is 3.5 %; alkali to cotton ratio is 0.095 g/g).

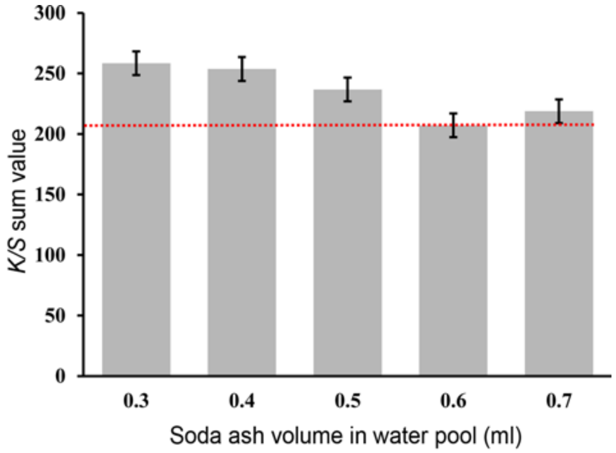

Figure 9. Color yield in different soda ash volumes (Solvent ratio is 10:1; Surfactant to co-surfactant mole ratio is 1:10; Surfactant to water mole ratio is 0.033:1; dye volume is 0.5 m*l*; time required for dyeing and fixation is 60 min; dyeing and fixation temperature is 70 °C; dye concentration is 3.5 %; alkali to cotton ratio is 0.095 g/g).

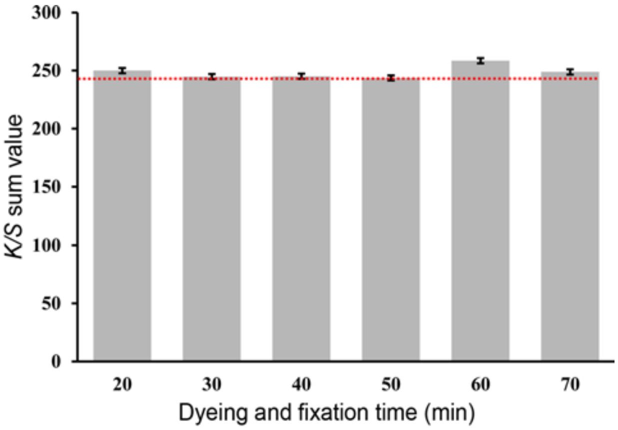

Figure 10. Color yield in different dyeing and fixation times (Solvent ratio is 10:1; surfactant to co-surfactant mole ratio is 1:10; surfactant to water mole ratio is 0.033:1; dye volume is 0.5 m*l*; soda ash volume is 0.3 m*l*; dyeing and fixation temperature is 70 °C; dye concentration is 3.5 %; alkali to cotton ratio is 0.095 g/g).

Dye and Soda Ash Volume in Water-pool

The result of APG-based reverse micellar dyeing of cotton with various dye volumes is presented in Figure 8. The color yield of dyed fabrics increases when dye volume increases from 0.3 m*l* and reaches the optimum value (>250) when 0.5 m*l* dye is dispersed in water-pool region of reverse micelle. On further increase in the dye volume to 0.6 m*l* or above, the color yield of the dyed samples decreases. When the water-pool volume is small, there is lack of free water for sufficient swelling of pores in the cotton fiber, inhibiting the diffusion of dye into fiber matrix whereas excess volume in water-pool may slightly weaken the dye-fiber interaction due to partial hydrolysis, lowering the dyeability of cotton.

The effect of varying volume of soda ash on color yield of dyed samples is illustrated in Figure 9. In general, the color yield shows a decreasing trend as the volume of soda ash increases. The optimal volume of soda ash in water-pool is 0.3 m*l* wherein soda ash is well solubilized in the reverse micelle for stable color fixation. Further addition of soda ash may lead to lower color yield since it may cause dye instability in water-pool medium, hindering the fixation efficiency of dye on cotton fiber surface.

