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Salt-free dyeing of cotton fabric modified with prepared chitosan-poly (propylene) imine dendrimer using direct dyes

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ABSTRACT

This study presents a novel method for eco-friendly dyeing of cotton fabrics with direct dyes. Cotton fabric was modified with chitosan-poly (propylene) imines dendrimer (CS-PPI), and its dyeing and fastness properties were investigated using three direct dyes. The impacts of important factors, i.e., CS-PPI concentration, dye concentration, dyeing time, dyeing temperature, and salt concentration were investigated and optimized. Results showed that cotton treatment with optimum CS-PPI concentration (15% owf) significantly improved dye up-take and decreased effective dye concentration required to obtain a given color depth. Also, optimum dyeing time and temperature were reduced ~50% and ~20 °C, respectively. Moreover, salt was eliminated from cotton dyeing process with direct dyes and "salt-free dyeing" was therefore developed. Colorimetric and color fastness data emphasized that this treatment had no negative effect on the hue and color fastness properties of dyed samples. So, it was concluded that the new eco-friendly process can help to considerably save time, energy, chemicals, and dyeing costs, and also can remedy the associated dyeing effluent problems from dyeing of cotton with direct dyes. Prog. Color Colorants Coat. 11 (2018), 21-32© Institute for Color Science and Technology.

1. Introduction

Cotton textiles can be dyed with diverse types of dyes such as direct, sulfur, vat and reactive dyes as well as azoic combinations. The most used dye in the textile industry after sulfur dye is direct dye, then vat and reactive dyes well behind [1, 2]. Direct dyes belong to salts of sulfonic acids, strong electrolytes, and almost absolutely dissociated in dye baths into colored anions and sodium cations. Dye anions are attached to cellulose macromolecules mostly through van der Waals forces [3]. The associated ions are formed owing to flat structure and large molecular weight of direct dye molecules. The degree of association reduces with the increasing of temperature, and consequently the cotton dyeing is carried out at higher temperature. Moreover, alkaline bath is the special treatment for collapse of the associates and sodium carbonate (Na_2CO_3) is often added to the dye bath. In addition, dyeing of cotton using direct dyes needs large quantities of salts such as sulfate or chloride [4, 5].

Direct dyes are desired due to their lower cost of dyeing, easier to apply with proper training, less

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affected by variations in liquor ratio, and environmentally less questionable than fiber reactive dyes, since much lower concentrations of Glauber's salt, a common salt, are required to attain a very high degree of dye exhaustion. According to EPA (US Environmental Protection Agency) and OECD (Organization of Economic Cooperation Development), the percentages of unfixed direct dyes that may be discharged in the effluents are 30% and 5-20%, respectively [6, 7]. Direct dyes discharged from different industries, especially textile industry cause many ecological problems [8-10]. With rising of environmental awareness and advancement of technologies, the textile industry is constantly seeking ecologically secure processes to alter the conventional dyeing methods [11]. In recent years, low-salt or salt-free dyeing techniques have been developed for ecological dyeing of textile fibers [12-19]. In the case of cellulosic fibers, particularly cotton fiber, it is well agreed that surface modification prior to dyeing would greatly favor in development of salt-free/low-salt dyeing process using anionic dyes [13-19].

Application of cationic groups such as amino or ammonium groups onto cellulose macromolecular chains, generally called "cationization of cotton", has been proposed with the aim to enhance the interactions with anionic dyes [13]. However, most of the chemicals used in cationization process are highly toxic and cause serious environmental hazards and health risks. Therefore, researchers are looking for non-toxic, biocompatible and biodegradable alternative materials for cationic modification of cotton. Chitosan and its derivatives have been successfully exploited in surface modification and improvement of dyeing and functional finishing of cotton textiles [20-23].

Chitosan, a linear polysaccharide, is obtained by treating the chitin shells of shrimp and other crustaceans with an alkaline substance, like sodium hydroxide. It is composed of randomly distributed β-(1→4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). In acidic media with pH<6, amine ($-NH_2$) groups of chitosan are protonated into $-NH_3^+$, so the chitosan behaves like poly-cationic polymer [20, 21]. Chemical activity and functional properties of chitosan can be modified using variety of materials. Grafting of multifunctional macromolecules such as sugars, cyclodextrins, crown ethers, or dendrimers onto chitosan backbone and consequent modification of textiles generates stronger linkage between chitosan derivatives and textiles. This phenomenon not only improves the stability of chitosan on the textiles, but also provides some further suitable properties such as antimicrobial, guest-molecule carriers, and chelating [22, 23].

Dendrimers, as novel class of chemical materials with unique structures and characteristics, have been recently used for chemical modification of chitosan. Dendrimer modified chitosan materials demonstrate exclusive features such as enhanced cationic nature, non-toxicity, biodegradability, antimicrobial activity, etc. Chitosan-polypropylene imine dendrimer (CS-PPI) is a novel hybrid material that its potential has been investigated in dye removal [22, 23], and functional finishing and eco-friendly dyeing of cotton, wool, and nylon textiles using reactive dyes and natural dyes [12, 24-29].

