



## Combined Salt Free Dyeing and Formaldehyde Free Finishing of Cotton Fabrics

Ahmed Mohammed Nuru <sup>a\*</sup>, Mohammed Hussien<sup>a</sup>, Seyoum Behonegn <sup>a</sup>

<sup>a</sup>School of Textile, Leather, and Fashion Technology of Textile Engineering,  
Kombolcha Institute of Technology, Wollo University, Ethiopia.

How to cite this paper:  
[https://xxxxx\\*](https://xxxxx*)

©2023 Kombolcha Institute of  
Technology, Wollo University



ISSN : 2788-6239 (Print)  
ISSN: 2788-6247 (online)

\*Corresponding  
Author: ahme2005a@gmail.com

---

### ABSTRACT

Cotton is the most widely used cellulosic material in the textile industry, especially for apparel purposes but has a tendency to wrinkle badly, degrading its aesthetic value and having poor smooth drying properties. Dyeing and crease resistance finishing process are applied to improve the wrinkle resistance and its aesthetic value respectively. Conventionally, dyeing and durable finishing of cotton is conducted separately by dyeing cotton first, then finished with a cross-linking agent. However, these traditional processes are time and chemical consuming processes. Many researchers have attempted to combine the dyeing and easy-care finishing process into one step. The challenge was difficult to produce fabrics that have deep shades, good Colour fastness and excellent crease recovery performance simultaneously. Hence, the aim of this work was to conduct combined dyeing and easy-care finishing of cotton fabrics with reactive dyes, citric acid and fibroin solution using a pad-dry-cure methods. In this work, fibroin is used as an additive to enhance the degree of cross-linking and as a cat ionizing agent to improve the exhaustion of the dye. The parameters were investigated and optimized with respect to colour strength, colour fastness and mechanical properties of the treated fabric. The efficiency of combined dyed and finished fabrics with reactive dye, citric acid and fibroin has been studied. Better colour strength, crease recovery angle, breaking strength, and fastness properties were obtained as compared with conventional processes. When the concentration of fibroin increased the K/S values, colour fastness properties, and crease resistance properties were improved.

Keywords: Citric Acid, Crease Recovery Angle, Dyeing, Fibroin, Strength Retention

---

### 1. INTRODUCTION

Cotton fabric is the most widely used natural cellulosic raw material in the textile industry, especially for apparel purposes due to its excellent properties such as

good strength, higher water absorbency, moisture content, comfortable to wear, non-toxic for health and easy for colour retention [1, 2]. The use of cotton-based products is not only limited to apparel purposes but used in different applications like functional textiles, technical

textiles, and much more demand. Among the total textile production, 50% of the application is based on cellulosic-cotton products. To increase the satisfaction of the customer colouration and finishing are imparted on the textile material to improve the appearance and functional properties of the fabric. Reactive dyes are the best colourants for the colouration of cellulose-based materials due to easy application and better fastness properties [3]. However, Cotton fabric has two main limitations. One of the main drawbacks of cellulosic materials is easy wrinkling after washing due to the swelling of cellulosic fibres by moisture [4]. During washing, the cellulosic fibres are stressed due to mechanical forces and swelling of the internal polymer chains of the amorphous areas to relieve the stress. Then, the stretched internal molecular chains form new hydrogen bonds in the stretched places so the fabric holds the creases [1]. The other limitation is dyeing the cotton fabric with reactive dye leads to electrostatic repulsion and makes the exhaustion of the dye difficult due to the development of a negative charge on cotton fabric and reactive dyes when immersed in water [5]. In order to overcome these problems many textile industries use an enormous amount of electrolyte and alkali for exhaustion and fixation purposes respectively. However, the salt added to the dye bath and alkalis are neither destroyed nor exhausted after the dyeing process that causes serious environmental pollution.

Easy-care finishing process is applied on cotton fabric in order to avoid crease formation by creating cross-linking between adjacent cellulose chains in cotton fibres. The most popular type of cross-linking agent is dimethyl dihydroxy ethylene urea (DMDHEU) which has the challenge of formaldehyde release that has an impact on human health and environmental issues with severe tensile strength loss, tear strength loss, and poor abrasion resistance properties[6, 7].

