

SALT FREE SULPHUR BLACK DYEING OF COTTON FABRIC AFTER CATIONIZATION

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Most dyeing processes need a large amount of salt for dye exhaustion from the dye-bath onto fabric, which ultimately results in the discharge of a large amount of saline effluent, producing threats to the aquatic environment. This research investigates the cationization of cotton fabric, which avoids the consumption of salt during dyeing. Pretreatment of fabric was carried out using a commercially available cationic agent named 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC). Then, pretreated fabric was subjected to dyeing using solubilized Sulphur Black dye. The pretreated fabric presented increased color strength values and colorfastness properties.

Keywords: cotton, dyeability, sulphur dye, pretreatment, cationization

INTRODUCTION

Cotton is a natural cellulosic fiber that is the backbone of the world's textile trade.¹ Cotton possesses some good properties, such as hydrophilicity, biodegradability and no static charge. After scouring and bleaching, cotton is almost 100% cellulose.²

Dyeing is a process of coloration of textile goods to make them more attractive. Direct, reactive, sulphur and vat dyes are usually used for dyeing cellulosic substrates.³⁻⁶ The polymer chain of cotton consists of many hundreds to thousands of β (1-4) D-glucose units, which are linked to each other, and upon immersion into water, a negative charge is created on cotton surface.⁷ The dyes used for cotton coloration also have negative charge, that is why a dye molecule moves away from cotton fibers because of electrostatic repulsion between two negatively charged species.^{8,9} To overcome this problem, in the textile industry, a large amount of salt is required to achieve high exhaustion of the dye from the dye-bath to cotton fibers.²

On an industrial level, when, during the dyeing

process, salt is mixed with dyes and other auxiliaries, it becomes very dangerous, because the loaded effluent causes environmental pollution. An excess of salt in water is very dangerous for drinking, agriculture and for marine life. Water containing a TDS (total dissolved solids) level of over 500 mg/L is unsuitable for irrigation and has an unpleasant taste. For dyeing cotton, its chemical modification can be done without the consumption of salt, modifying the hydroxyl groups present on the cotton polymeric structure.¹⁰ The approach of cotton yarn cationization was used on a commercial level by Japanese companies, such as Kurabo Industries, Toyobo. The fabrics made from these cationized dyed yarns exhibit different colors and cross-dye effect.^{11,12} Ali *et al.* cationized cotton using a cationic polymer under alkaline conditions by the exhaust method to enhance the dyeability for natural dyes, which enhanced the dye uptake and fastness properties of the treated textiles.¹³

Lewis used 2,4-dichloro-6-(2-pyridinoethylamino)-s-triazine (DCPEAT) to

modify cotton under alkaline conditions, to improve dye substantivity without salt. The modified cotton became more reactive, compared to the original cotton.¹⁴ Bhuiyan *et al.* also worked on the modification of cotton for reactive dyeing using chitosan and their research led to the conclusion that the dye uptake was improved and no fastness deterioration had occurred in the dyed fabric treated with chitosan.⁷

Wang *et al.* worked on the modification of cotton for reactive dyeing using 1-chloro-2-hydroxy-3-trimethylammoniumpropane chloride. This modification resulted in improved dyeability of the cotton fabric, along with wash and light fastness.¹⁰ S. Draper *et al.* worked on the cationization of cotton using the CHPTAC cationic agent. Their research showed that dyeing using modified cotton results in increased K/S and reduced dyeing cycle time using direct dyes. It was also established that if an excess amount of CHPTAC was applied, it might cause yellowing of cotton fabric.¹⁵

Lewis *et al.* modified cotton by using N-methylolacrylamide (NMA), which was further aminated using ammonia containing various amines, *e.g.* methylamine and ethanolamine. After this treatment, cotton fabric was dyed with a reactive dye in a slightly acidic bath without an electrolyte. It was concluded that dye buildup and fixation were improved by introducing primary and secondary amino groups. The presence of tertiary amino groups caused high improvement in exhaustion, but under mild acidic conditions, fixation was badly affected.¹⁶

Sulphur dyes are one of the most popular class of dyes used for coloration of cellulosic fibers in deep black shades.^{17,18} Sulphur dyes are called like this because they contain a di-sulphide linkage in their chemical structure. Sulphur dyes are complex organic compounds synthesized by heating simple amines or phenolic compounds in the presence of sulphur. As sulphur dyes are water insoluble, they need to be solubilized before application on cotton using sodium sulphide.