To the best of our knowledge, CS-PPI has not been used in dyeing of cotton with direct dyes. In the present study, with the aim to develop a salt-free dyeing process for direct dyes, cotton fabric was pre-treated with CS-PPI in the presence of CA as a cross-linking agent. The effects of important factors such as CS-PPI, direct dye and salt concentrations as well as dyeing time and temperature on the color strength were then studied. Moreover, fastness properties of untreated and CS-PPI modified cotton dyed by means of two separate processes (salt-free and conventional dyeing) were investigated.

2. Experimental

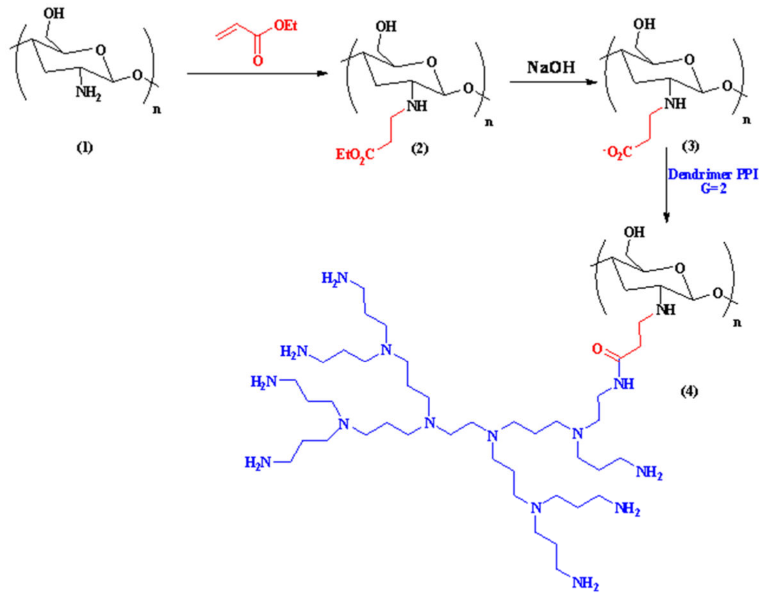
2.1. Materials and methods

Plain weave cotton fabric with weft/cm: 36 and warp/cm: 32 (density: 150 g/m^2) was used in this study. The scouring of fabrics was carried out using a nonionic detergent (Lotensol, Hansa). Three commercially available direct dyes, namely, C.I. Direct Blue 78 (DB78), C.I. Direct Red 80 (DR80) and C.I. Direct Yellow 106 (DY106) were supplied by Ciba Ltd., and used for dyeing of cotton as received without further purification. The specifications of direct dyes are summarized in Table 1. All other chemicals used were of analytical laboratory grade provided by Merck, Germany. Distilled water was used for preparation of solution and dyeing.

2.2. Synthesis of CS-PPI

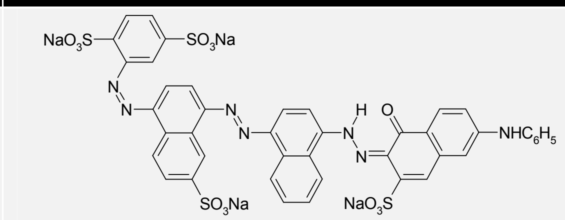
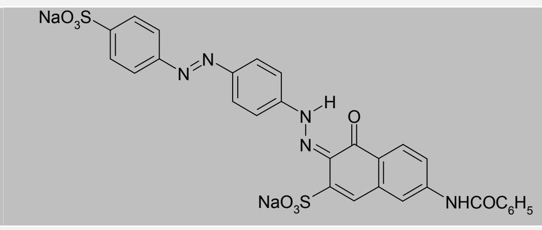
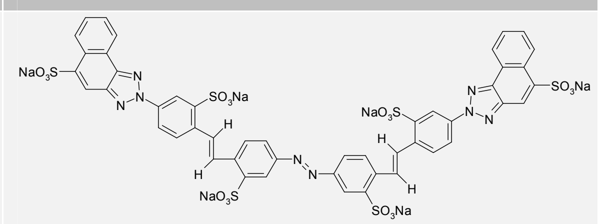
The preparation steps of chitosan-polypropylene imine

(CS-PPI) have been summarized in Scheme 1, and thoroughly described in our previous study [29]. Chitosan (1) was dissolved in water/methanol mixture using acetic acid (pH= 4). Then, ethyl acrylate was added into the solution. After stirring at 50 °C, and upon completion the reaction, the solution was precipitated in acetone saturated with $NaHCO_3$. After that, the filtration was done, and the precipitated powder was achieved with the yield of 95%. Compound (3) was dispersed in methanol; polypropylene imine (PPI) (G=2) was added to the prepared suspension, and the mixture was stirred at ambient temperature for three days. After that, the solvent was evaporated and the obtained powder was dried to achieve CS-PPI.



Scheme 1: Preparation method of chitosan-polypropylene imine dendrimer (G=2) hybrid (CS-PPI) [29].

Table 1: The specification of the used direct dyes.