Dyeing and Fixation Time

The maximum color yield is obtained with a total time of 60 min (Figure 10) under working temperature of 70 °C. However, it is found that as the dyeing and fixation time increases (from 20 to 70 min) while keeping other variables constant, color yield is maintained in a range between 240 and 260 without significant change. The use of one-bath one-step dyeing process may shorten the processing time for both dyeing and fixation equilibrium within 60 min while sacrificing color yield of the fabric to a small extent. Further extension of dyeing and fixation time (beyond 60 min) may consume more energy whereas the color yield of the dyed samples does not improve significantly.

Dyeing and Fixation Temperature

The effect of dyeing bath temperature is significant in terms of both reactivity and affinity of dye on cotton fiber. The change in temperature influences the migration rate of dye from solvent to cellulosic fiber surface. Figure 11 shows that the optimal dyeing and fixation temperature for APG-

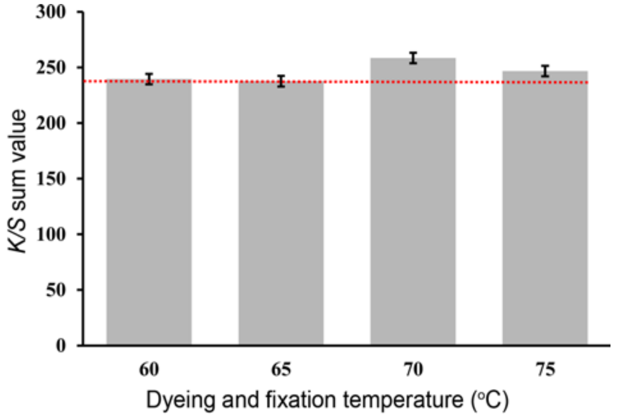

Figure 11. Color yield in different dyeing and fixation temperatures (Solvent ratio is 10:1; surfactant to co-surfactant mole ratio is 1:10; surfactant to water mole ratio is 0.033:1; dye volume is 0.5 m*l*; soda ash volume is 0.3 m*l*; time required for dyeing and fixation is 60 min; dye concentration is 3.5 %; soda ash to cotton ratio is 0.095 g/g).

based reverse micellar dyeing of cotton is 70 °C which is similar to previously studied PEG-based system. When the dyeing temperature is 60 °C and 65 °C, color yield of the dyed samples in terms of *K/S* sum value is nearly constant (around 240). Moreover, there is a reduction in dyebath exhaustion leading to slightly lower color yield as the temperature was increased to 75 °C since the migration rate should be controlled in order to maximize dye affinity on fiber surface.

Soda Ash Concentration

In order to improve the quality of color fixation, the soda ash concentration in water-pool needs to be adjusted for each dye concentration in terms of color yield (*K/S* sum value). Table 3 provides the color yield (*K/S* sum value) and optimized soda ash concentrations of the dyed samples in dye concentration ranging from 0.1 % to 3.5 %. For dye concentrations from 0.1 % to 3.5 %, the optimized soda ash to cotton (g/g) ratios are 0.04, 0.04, 0.08, 0.085, and 0.095 respectively.

Optimal Dyeing Parameters for APG-based Reverse Micellar System

Based on the study on (i) solvent ratio, (ii) surfactant to water mole ratio, (iii) surfactant to co-surfactant mole ratio, (iv) dye and soda ash volume in water-pool, (v) dyeing and fixation time, (vi) dyeing and fixation temperature, and (vii) soda ash concentration, the optimum conditions for APG-based reverse micellar dyeing system on cotton fabrics using D5 solvent are summarized in Table 4.