In order to overcome the problem with respect to colouration and finishing many researchers have investigated and developed formaldehyde-free easy-care agents for finishing and chemical and physical modifications of cotton fabric with amide compounds for colouration problems.

However, conventionally, dyeing and finishing of textile materials are conducted separately, by dyeing cotton first, then finished with a cross-linking agent to obtain the desired colour and durable finish properties. But these traditional processes are water, energy and chemical intensive processes. Nowadays, due to global awareness on environmental pollution, climate change, global warming, and sustainability, both academic research and industrial product development have been intensified to seek for sustainable dyeing and finishing processes would be merged for significant saving in energy, chemicals, water, labour, time and safe the environment using biodegradable plant extract polymers[8]. Combined dyeing and finishing of cotton fabric are carried out based on incorporating the dyestuff into the finishing bath which is a relatively more economical process due to reduced energy consumption, production time, dyeing and finishing chemicals, water usage, and also physical properties of the fabric [9, 10]. Many researchers have attempted to combine dyeing and easy-care finishing process in to one step. But the main challenge has been producing treated fabrics that have deep shades, good washing fastness and excellent crease recovery performance simultaneously.

Dong et al. [1, 9] Conducted simultaneous dyeing and durable press finishing of cotton fabric with reactive dyes and citric acid finishing agent by using a pad-dry-cure process and obtained relatively satisfactory properties of dyed and finished cotton fabric with appropriate adjustment of the treating conditions.

Choi [1] studied combined dyeing and durable press finishing of cotton fabric with aldehyde finishing agent and

monochlorotriazine reactive dye with glyoxal and glutaraldehyde in the dye-finishing bath tend to inhibit dye sorption but increase dye fixation. The present study has been come up with the biodegradable natural polymer which is used as a durable finish cross linking agent treatment on cotton fabric and used as a cationization agent which is comparatively cheap, environmentally safe, and worthwhile product for textile.

In the present study, an attempt has been made to find the best optimum parameters used for CA and fibroin solution as a DP finish cross linking agent treatment on cotton fabric and reactive colourants to obtain better colour shade, colour fastness properties and excellent crease recovery performance of combined dyeing and finishing of cotton fabric simultaneously.

## 2. MATERIALS AND METHODS

### 2.1 Materials and chemicals

Full bleached 100% plain weave cotton fabric (100%), having the following structural characteristics, was used: 34Nm count yarn (warp, weft), 65end per inch; 54 Picks per inch; and fabric mass per unit area with 150 g/m<sup>2</sup> fabric was sourced from Kombolcha Textile Share Factory, Kombolcha, Ethiopia. Bombyx mori silk cocoon was obtained from Wereta Agriculture College, Gondor, Ethiopia. Fibroin solution and citric acid were used as a crease resistance finishing agent. Sodium carbonate Ethanol, Calcium chloride, and hydrochloric acid are laboratory reagent grade. Sodium dihydrogen phosphate was used to catalyse the crosslinking reaction. The reactive dyes used in this study was CI Reactive Red 5 Mono - chloro triazine. Deionized water was used in all experiments.

### 2.2 Preparation of silk fibroin solution

Degumming raw cocoon was done using aqueous sodium carbonate solution (0.5% o.w.f.) for 60 minutes with soap (0.5% o.w.f.) and then washed with distilled water at boiling point. This was done to remove sericin plus other impurities and then rinsed thoroughly in

warm water. The degummed silk fibroin was then dissolved in a ternary solvent system of calcium chloride, water and ethyl alcohol (CaCl<sub>2</sub>: water: ethyl alcohol = 1:8: 2, molar ratio) with a liquor ratio of 1:15 at 85 °C for 30 minutes (9). The aqueous silk fibroin solution was hydrolyzed at 100 °C for 3 hrs.