Dye	Molecular formula	Molecular Weight (g/mol)	Chemical structure
DB78	$C_{42}H_{25}N_7Na_4O_{13}S_4$	1055	
DR81	$C_{29}H_{19}N_5Na_2O_8S_2$	675	
DY106	$C_{48}H_{26}N_8Na_6O_{18}S_6$	1333	

2.3. CS-PPI grafting on cotton fabric

Desized, mercerized and scoured cotton fabric was used for grafting process. Prior to grafting, cotton fabric was scoured with 2 g/L nonionic detergent at 60 °C for 30 min, liquor ratio (L:R) of 40:1. Then, fabrics were rinsed and air dried. A fine powder of CS-PPI was dissolved in citric acid solution (pH=4-5) and the grafting of cotton fabric was carried out as follows: Cotton fabric was dipped in various concentrations of CS-PPI solutions (5, 10, 15, 20 and 25% owf (over weight of fiber)) for 2 h at 65 °C. The fabrics were then dried for 5 min at 80 ˚C, cured in an oven at 120 °C for 3 min. Afterwards, treated fabrics were rinsed with water at room temperature for 30 min to remove un-grafted materials, squeezed, air dried, and used in dyeing trials.

2.4. Dyeing method

2.4.1. Conventional dyeing:

Untreated and modified cotton fabrics were dyed at various temperatures (60, 80, 100 °C) for 10-60 min time intervals with direct dyes in the bath containing dye 1-8% owf, sodium sulfate 10-40 g/L. Dyeing was performed in a laboratory dyeing machine (Smart dyer rapid sd-16, India) with L:R 1:40 (Figure 1). Finally, dyed fabrics were rinsed with tap water, dried at room temperature, and analyzed.

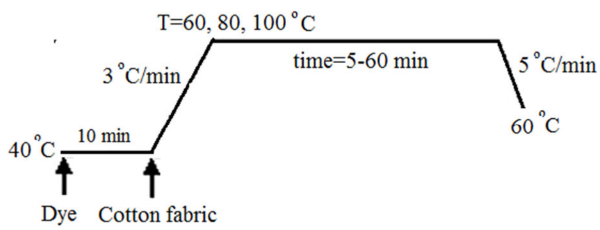


Figure 1: Dyeing procedure of cotton fabrics with direct dyes.

2.4.2. Salt-free dyeing

Salt-free dyeing was performed without salt addition. The rest of dyeing procedure was the same as conventional dyeing (section 2.4.1).

The color strength of treated cotton was measured by the reflectance spectrometer (Gretag Macbeth 7000 A spectrophotometer under D65 illuminant at 10° observer), and calculated at λ_{max} (wavelength of maximum absorption) from the Kubelka-Munk (Eq. 1). During measurements, fabric samples were held flat and securely using a spring-loaded sample clamp. Measurements were repeated three times on each dyed fabric and the average was calculated and reported.

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

where K is the absorbance coefficient, S is the scattering coefficient, R is the reflectance value at λ_{max} (wavelength of maximum absorption).

2.5. Fastness properties

Wash fastness was evaluated by the standard ISO 105 C06 C2S:1994 (E) method. The washing was conducted at 60 °C for 30 min, rinsed with cold water. air dried, and analyzed by gray scale.

Light fastness test ISO 105 B02:1988 (E) was evaluated with the xenon arc lamp using blue reference samples. Light fading was evaluated using blue scale (severe fading=1 and no fading=8).

The rub fastness test was performed according to ISO105-X12:1993 (E) using a crockmeter. The testing squares were thoroughly immersed in distilled water for the wet rub test. The rest of the procedure was the same as the dry test. The staining on the white test cloth was assessed according to the gray scale.

3. Results and Discussion

3.1. Effect of CS-PPI concentration on color strength

Color strength variation as a function of CS-PPI concentration used for treatment of cotton fabrics is shown in Figure 2. Results showed that, independent from type of direct dye, K/S steadily increased with the increase of CS-PPI concentration and reached plateau around 15% owf CS-PPI. Further increase in CS-PPI concentration did not bring about appreciable change in K/S values. So, CS-PPI 15% owf can be selected as optimum concentration for modification of cotton fabric with highest color strength values with direct dyes. In addition, *K/S* values of treated samples were even higher than that of the untreated cotton dyed using 30% owf salt. This can be attributed to the presence of amine groups on treated cotton and consequently, increasing the dye absorbing sites on fiber surface which contributes to enhance absorption of direct dyes [12, 14]. As a result, CS-PPI treatment effectively enhanced color strength of dyed cotton fabrics by 11, 8 and 3 grades for blue, red and yellow direct dyes, respectively.

The possible interaction mechanism between untreated/modified cotton and direct dye molecules is schematically shown in Scheme 2. In addition to van der Waals forces in untreated cotton, hydrogen bonding is also responsible for interaction forces between macromolecular chains of cellulose and direct dyes [1-5]. In addition to these forces, in CS-PPI treated cotton, numerous protonated amino groups significantly participate in electrostatic interactions with anionic groups of direct dyes. Therefore, synergistic effect of these interaction forces would result in enhanced dye absorption, and consequent higher color strength of dyed modified cotton.