Table 3. Color yield in different soda ash concentrations corresponding to percentage of dyes (0.1, 0.5, 1.5, 2.5, and 3.5 %) and the optimized soda ash concentration under APG reverse micellar system (Solvent ratio is 10:1; surfactant to co-surfactant mole ratio is 1:10; surfactant to water mole ratio is 0.033:1; dye volume is 0.5 m*l*; soda ash volume is 0.3 m*l*; time required for dyeing time and fixation time is 60 min; dyeing and fixation temperature is 70 °C)

Dye concentration (% owf)	Color fixation agent to cotton weight ratio (g/g)	*K/S* sum value	Optimized color fixation agent to cotton weight (g/g)
0.1 %	0.02	11.43	0.04
	0.04	12.32	
	0.06	12.10	
0.5 %	0.02	36.67	0.04
	0.04	42.85	
	0.06	42.47	
1.5 %	0.06	122.33	0.08
	0.07	122.61	
	0.08	135.39	
2.5 %	0.08	198.85	0.085
	0.085	201.25	
	0.09	199.68	
3.5 %	0.09	244.67	0.095
	0.095	263.21	
	0.10	259.54	

Table 4. Optimized parameters for dyeing and fixation in D5

Dye concentration (% owf)	0.1	0.5	1.5	2.5	3.5
Solvent to cotton weight ratio (v/w)	10:1				
Surfactant to co-surfactant mole ratio	1:10				
Surfactant to water mole ratio	0.033:1				
Dye volume (m*l*)	0.5				
Soda ash volume (m*l*)	0.3				
Dyeing and fixation time (min)	60				
Dyeing and fixation temperature (°C)	70				
Dye concentration (% owf)	0.1	0.5	1.5	2.5	3.5
Soda ash to liquor (g/*l*)	4	4	8	8.5	9.5
Soda ash to cotton weight ratio (g/g)	0.04	0.04	0.08	0.085	0.095

Color Yield of Dyed Cotton in Aqueous and Non-aqueous Medium

Table 5 displays color yield (*K/S* sum values) of cotton woven fabrics dyed in both water and APG-based reverse micellar dyeing systems. Levafix CA Red was used as

Table 5. Color yield of dyed cotton fabrics in water and D5 solvent

Color	Dye conc. (% owf)	Solvent		
		Water	D5	
		K/S sum	*K/S* sum	Percentage (%)
Red	0.1	4.96	8.87	↑78.62
	0.5	17.20	34.87	↑102.70
	1.5	58.89	105.09	↑78.44
	2.5	105.43	177.84	↑68.68
	3.5	145.35	234.97	↑61.66
Yellow	0.1	6.51	8.19	↑25.77
	0.5	26.45	34.73	↑31.29
	1.5	80.55	94.96	↑17.88
	2.5	131.92	139.43	↑5.70
	3.5	169.87	172.54	↑1.58
Blue	0.1	6.01	5.62	↓6.44
	0.5	25.47	26.41	↑3.69
	1.5	88.11	75.77	↓14.00
	2.5	150.00	111.54	↓25.64
	3.5	195.60	144.56	↓26.09

model reactive dye for optimization of process parameters and applying the results to Levafix CA Yellow and Levafix CA Blue reactive dyes. The optimal *K/S* sum value achieved is based on the properties of reactive group structures of Levafix CA Red dye. In reverse micellar approach, *K/S* sum values of fabrics dyed with Levafix CA Red dye are higher than fabrics dyed in conventional water-based dyeing approach. Meanwhile, higher color strength was observed from the encapsulated reactive red dyes in APG-based reverse micelle compared with reactive yellow and blue dyes. The possible reasons are mainly concerned with reactivity of reactive groups and the process conditions for the fixation reaction.

In terms of chemical properties of reactive dyes, dye affinity on cellulose surface for vinyl sulphone (VS) and difluoropyrimidine (DFP) groups is alkali-controllable while monofluorotriazine (MFT) group is salt-controllable. Reactive dyes possess negative charged functional groups and cellulosic fibers are electronegative in aqueous solution; hence the interaction between anionic reactive dyes and cellulosic fibers is hindered by the electrostatic repulsion. However, addition of salt (NaCl) can be considered as dyeing promoter because Na^+ ions in aqueous system are chemically adsorbed on cellulosic fibers by electrostatic attraction between Na^+ ions and cellulosic fibers. The repulsion between reactive dyes and cellulose surface is weakened and that facilitates reactive dyes affinity towards cellulosic fiber surface. All three types of hetero-bifunctional reactive dyes have MFT group and the difference in color yield of the reactive dyes is the chemical structure of the second reactive group. The second functional group of Levafix CA Red dye is difluoropyrimidine (DFP) [53]. For Levafix CA Yellow and Blue dyes, the second functional group involved in the interaction with cellulose fibers is vinylsulphone (VS) [53].