### 2.3 Simultaneous dyeing and finishing process

The fabric was padded at 80% wet pick-up with a bath containing various amounts of cross-linking agent (Citric acid), fibroin solution, reactive dyes, catalyst (Sodium di-hydrogen phosphate), sequestering agents, and wetting agent. Fabric was dried at 100°C for 2 minutes and cured at various curing temperatures (130°C, 154°C, 150°C, and 160°C) for 2 min. Soaping was carried out at 50°C for 30 min with 2 g/L sodium carbonate and 5 g/L non-ionic detergent. Finally, cold wash was given followed by drying

### 2.4 Evaluation of fabric properties

Colour Strength (k/s) (using a computer colour matching system X 4000 spectrophotometer under illuminant D65 using a 10° standard observer), Breaking strength (ASTM - D 5034 method), tear strength (ASTM-D 1424method), wrinkle recovery angle (AATCC Test Methods 66), and colour fastness are the properties of the combined dyed and finished cotton fabric that were evaluated after treatment.

## 3. RESULTS AND DISCUSSION

### 3.1 Effect of citric acid on colour strength

When the citric acid concentration was increased from 20g/l to 50g/l by keeping the other variables constant the colour yield decreases significantly. The reason for decreasing the colour yield with increasing the concentration of citric acid due to shifting of the dye bath PH towards acidic conditions which is not compatible with the satisfactory fixation of reactive dyes. However, when citric acid with fibroin used as finishing agent and even if the dye bath PH shifted to acidic condition the

colour yield is not significantly decreased. Due to imparting more amino groups on the surface of cotton fabric which comes from fibroin solution and turned to a positive charge under acidic conditions during dyeing, and which increased the attraction potential of reactive dyes towards cotton fabric under acidic conditions. Effect of citric acid concentration on colour yield was shown in Figure 1.

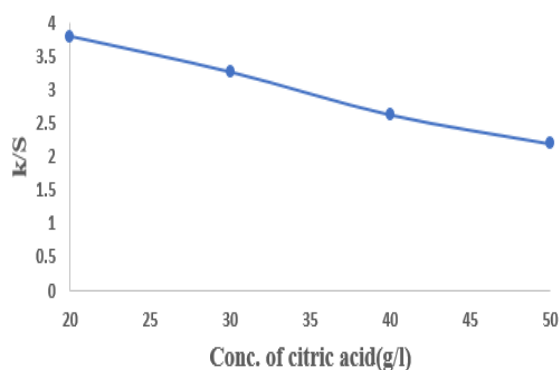


Fig. 1 Effect of citric acid concentration on colour yield

### 3.2 Effect of fibroin concentration on colour strength

The effect of the fibroin concentration on the colour strength of the treated cotton fabric was studied. When the concentration of fibroin solution increases and keeping the other variables constant the colour strength of the dyed fabric also increases as shown in the Figure 2. As the result indicates, the K/S value of the sample treated with citric acid alone is 2.63, while the sample treated with citric/fibroin is 6.86. This shows a combination of citric acid and fibroin for combined dyeing and finishing gradually increases K/S values with increasing fibroin concentration. Colour strength of treated dyed cotton fabrics increase as a function of silk fibroin concentration in the finishing solution increases. The result indicates that more amino groups from silk fibroin are present on the surface of cotton fabric. The amino groups turned to a positive charge under acidic conditions during dyeing, which increased the potential of ionic attraction and thus led to increased reactive dye

uptake. Effect of fibroin solution on Colour Yield was shown in Figure 2.

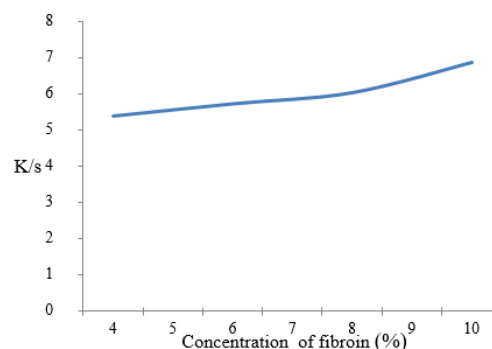


Fig. 2 Effect of fibroin solution on colour yield

### 3.3 Effect of curing temperature on colour strength

In conventional dyeing methods of cotton fabric with Monochlorotriazine reactive dyes require high temperature for fixation and also for esterification /cross-linking of cellulose with cross-linking agent or citric acid. However, at curing temperature of 160 °C the K/S of the fabric was lower due to depolymerization of reactive dyes and also the fabric tends to turn yellow at high curing temperatures which influences the shade of hue. Effect of curing temperature on colour strength was shown in Figure 3.