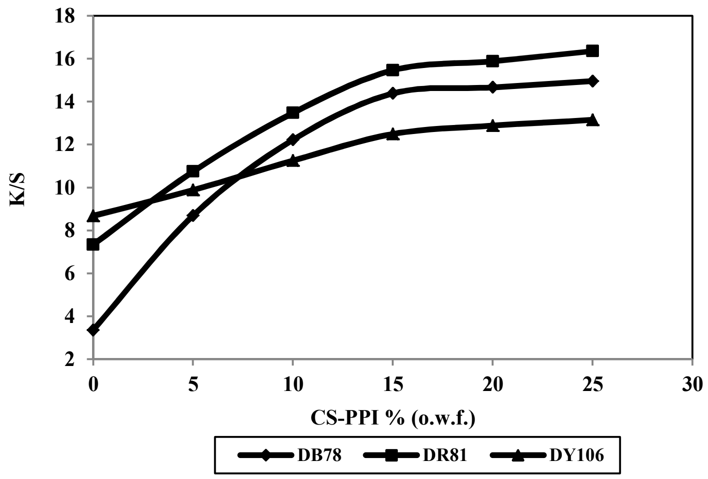
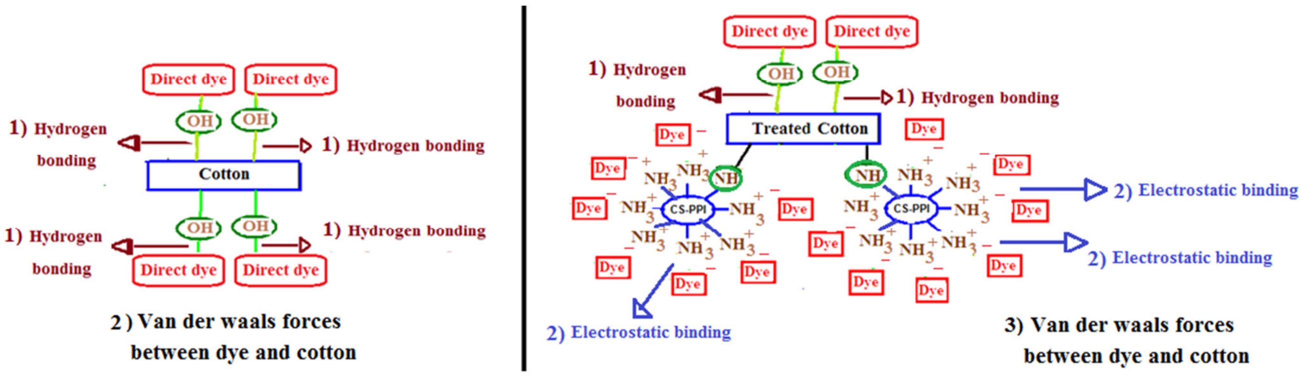


Figure 2: The effect of CS-PPI concentration on color strength of cotton fabrics (dye concentration= 4% owf; dyeing temperature= 100 °C; time= 60 min); for untreated cotton dyeing salt 30 % owf was also used.



Scheme 2: Proposed mechanism for the interaction of direct dyes with untreated and CS-PPI modified cotton.

3.2. Effect of dyeing parameters on color strength

3.2.1. Effect of dye concentration

Figure 3 shows the effect of direct dye concentration (1-8% owf) on color strength values (dye-ability) of untreated and modified cotton. Several important results are evident from this figure explained as follows:

I) The shapes of graphs for all direct dyes show that independent of the type of cotton (untreated or modified), K/S values followed a similar trend as a function of dye concentration. However, K/S values depended strongly on the type of cotton used, and modified cotton possessed relatively higher K/S values compared to untreated cotton.

II) Initial dye concentration had prominent role on K/S values, and higher initial dye concentration brought about higher K/S values. This behavior can be related to greater difference in chemical potential of dye between dyeing solution and fiber at higher dye concentration and subsequent increased driving force for movement of dye molecules from solution toward cotton fibers.

III) It is also observed that dye up-take on modified cotton was relatively fast and reached equilibrium at around 4% owf dye concentration (within 60 min with no salt usage) while in conventional dyeing (using 8% owf dye with 30 g/L salt) equilibrium was not still achieved for untreated cotton, and more likely further increase in dye concentration would result in more dye absorption and higher color strength. Indeed, changes in surface properties of cotton after modification with CS-PPI and subsequent altered dyeing mechanisms are responsible for such different dyeing behavior with direct dyes, as explained in previous section. Therefore, 4% owf dye concentration can be chosen as the optimum dye concentration to achieve the highest dye absorption and color strength on modified cotton.

IV) From comparison of color strength data for untreated and modified cotton, it was found that modified cotton dyed with 1-2% owf of dyes possessed similar or even higher color depth than those of untreated cotton dyed with 8% owf of direct dyes. This finding proved that the treated cotton can be successfully dyed with same color depth as conventional dyeing using considerably lower amount of direct dyes. In other words, to produce a given color depth on cotton, not only significantly lower concentration of direct dye is required, but also heavy color shades (higher color strengths) which are not achievable in conventional dyeing, could be produced after a simple treatment of cotton with CS-PPI. This finding has great importance in terms of significant saving of direct dyes as well as development of an environmentally friendly process for cotton dyeing with fewer hazards of remained direct dyes in wastewater needed to be treated prior to discharge into the environment.