In aqueous dyeing system, difluoropyrimidine (DFP) group is more reactive and less resistant to hydrolysis than vinyl sulphone [54]. The bond formed with the cellulose fiber surface is less stable in mild alkaline medium upon addition of soda ash (Na_2CO_3). It is characterized by lower *K/S* sum values for reactive red dyes compared to reactive yellow and blue dyes (Table 5).

Generally speaking, soda ash can increase the pH of the dyeing bath and further accelerate the fixation reaction via formation of the covalent bond between dye and the cellulosic fibers. In the meantime, reactive dyes released from reverse micelles continue to get adsorbed on cellulose fibers. The *K/S* sum value first increases at the initial stage of soda ash addition and then decreases as the pH increases to around 8. At this alkaline pH condition, the dye fixation rate is improved until more negative charges are distributed on cellulose fibers due to enhanced ionization of surface hydroxyl groups. Furthermore, the binding of reactive dyes on cellulosic fibers is hindered by electrostatic repulsions between anionic reactive dyes and the cellulose fibers.

In reverse micellar dyeing, the dye fixation process is mainly alkaline pH dependent in water-pool environment and no salt is introduced into the dyeing bath. Electrostatic repulsion between reactive dyes and cellulosic surface can be minimized as reactive dyes encapsulated in non-ionic reverse micelle and therefore reactive dyes can well migrate to the cellulose fiber surface via random molecular motion. The reactive dyes are then released from reverse micelle and rapidly interact with hydroxyl group of cellulose for effective dye fixation.

The reactive dyes in water-pool environment can be explained in the following. The amount of water molecules inside the core of reverse micelle is expected to be small and eventually reduces the availability of carbonate ions dissociated from soda ash. Thus, low availability of carbonate ions inside the core denotes that reactive dyes are more resistant to hydrolysis.

The rate of hydrolysis is directly proportional to polarity of the water-pool. In other words, it is conceivable that the inherent water polarity in reverse micelle is much lower than that in bulk water. As the water-pool is confined in reverse micelle cavity, water molecules are mostly located at the inner surface of reverse micelle (hydrophilic group of APG surfactant), as for water molecules located in the core of water pool, the so-called “free water”, the partitioning of carbonate ions dissociated from soda ash located at inner surface reduces the rate of dye hydrolysis. On the other hand, the dynamic characteristic of “free water” is totally different from bulk water phase because the dielectric relaxation of “free water” in confined water-pool region is slower than bulk water [55].

The second functional group of reactive red dye (Levafix CA Red) consists of difluoropyrimidine (DFP) group which reacts with cellulosic fibers via nucleophilic substitution with a good leaving group such as fluorine [53]. This type of halo-pyrimidine-based reactive dyes in hetero-bifunctional groups consists of at least two halogen leaving groups.

These carbon-halogen bonds are selectively activated; because of the asymmetric structure of the pyrimidine ring, 2,4-fluorocarbon bonds of difluoropyrimidine (DFP) group are strong electrophilic and highly reactive in dye-cellulose interaction in the presence of soda ash at optimized dyeing temperature of 70 °C.

The second functional group for both yellow and blue dyes consists of vinyl sulfone group that reacts with nucleophilic hydroxyl group of cellulose structure via Michael addition reaction through carbon-carbon double bonds [53]. In this regard, the electron withdrawing effect of vinyl sulphone group is less reactive than that in difluoropyrimidine and its derivatives [56]. Thus the dye functional group with higher reactivity tends to form stable covalent bonds under mild alkaline condition and can be evaluated by color strength measurement as indicated in

Table 5.