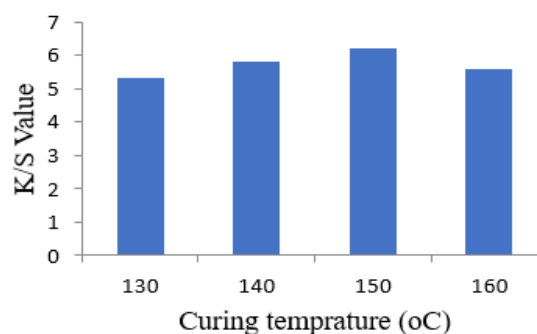


Fig. 3 Effect of curing temperature on colour strength

### 3.4. Effect of citric acid on crease recovery

The concentration of cross linking agents in the treatment bath showed significant effect on the DCRA of combined dyed and finished fabrics. As compared to bleached fabric the percentage increase in DCRA of combined dyed and finished fabrics was observed when the citric acid concentration was varied from 20g/l,

30g/l, 40g/L and 50 g/L whereas other variables were constant. The percent increase was recorded as 58.8%,63.4%,71% and 76.6 for the citric acid concentration of 20%, 30%,40% and 50% respectively, while the percentage increase in DCRA of combined dyed and finished fabrics with alone citric acid is less than the percentage increase in DCRA of combined dyed and finished fabrics with citric acid/fibroin. Effect of Citric Acid Concentration on DCRA was shown in Figure 4.

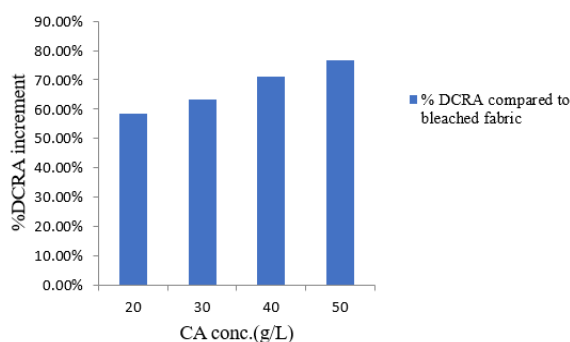


Fig. 4 Effect of citric acid concentration on DCRA

### 3.5 Effect of fibroin solution concentration on crease recovery angle

When the concentration of fibroin solution increases the Crease recovery angle of combined dyed and finished cotton fabrics both in warp and weft directions increases. As the concentration of fibroin solution increases the crease recovery angle of the fabric increases but the strength of the fabric decreases.

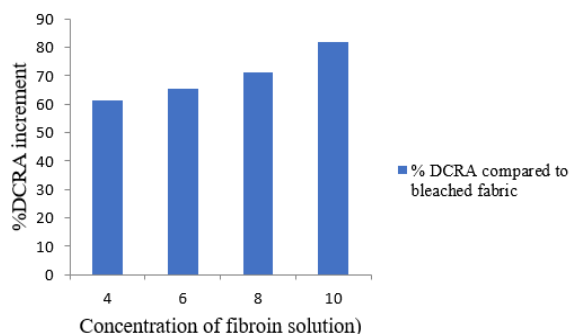


Fig. 5 Effect of fibroin solution on DCRA

Effect of fibroin solution on DCRA was shown in Figure 5. As compared to the crease recovery angle value of the un-dyed and finished cotton fabric the percentage increase in DCRA of combined dyed and finished fabrics was observed. The percent increase was recorded as 61.4 %, 65.5 %, 71 % and 82% for the fibroin concentration of 4 %, 6 %, 8 % and 10% respectively. The introduction of fibroin solution in the finishing solutions additionally better enhances the crease recovery angle of a fabric which was finished with citric acid alone.

### 3.6 Effect of curing temperature on crease recovery angle

To study the effect of curing temperature on DCRA of crease resistance finishing of cotton fabric the curing temperature is varied from 130 °C, 140 °C, 150 °C and 160 °C by keeping other variables constant.