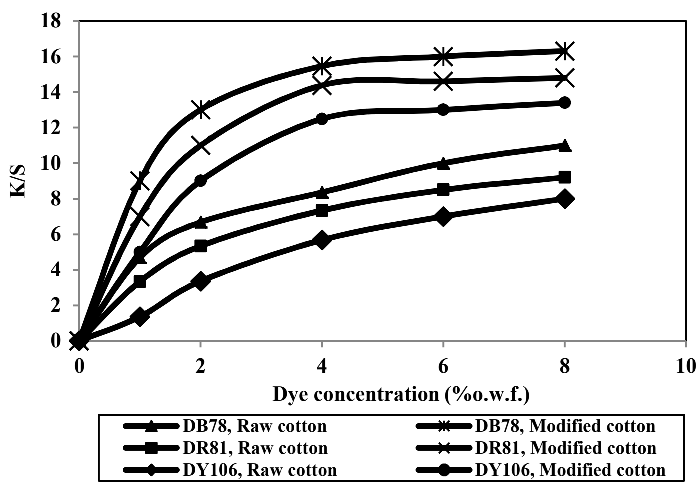


Figure 3: Effect of dye concentration on color strength of dyed untreated and modified (CS-PPI 15% owf) cotton fabrics (dyeing condition: temperature= 100 °C; time=60min); for untreated cotton dyeing salt 30 % owf was also used.

3.2.2. Effect of time

Color strength variation of untreated and modified cotton as a function of dyeing time is demonstrated in Figure 4. It is obvious from Figure 4 that the K/S values increased with appreciably faster rate than untreated cotton. Moreover, modified cotton reached equilibrium (the highest K/S value) after about 20 min of dyeing time while untreated cotton still needed more time (at least 40 min) to achieve the highest possible color strength. Besides, at any given time, it was seen that modified cotton was able to up-take higher amount of dye molecules from colored solution, therefore, possessed higher K/S values as compared to untreated cotton.

As discussed earlier, this behavior may be related to the surface properties of cotton. In modified cotton, not only the surface morphology is completely different from than that of untreated cotton, but also the large number of active functional groups such as amine and hydroxyl groups are introduced on the fiber surface which enhance dye absorbing capacity of cotton via ionic interactions and hydrogen bonding and thus bringing bout higher K/S values and deeper color shades [1-5, 12, 24]. However, in untreated cotton, the interaction forces are only limited to hydrogen bonding between hydroxyl groups of cellulose chains and functional groups of dye molecules and thus the dyeing rate and dye absorbing capacity remained comparatively low [1-5].

So, it can be concluded that a decrease in dyeing time as well as the enhancement in the amount of dye up-take are worthwhile since remarkable amount of time (~50%), energy, and chemicals can be saved which is very important from both ecological and economical points of view. In fact, this goal can be realized through simple surface modification of cotton with bio-compatible CS-PPI.

3.2.3. Effect of temperature

Temperature has several effects in dyeing of textile fibers. Temperature has swelling effect on fiber material and facilitates the breaking down of dye agglomerates and diffusion of dye molecules within fiber structure [1]. The effect of dyeing temperature (60, 80 and 100 °C) on color strength of untreated and modified cotton is shown in Figure 5. As it is clear, the effect of temperature is somewhat different for the modified cotton. In the case of untreated cotton, color strength steadily increased with temperature, while for modified cotton, at first, color strength increased rapidly with increasing the temperature from 60 to 80 °C, but further temperature increase to 100 °C had less impact on the increase of K/S values. Interestingly, comparison of K/S values showed that the modified cotton dyed at 80 °C possessed higher K/S than the untreated cotton dyed at 100 °C. This means that the optimum dyeing temperature has been shifted to lower temperatures when modified cotton used in dyeing. As a result, lower energy is required compared to conventional dyeing with direct dyes.

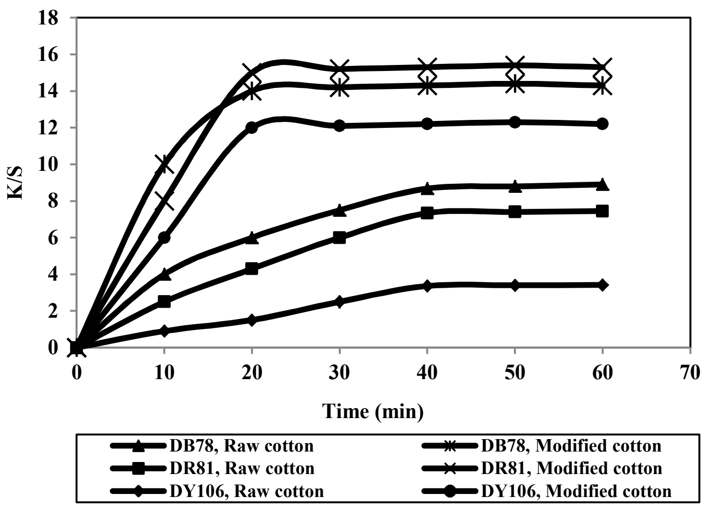


Figure 4: Effect of time on color strength values of dyed untreated and modified (CS-PPI 15% owf) cotton fabrics (dyeing condition: dye concentration=4% owf; dyeing temperature= 100 °C); for untreated cotton dyeing salt 30 % owf was also used.