Sulphur dyes are also used because of their low price and excellent color fastness properties, except against chlorine.¹⁹⁻²⁶ Worldwide consumption of sulphur dyes for dyeing cellulose fibers is of 7%.²⁷ On cellulosic fibers, sulphur dyes provide inexpensive medium to heavy shade depths, moderate to good light fastness and good wet fastness.^{18,28} This research work is focused on cationization of cotton fabric with cationic agent CHPTAC, in different concentrations, for optimization of sulphur dyeing without salt to obtain different shades.

EXPERIMENTAL

Materials

The pretreated and mercerized cotton fabric (ends/inch 120, picks/inch 121, warp 35s, weft 40s and GSM 130) used in this study was available from the lab the authors are affiliated to. The cationic agent, 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC 60 wt% in water), was purchased from Aldrich. The leuco form of sulphur black dye, Diresul Black RDT D liquid, provided by Archroma, Pakistan, was used in this research.

Cationization

Cationization of cotton fabric was carried out using four different concentrations of CHPTAC, as mentioned in Table 1, by keeping constant the liquor ratio of 1:10. Distilled water was taken in a beaker and CHPTAC was slowly added to it under continuous stirring on a magnetic stirrer, followed by the addition of 50% NaOH, as mentioned in Table 1, to maintain the pH around 13.5. Cotton fabric was immersed in the solution for 15 min at room temperature, followed by squeezing using a padder at 100% pickup. Then, the samples were batched in an air-tight polyethylene bag for 24 h. The batched fabric was then washed five times with water and dried in an oven.

Mechanism of cationization

As shown in Figure 1, in the first stage, CHPTAC converts to its epoxide form, due to the presence of chlorine in its molecule, which is highly electronegative. This epoxide species is a good nucleophile, which will be covalently bonded with the cellulosate anion, as shown in Figure 2.

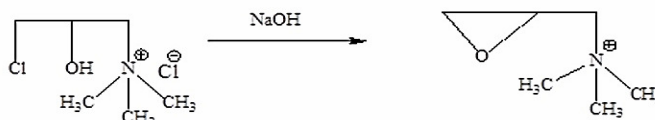


Figure 1: Conversion of CHPTAC to its epoxide form

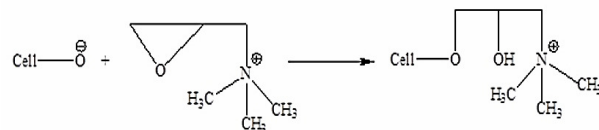


Figure 2: Reaction of cellulose with CHPTAC (epoxide form)

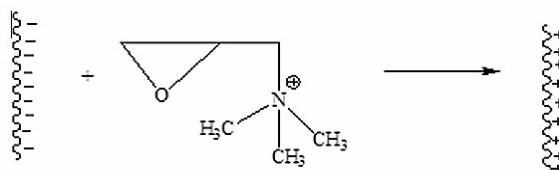
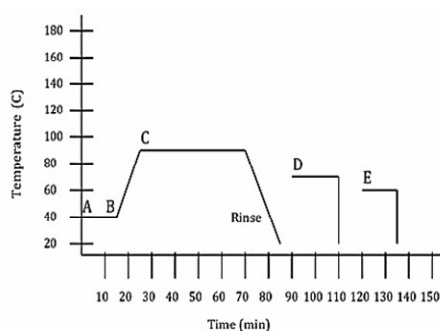


Figure 3: Cationic cellulose after the reaction with CHPTAC



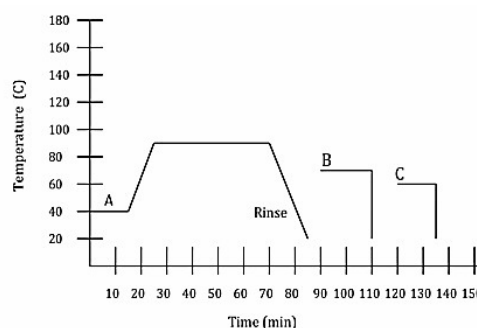
A	<ul style="list-style-type: none"> • Squestrant • Wetting agent • Caustic soda • Sodium sulphide • Solublized sulphur dye
B	<ul style="list-style-type: none"> • Half amount of salt
C	<ul style="list-style-type: none"> • 2nd half amount of salt
D	<ul style="list-style-type: none"> • Oxidation
E	<ul style="list-style-type: none"> • Detergent