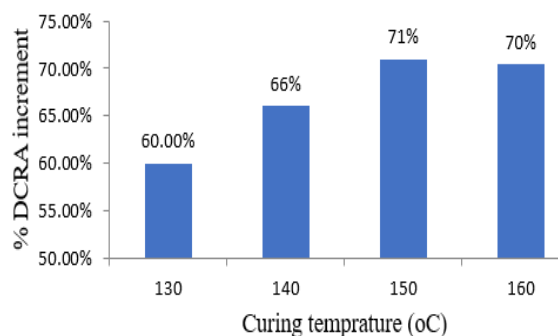


Fig. 6 Effect of curing temperature on DCRA

Citric acids required higher curing temperature in order to cross-link the hydroxyl group of cellulose molecules. The percent increase in DCRA of the combined dyed and finished fabric as compared to un-dyed and finished bleach fabric is 60 %, 66 %, 71 % and 70 % for the curing temperature of 130 0C, 140 0C, 150 0C and 160 0C respectively. Effect of curing temperature on DCRA was shown in Figure 6.

### 3.7 Effect of v citric acid on the physical properties of cotton fabric

After combining dyeing and finishing of cotton fabric the flexibility of a cotton fabric is reduced, which decreases fabric strength, especially tensile strength, tear

strength, and adversely affects fabric hand. The results in Table 1 shows, tensile strength and tear strength of the treated fabrics decreases when concentration of citric acid increases. The reason is as the concentration of citric acid increases the cross-linking of the hydroxyl groups of the cellulose increases which reduces the sliding movement of the cellulose chains in cotton fiber that cause drop in strength. According to the test results the percentage tensile strength retention of treated fabrics compared to untreated bleached fabric is 96 %, 94 %, 85.6% and 76.6% in warp direction and 93 %, 86.4 %, 75.6 %, 71 % in weft direction for citric acid concentrations 20 g/L, 30 g/L, 40g/L and 50 g/l respectively.

Table 1. Effect of citric acid on the physical properties

CA Conc. (g/L)	Tensile strength(N)		%tensile retention		Tear strength(N)		%tear retention	
	warp	weft	warp	weft	warp	weft	warp	Weft
untreated	236	198	100	100	25	23	100	100
20 g/L	226	185	96	93	24.2	22.5	96.8	97.8
30 g/L	222	171	94	86.4	23.5	21.8	94	94.8
40 g/L	202	150	85.6	75.6	23	21.5	92	93.5
50 g/L	181	141	76.6	71	21.5	20	86	87

### 3.8 Effect of curing temperature on strength

As results show, as curing temperature increases the tensile strength of the fabric significantly decreases. The reason is poor resistance of cotton fibers to high curing temperature. In addition, at high curing temperature acids depolymerize cellulose molecules and cross-linking also increases as temperature increases, these all affect the tensile strength of cotton fabrics. The percentage tensile strength retention of finished fabrics as compared to untreated finished fabric is 95 %, 44 %, 85.6 %, and 76%, in warp direction and 87 %, 82 %, 77.60 %, 66 % in weft direction for curing temperatures of 130 °C, 140 °C, 150 °C and 160 °C respectively.

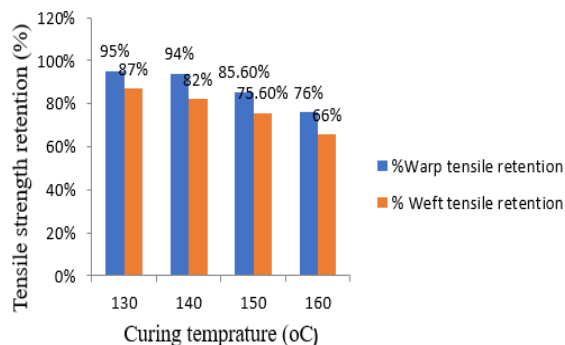


Fig.7 Effect of curing temperature on tensile strength

Effect of curing temperature on tensile strength was shown in Figure 7. At curing temperature of 160 0C the tensile strength of finished fabric shows high tensile strength loss.

### 3.9 Effect of curing temperature on tear strength

As the result shows in figure as curing temperature increases the tear strength of the fabric decreases. The reason is poor resistance of cotton fibers to high curing temperature and cross-linking also increases as temperature increases. Effect of curing temperature on tear strength was shown in Figure 8.