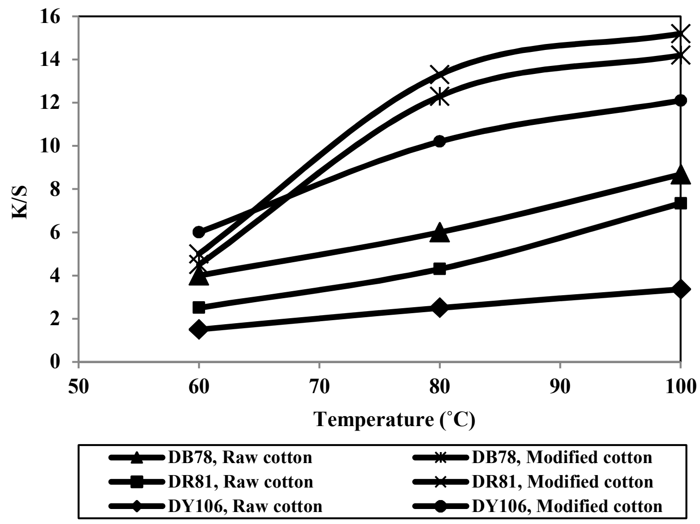


Figure 5: Effect of temperature on color strength values of dyed untreated and modified (CS-PPI 15% owf) cotton fabrics (dyeing condition: dye concentration=4% owf; time=60 min); for untreated cotton dyeing salt 30 % owf was also used.

In fact, the increase in dyeing temperature can enhance the solubility of direct dyes and also produce a swelling effect within the internal structure of fiber, so enables large dye molecules to penetrate easily into fiber. However, temperature can affect dye up-take rate in different ways by changing the solubility of dye molecules and molecular interactions between dye and fiber. Therefore, different effects of temperature on color strength of untreated and modified cotton can be ascribed to different chemical reactions taking place among the functional groups of the cotton and direct dyes.

Based on the results obtained, it can be concluded that CS-PPI treatment of cotton can effectively reduce (at least 20 °C) the optimum dyeing temperature with direct dyes, so that less amount of dye is required for dyeing and significant amount of energy can be saved in this way.

3.2.4. Effect of salt concentration

Inorganic salts like sodium sulfate were extensively used to increase the affinity of direct dyes in cotton dyeing. In dye bath, salts also delay dye migration toward substrate and so the better levelness in dyeing could be attained [5]. Figure 6 shows the influence of salt concentration (0-40% owf) on the color strength of dyed untreated cotton fabric. For comparison, the CS-PPI treated cotton dyed without salt addition is also shown in Figure 6. It is evident that salt addition was quite effective in neutralization of negative charge and improvement of K/S values of untreated cotton up to nearly 30% owf. Therefore, 30% owf salt concentration was considered as the optimum concentration for dyeing of untreated cotton with direct dyes. Interestingly, it is obvious that K/S values of dyed CS-PPI treated cotton were higher than those of untreated cotton dyed using 30% owf salt (conventional dyeing). This finding confirmed that compared to untreated cotton, the treated cotton could be successfully dyed with same or even higher color depth with no salt usage. In other words, after CS-PPI treatment of cotton, the salt can be eliminated from dyeing process without impairing the color strength, and thus the dyeing process of cotton with direct dyes becomes “salt-free dyeing”. This finding is very important sinceelimination of salt from dyeing process remedied the problems associated with the high load of salt in dyeing effluents.

3.3. Colorimetric properties of the direct dyes

Dyed untreated and modified cotton fabrics were all characterized with a reflectance spectrophotometer to evaluate their colorimetric properties. Surface reflectance spectra were measured and related color parameters were then calculated in CIE L*a*b* color coordinates. The colorimetric data are presented in Table 2. Data showed that there were some changes in colorimetric values of dyed modified samples. Although there were gradual increase in a* and b* values with the increase of CS-PPI concentration which was indicative of an increase in color chroma or color vividness of dyed modified cotton, color hue has not changed. The lightness (L*) decreased with increase of CS-PPI concentration which indicated darker color shades for modified samples. Comparison of colorimetric data showed that CS-PPI modification would not impair color hue but produce darker color shades on cotton fabrics.

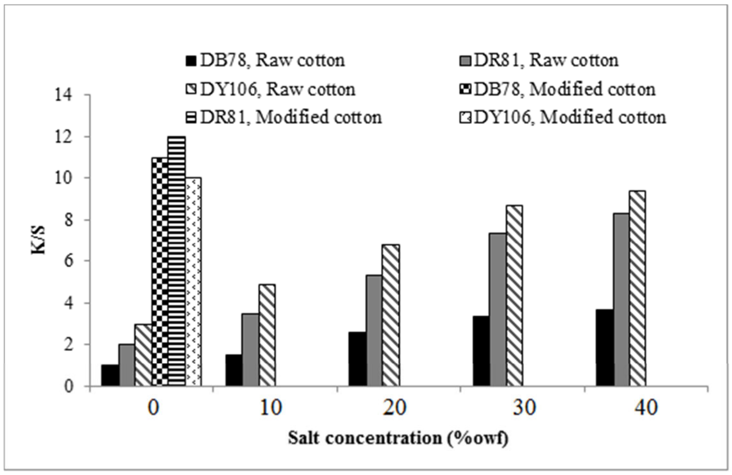
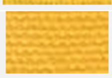
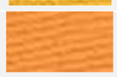


Figure 6: Comparison of the color strength values; Untreated cotton dyed with different salt concentrations vs. CS-PPI (15 %owf) modified cotton dyed with no salt (dyeing condition: dye concentration=4% owf; dyeing temperature= 100 °C; time= 60min).

Table 2: Colorimetric data of cotton dyed with direct dyes.