Due to the difference in reactivity in covalent bond formation between dye and cellulosic surface, the optimal dyeing parameters of different types of reactive dyes such as working temperature, dyeing time, types of dye auxiliaries and pH condition, etc. also vary. Therefore, more investigations are needed to further improve the coloration of cotton fiber using APG-based reverse micelles in dyeing process.

Table 6. Color change of water-dyed and solvent-dyed cotton (washing fastness)

Specimen	Conventional dyeing	APG reverse micellar dyeing
	Rating	Rating
Blue 0.1 %	5	5
Blue 0.5 %	5	5
Blue 1.5 %	5	5
Blue 2.5 %	5	5
Blue 3.5 %	5	5
Yellow 0.1 %	5	5
Yellow 0.5 %	5	5
Yellow 1.5 %	5	5
Yellow 2.5 %	5	5
Yellow 3.5 %	5	5
Red 0.1 %	5	5
Red 0.5 %	5	5
Red 1.5 %	5	5
Red 2.5 %	5	5
Red 3.5 %	5	5

Color Fastness to Laundering

The findings about color change in Table 6 and color staining in Tables 7 and 8 exhibit washing fastness properties of the dyed samples under AATCC-61 accelerated laundering test. The results reveal that both conventional aqueous dyed cotton and APG reverse micellar dyed cotton can achieve excellent color change (rating of 5) and color staining (rating of 4-5 to 5) against accelerated laundering. Rating 4-5 is mainly obtained when fabrics are dyed in high concentration with a darker shade. This attests that the dyed fabrics are thoroughly cleaned after the soaping and rinsing process so that the residuals of dye and auxiliaries are removed from the fabrics.

Figure 12 shows visual images of woven cotton fabrics dyed in water and D5 medium. Experimental findings demonstrate that D5-dyed cotton fabrics using APG-based reverse micelles as reactive dye carrier can achieve acceptable dyeing effect as compared to conventional water-based dyeing system and the quality of D5-dyed cotton fabrics can be confirmed in terms of color yield data.

Breaking Strength Properties of Cotton Fabrics Dyed in Water and D5

The values of breaking strength for water-dyed and D5-dyed cotton woven fabrics in warp and weft directions are showed in Table 9(a). The tensile strength of the undyed cotton fabric is 401.61 N and 202.14 N in warp and weft directions. Whereas the tensile strength of the water-dyed cotton fabric ranged between 233.55-336.51 N in warp

Table 7. Color staining (conventional water-dyed cotton)

Specimen	Rating of multifiber strips					
	Wool	Acrylic	Polyester	Nylon	Cotton	Acetate
Blue 0.1 %	5	5	5	5	5	5
Blue 0.5 %	5	5	5	5	5	5
Blue 1.5 %	5	5	5	5	5	5
Blue 2.5 %	5	5	5	5	5	5
Blue 3.5 %	5	5	5	5	4-5	5
Yellow 0.1 %	5	5	5	5	5	5
Yellow 0.5 %	5	5	5	5	5	5
Yellow 1.5 %	5	5	5	5	5	5
Yellow 2.5 %	5	5	5	5	5	5
Yellow 3.5 %	5	5	5	5	5	5
Red 0.1 %	5	5	5	5	5	5
Red 0.5 %	5	5	5	5	5	5
Red 1.5 %	5	5	5	5	5	5
Red 2.5 %	5	5	5	5	5	5
Red 3.5 %	5	5	5	5	4-5	5

Where rating: 5=Excellent washing fastness, 1=Poorest washing fastness.