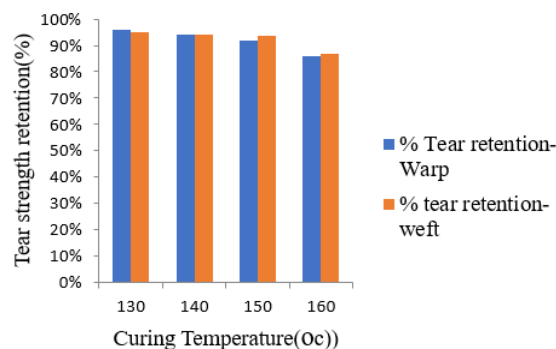


Fig. 8 Effect of curing temperature on tear strength

### 3.10 Colour Fastness property

The colour changes of the dyed samples, and the staining of the white fabrics, were assessed using the grey-scale, and the results are shown in Table2. The rubbing fastness of the combined dyed and finished with citric acid alone is better than the combined dyed and finished with citric/fibroin due to darker shade was obtained with

combined dyed and finished with reactive dye with citric acid/fibroin solution while the Washing and Perspiration fastness of dyed and finished of cotton fabric with reactive dye/citric/fibroin ranging from very good to excellent.

Table 2. Fastness property of the dyed fabric

Fastness properties		Conventional dyed fabric	Combined with CA	Combined with CA/fibroin
Washing fastness		5	4/5	5
Rubbing Fastness	Dry	5	5	5
	Wet	4/5	4/5	4
Perspiration fastness		4/5	4	5

#### 4. CONCLUSION

In this study, combining reactive dyes padding with Citric acid/fibroin solution for combined dyeing and resin finishing in one step using pad-dry-cure technique was undertaken. The results obtained indicate that the properties of the dyed and finished cotton fabrics (such as colour strength, dry wrinkle recovery angle, tensile and tear strength) are affected by a variety of factors. These include the concentrations of the citric acid, fibroin and the curing temperature. Relatively satisfactory properties of dyed and finished cotton fabric can be obtained with optimum treating conditions of citric acid (40g/l), fibroin solution (8%) and at curing temperature of 150oc. The significant increase in wrinkle recovery and colour strength (k/s) value of the Dyed fabric were obtained with adding high concentration of fibroin solution in combined processes., but had a slightly negative influence on the tensile strength property of the treated fabric samples.

#### REFERENCES

- [1] P.S.Özdemir and S.J.E.C.Şaşmaz, "Economical one step process for simultaneous application of pigment dyeing and wrinkle recovery finishing of cotton fabrics", 5(2), pp 425-436, 2018.
- [2] Huaifang Wang, Chuanjie Zhang, Xudong Chu and Ping Zhu, "Mechanism of ant wrinkle finishing of cotton fabrics using mixed polycarboxylic acids", International Journal of Polymer Science, 2020.
- [3] E.Solomon, "Finishing of Cotton Fabrics using Monochlorotriazine Reactive Dyes and Citric Acid with Pad-Dry-Cure Methods".
- [4] M.D.Teli, O.E.J.I.R.J.o.E. Gurmu, and Technology, "Simultaneous acid dyeing and modified DMDHEU finishing of cotton fabrics for process intensification", 4(3), pp 163-172, 2017.
- [5] O.K.Alebeid and T.J.T.J.O.T.T.I. Zhao, "Simultaneous dyeing and functional finishing of cotton fabric using reactive dyes doped with TiO<sub>2</sub> nano-sol", 107(5): pp 625-635, 2016.
- [6] M.K. Uddin et al. "Effective Cross-linking Dyeing Method for Jute Fabric with Reactive Dyes", 15(27): p. 125-135, 2019.
- [7] E.J.Blanchard, et al., "Dyeable cross-linked cellulose from low formaldehyde and non-formaldehyde finishing systems", 33(4), pp 1030-1034, 1994.
- [8] A.Nathany, et al., "Optimization of concentration of ingredients for simultaneous dyeing and finishing using response surface methodology", 105(11): p. 1146-1159, 2014.
- [9] Y.Dong, J.Wang and P.J.C.T. Liu, "Dyeing and finishing of cotton fabric in a single bath with reactive dyes and citric acid", 117(5), pp 262-265, 2001.
- [10] H.Choi, "One-bath dyeing and nonformaldehyde durable press finishing of cotton using dialdehyde and a monochlorotriazinyl reactive dye", 2002. 72(6), pp 469-473, 2002.