Dye	CS-PPI %(o.w.f.)	L*	a*	b*	Image
DB78	0	56.7	-1.4	-12.1	
	5	50.2	-1.5	-12.4	
	10	46.6	-1.2	-13.3	
	15	41.9	-2.7	-14.1	
DR81	0	60.9	37.1	5.6	
	5	57.2	37.5	5.9	
	10	55.2	38.0	6.3	
	15	51.4	38.6	6.4	
DY106	0	74.3	17.4	66.3	
	5	71.5	17.8	67.1	
	10	68.6	18.0	67.7	
	15	66.1	18.4	68.2	

3.4. Color fastness properties

Color fastness of dyed cotton fabric against wash, rub, and light was measured according to standard methods and the results are summarized in Table 3. In general, wash fastness of the treated cotton was satisfactory, and change of shade and staining on adjacent fabrics were equal to or even higher than untreated cotton. It should be mentioned that the improvement in color change is observed at higher CS-PPI concentrations. In fact, the molecular structure of direct dyes (Table 1) may be an influencing factor on wash fastness. DY106 contains more amino and hydroxyl groups than other dyes, which is advantageous in formation of hydrogen bonds between dye molecules and CS-PPI treated cotton, so that the dye molecules are tightly fixed onto the cotton fabrics, displaying better wash fastness. It is very interesting that the modified samples show an obvious improvement in color staining compared to untreated cotton. A visible improvement in color staining may be the result of the mechanical blockage of dye.

Rub fastness (dry and wet) of dyes on treated fabrics were satisfactory and similar to those of untreated cotton. In general, the deeper shades showed somewhat inferior rub fastness than lighter shades. As discussed above, the treatment of cotton fabric enhanced the dye up-take and brought about deeper shades. Generally, when the concentration of dye molecules on fiber is high, the chance of dye to detach and stain adjacent test cloth is also high. Hence, as a general result of achieving deeper shades, the treated fabric samples have shown slightly lower fastness rating in comparison to lighter untreated fabric.

Direct dyes on untreated cotton fabrics exhibited different stability against light. This might be due to the type of direct dye used, because the resistance of a dye to chemical or photochemical attack is directly related to its chemical structure, so that direct dyes with large chemical structures exhibit higher light fastness. In addition, treated cotton dyed with DB78 and DY106 exhibited light fastness similar to untreated cotton, while some minor improvement in light fastness of DR81 was observed for treated cotton.

Overall, fastness results indicated that the CS-PPI pretreatment of cotton not only would not impair the fastness properties of direct dyes, but also allowed obtaining darker colors, with a better level of staining which can satisfactorily meet the application requirements.

Table 3: Fastness properties of dyed cotton fabrics.

Dye	CS-PPI % (owf)	Fastness					
		Wash			Rub		Light
		CC	SC	SN	Dry	Wet	
DB78	0	3	4	4	4-5	4-5	6
	5	3-4	4	4	4-5	4-5	6
	10	3-4	4	4	4-5	4-5	6
	15	3-4	4-5	4-5	4-5	4-5	6
DR81	0	3	2-3	4-5	4-5	2-3	3
	5	3-4	3	5	5	3	3-4
	10	3-4	3	5	5	3	3-4
	15	3-4	3	5	5	3	3-4
DY106	0	4	4-5	5	4-5	4-5	6
	5	4-5	5	5	5	5	6
	10	4-5	5	5	5	5	6
	15	4-5	5	5	5	5	6

4. Conclusions

The results showed that chitosan-polypropylene imine dendrimer (CS-PPI) can be used as a novel modified biopolymer to improve the color strength of cotton fabrics with direct dyes. The introduction of numerous polar groups, mainly new amino groups from CS-PPI onto cotton fiber surface was responsible for the improvement of color strength of the treated cotton. Colorimetric and color fastness results confirmed that the modification has no adverse influence on other properties of dyed cotton. Indeed, CS-PPI treatment of cotton brought about I) significant enhancement in dye up-take and decrease in the concentration of dye required to obtain a given color depth on cotton; II) a decrease in optimum dyeing time (~50%); III) decrease of optimum dyeing temperature with direct dyes (~20 °C); IV) elimination of salt and development of "salt-free dyeing". Thus, using a simple CS-PPI treatment of cotton in dyeing with direct dyes not only remarkable amount of time, energy, chemicals and dyeing costs are saved, but also the problems associated with dyeing effluents are remedied.