Table 8. Color staining (APG reverse micellar dyed cotton)

Specimen	Rating of multifiber strips					
	Wool	Acrylic	Polyester	Nylon	Cotton	Acetate
Blue 0.1 %	5	5	5	5	5	5
Blue 0.5 %	5	5	5	5	5	5
Blue 1.5 %	5	5	5	5	5	5
Blue 2.5 %	5	5	5	5	5	5
Blue 3.5 %	5	5	5	5	4-5	5
Yellow 0.1 %	5	5	5	5	5	5
Yellow 0.5 %	5	5	5	5	5	5
Yellow 1.5 %	5	5	5	5	5	5
Yellow 2.5 %	5	5	5	5	5	5
Yellow 3.5 %	5	5	5	5	5	5
Red 0.1 %	5	5	5	5	5	5
Red 0.5 %	5	5	5	5	5	5
Red 1.5 %	5	5	5	5	5	5
Red 2.5 %	5	5	5	5	5	5
Red 3.5 %	5	5	5	5	4-5	5

Where rating: 5=Excellent washing fastness, 1=Poorest washing fastness.

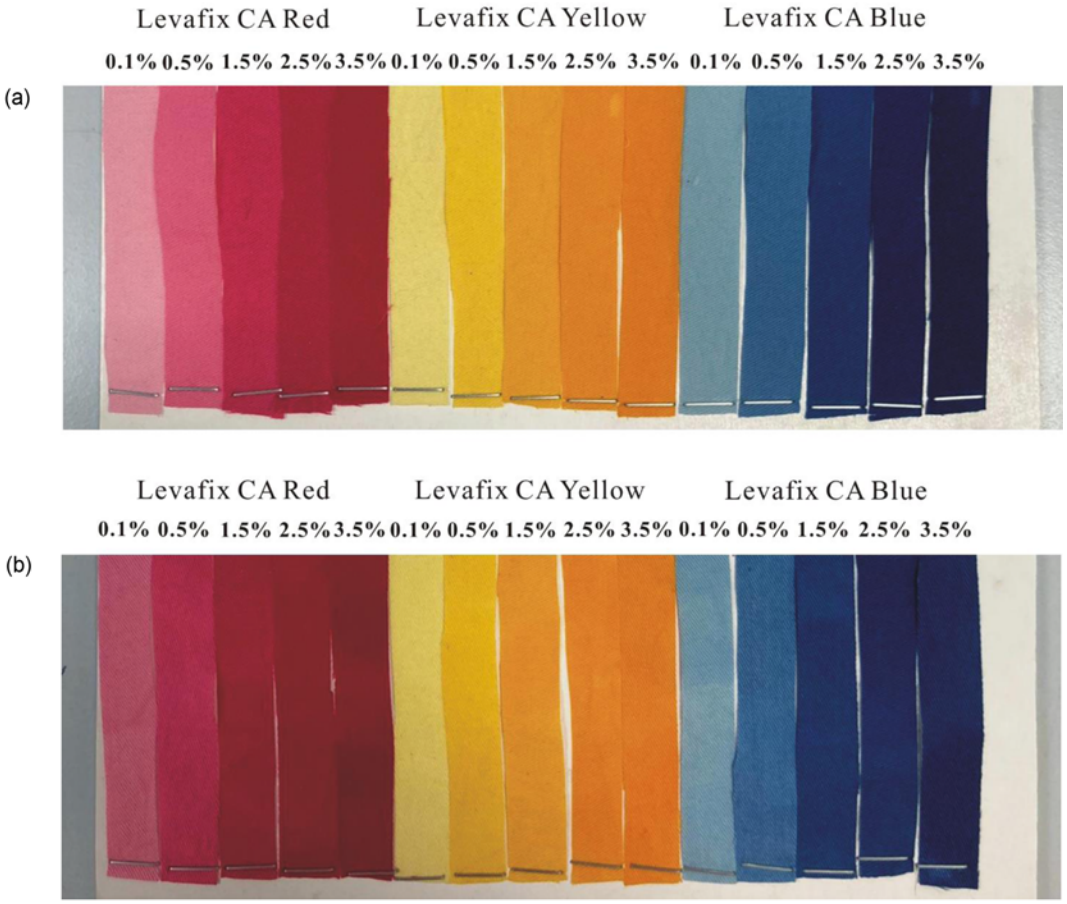

Figure 12. Color swatches of cotton woven fabrics dyed in water and D5; (a) dyeing in water and (b) dyeing in D5. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 9. (a) Breaking strength (N) of undyed, water-dyed, and solvent-dyed specimens, (b) breaking extension (mm) of undyed, water-dyed, and solvent-dyed specimens, (c) breaking extension (%) of undyed, water-dyed, and solvent-dyed specimens

(a)

Tensile strength		Undyed		Water		D5	
Specimen		Warp (N)	Weft (N)	Warp (N)	Weft (N)	Warp (N)	Weft (N)
Red	3.5 %	401.61	202.14	336.51	150.06	303.48	133.28
Blue	3.5 %			322.55	171.81	348.05	169.79
Yellow	3.5 %			233.55	132.48	242.14	146.04

(b)

Breaking extension (mm)		Undyed		Water		D5	
Specimen		Warp (mm)	Weft (mm)	Warp (mm)	Weft (mm)	Warp (mm)	Weft (mm)
Red	3.5 %	17.92	8.17	19.66	8.91	17.65	8.91
Blue	3.5 %			19.18	9.32	17.58	8.10
Yellow	3.5 %			18.43	9.66	15.41	8.41

(c)

Breaking extension (%)		Undyed		Water		D5	
Specimen		Warp (%)	Weft (%)	Warp (%)	Weft (%)	Warp (%)	Weft (%)
Red	3.5 %	23.89	10.89	26.21	11.88	23.53	11.88
Blue	3.5 %			25.57	12.43	23.44	10.80
Yellow	3.5 %			24.57	12.88	20.55	11.21

direction and ranged between 132.48 N-171.81 N in weft direction. For APG reverse micellar dyed cotton fabric in D5 solvent, the breaking strength in warp and weft directions is in the range of 242.14 N-348.05 N and 133.28 N-169.79 N, respectively. Both water-dyed and D5-dyed cotton fabrics exhibited a slight decrease in tensile strength as compared to undyed cotton fabrics. As observed from the tensile strength at the breaking point in Table 9(a), the fibers in warp threads were subjected to a higher binding force than yarn threads in weft direction after dyeing. However, the tensile strength data suggests binding force enhancement in woven fabrics is due to compressive shrinkage after textile finishing such as dyeing and washing treatments [57].

Breaking extension length and percentages of undyed, water-dyed, and D5-dyed woven cotton fabric samples are shown in Table 9(b) and 9(c). It is observed that elongations at break along warp direction are higher than elongations at break along weft direction. Moreover, D5-dyed samples are almost in similar range of breaking extension length to that of undyed and water-dyed cotton fabrics. Based on the findings, it is evident that the breaking strength behavior of water-dyed and D5-dyed cotton fabrics using APG reverse micellar approach are similar, indicating that D5 solvent as reactive dyeing medium does not alter the physical structure of dyed cotton fabric significantly.

Conclusion

The color yield and color fastness of dyed cellulosic fabrics in decamethylcyclopentasiloxane (D5) medium was investigated using an environment-friendly alkyl polyglucosides-based reverse micelles and compared with same properties of fabrics dyed with a water-based dyeing system. The experimental findings indicated that cotton fabrics dyed by cyclosiloxane-assisted reverse micellar approach may improve color yield under optimization of various dyeing parameters. Among three types of reactive dyes, red and yellow reactive-dyed cotton fabrics achieve higher color yield (*K/S* sum value) than blue reactive-dyed cotton in cyclosiloxane-based solvent. The *K/S* sum values of cyclosiloxane-dyed samples were comparable to water-dyed samples at each calibrated dye concentration. Moreover, color fastness to laundering test was carried out and the ratings were in the range from 4-5 to 5 indicating that the samples had excellent color fastness properties after thorough soaping and washing process.

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