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5. References

1. J. Shore, Cellulosics Dyeing, Society of Dyers and Colourists, (1995).
2. W. Ingamells, Colour for textiles A user's handbook, Society of Dyers and Colourists, (1993).
3. K. Hunger, Industrial Dyes: Chemistry, Properties, Applications, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, (2003).
4. J.R. Aspland, Direct Dyes and Their Application, Textile Chemist and Colorist, (1991).
5. C. Preston, The Dyeing of Cellulosic Fibres, Society of Dyers and Colourists, (1986).
6. M. Wawrzkiewicz, Comparison of gel anion exchangers of various basicity in direct dye removal from aqueous solutions and wastewaters, *Chem. Eng. J.*, 173(2011) 773-781.
7. M. T. Yagub, T. K. Sen, S. Afroze, H. M. Ang, Dye and its removal from aqueous solution by adsorption: a review, *Adv. Colloid Interface Sci*., 209(2014) 172-184.
8. N.M. Mahmoodi, R. Salehi, M. Arami, H. Bahrami, Dye removal from colored textile wastewater using chitosan in binary systems, *Desalination*, 267(2011) 64-72.
9. T. A. Arica, E. Ayas, M. Y. Arica, Magnetic MCM-41 silica particles grafted with poly (glycidylmethacrylate) brush: Modification and application for removal of direct dyes, *Micropor. Mesopor. Mat.,* 243(2017): 164-175.
10. V.K. Gupta, Suhas, Application of low-cost adsorbents for dye removal-a review, *J. Environ. Manage.,* 90 (2009) 2313-2342.
11. A.Khatri, M. H. Peerzada, M. Mohsin, M. White, A review on developments in dyeing cotton fabrics with reactive dyes for reducing effluent pollution, *J. Clean. Prod.*, 87(2015): 50-57.
12. M. Sadeghi-Kiakhani, S. Safapour, Eco-friendly dyeing of treated wool fabrics with reactive dyes using chitosan-poly(propylene imine) dendreimer hybrid, *Clean Technol. Environ. Policy*, 17(2015) 1019-1027.
13. D. P. Chattopadhyay, Cationization of cotton for low-salt or salt-free dyeing. *Ind. J. Fibre Tex. Res.,* 26(2001) 108-115.
14. T. E. N. G. Xiaoxu, M. A. Wei, S. Zhang, Application of tertiary amine cationic polyacrylamide with high cationic degree in salt-free dyeing of reactive dyes, *Chin. J. Chem. Eng.,* 18(2010): 1023-1028.
15. F. Zhang, Y. Chen, H. Lin, Y. Lu, Synthesis of an amino-terminated hyperbranched polymer and its application in reactive dyeing on cotton as a salt-free dyeing auxiliary, *Color. Technol.,* 123(2007): 351-357.
16. F. Zhang, Y. Chen, H. Lin, H. Wang, B. Zhao, HBP-NH_2 grafted cotton fiber: preparation and salt-free dyeing properties, *Carbohydr. Polym.* 74(2008): 250-256.
17. M. Montazer, R. Malek, A. Rahimi, Salt free reactive dyeing of cationized cotton, *Fiber Polym.*, 8 (2007) 608-612.
18. Z. Bahreini, A. Kiumarsi, A Comparative Study on the Dyeability of Stabraq (Milkweed) Fibers with Reactive Dyes, *Prog. Color Colorants Coat.*, 1(2008) 19-26.
19. L. Wang, W. Ma, S. Zhang, X. Teng, J. Yang, Preparation of cationic cotton with two-bath pad-bake process and its application in salt-free dyeing, *Carbohydr. Polym.*, 78 (2009), 602-608.
20. M. Feiz, S. Salimpour, Improvement in Wash Fastness of Dyed Silk by Aftertreatment with Commercial Syntan/Metal Salts, *Prog. Color Colorants Coat.,* 1(2008) 27-36.
21. M. A. R. Bhuiyan, A. Shaid, M. A. Khan,

Cationization of cotton fiber by chitosan and its dyeing with reactive dye without salt, *Chem. Mater. Eng.*, 2(2014): 96-100.
22. M. Sadeghi-Kiakhani, M. Arami, K. Gharanjig, Application of Chitosan-Dendrimer PPI Hybrid in Direct Dyes Removal: Optimization by RSM, Kinetic and Isotherm Studies, *J. Color Sci. Tech.*, 6(2013), 355-368.
23. M. Sadeghi-Kiakhani, M. Arami, K. Gharanjig, Dye removal from colored textile wastewater using chitosan-PPI dendrimer composite as a biopolymer: optimization, kinetic and isotherm studies, *J. Appl. Polym. Sci.*, 127(2013) 2607-2619.
24. M. Sadeghi-Kiakhani, S. Safapour, Salt-free Reactive Dyeing of the Cotton Fabric Modified with Chitosan-Poly(propylene imine) Dendrimer Hybrid, *Fiber Polym.*, 16(2015) 1075-1081.
25. L. Mehrparvar, Siyamak Safapour, M. Sadeghi-Kiakhani, K. Gharanjig, Chitosan-polypropylene imine dendrimer hybrid: a new ecological biomordant for cochineal dyeing of wool, *Environ. Chem. Lett.,* 14(2016): 533-539.
26. L. Mehrparvar, S. Safapour, M. Sadeghi-Kiakhani, K. Gharanjig, A cleaner and eco-benign process for wool dyeing with madder, Rubia tinctorum L., root natural dye, *Int. J. Environ. Sci.,* 13(2016): 2569-2578.
27. M. Sadeghi-Kiakhani, S. Safapour, Improvement of dyeing and antimicrobial properties of nylon fabrics modified using chitosan-poly (propylene imine) dendreimer hybrid, *J. Ind. Eng. Chem.* 33(2016): 170-177.
28. M. Sadeghi-Kiakhani, M. Arami, K. Gharanjig, Application of a biopolymer Chitosan-Poly (Propylene) Imines Dendrimer Hybrid as an antimicrobial agent on the wool, *Iranian Polym. J.*, 22(2013) 931-940.
29. M. Sadeghi-Kiakhani, K. Gharanjig, M. Arami, Grafting of prepared chitosan-poly(propylene) imines dendrimer hybrid as a biopolymer onto cotton and its antimicrobial property, *J. Ind. Eng. Chem.*, 28(2015) 78-85.

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