Figure 4: Conventional dyeing profile

After the reaction of CHPTAC with cellulose, the cellulosic substrate is cationized due to the presence of quaternary amines in the CHPTAC molecule. The schematic of the reaction is shown in Figure 3. There is also an amount of active CHPTAC, which might be hydrolyzed.

Conventional dyeing

Conventional dyeing was carried out with four different shade percentages, of 1, 2, 4 and 6 o.w.f. (on weight of fabric), as mentioned below in design of experiments (DOE). The dyeing solution was made using 1 g/L of wetting agent, 1 g/L of sequestering agent, 5-10 g/L sodium sulfide, 1-4 g/L caustic soda (as a function of shade depth), 20 g/L of Glauber's salt (for all the shades) and solubilized sulphur dye. Figure 4 shows the dyeing procedure for conventional dyeing; the dyeing process was carried out in a high



A	<ul style="list-style-type: none"> • Squestrant • Wetting agent • Caustic soda • Sodium sulphide • Solublized sulphur dye
B	<ul style="list-style-type: none"> • Oxidation
C	<ul style="list-style-type: none"> • Detergent

Figure 5: Modified dyeing profile after cationization

temperature pot dyeing machine at a liquor ratio of 1:20. Salt was added in two portions, at point B and C, to achieve level exhaustion. The dye bath pH was maintained at 11, and dyeing was carried out for 45 min at 90 °C. The dyed fabric was oxidized at stage D, using potassium dichromate (2% o.w.f) with 2-3 drops of acetic acid at 70 °C for 20 min. The fabric was washed with tap water and then hot washing was performed, using 1 g/L detergent at 60-70 °C. Finally, the samples were dried in an oven.

Dyeing of cationized cotton

Cationized cotton was dyed using a wetting agent, a sequestering agent, sodium sulfide, caustic soda and solubilized sulphur dye of four different shade percentages of 1, 2, 4 and 6 o.w.f., as used in the case of conventional dyeing. The amount of all dyeing auxiliaries was used exactly as mentioned above with

regard to conventional dyeing. No salt was added during dyeing of cationized cotton. The dyeing was carried out in a high temperature pot dyeing machine at a liquor ratio of 1:20. The modified dyeing procedure is described in Figure 5. The dye bath pH was maintained at 11 and dyeing was carried out for 45 min at 90 °C. The dyed fabric was oxidized using potassium dichromate (2% o.w.f) at stage B, with 2-3 drops of acetic acid at 70 °C for 20 min. Then, the fabric was washed with tap water and subsequently hot washing was done using 1 g/L detergent at 60 °C.

Finally, the samples were dried in an oven.

Design of experiment

Table 1 indicates the design of experiments (DOE), for a total number of experiments of 20. The first 4 cotton fabric samples were dyed using salt (the conventional method) and the rest, representing CHPTAC cationized cotton fabric, were dyed by the modified procedure with different dye concentrations to achieve various shade depth.

Table 1
Design of experiments

Run order	CHPTAC (g/L)	NaOH (50%)	Shade depth (%)
1	0	0	1
2	0	0	2
3	0	0	4
4	0	0	6
5	10	10	1
6	10	10	2
7	10	10	4
8	10	10	6
9	20	20	1
10	20	20	2
11	20	20	4
12	20	20	6
13	40	40	1
14	40	40	2
15	40	40	4
16	40	40	6
17	60	60	1
18	60	60	2
19	60	60	4
20	60	60	6

RESULTS AND DISCUSSION

Washing fastness

Figure 6 shows the washing fastness of conventionally dyed uncationized fabric and that of cationized fabric, while the washing fastness of the control fabric was 4, according to the grey scale. ISO 105 C06 testing standard was followed to determine the washing fastness. The dyed fabric, cationized with 60 g/L of CHPTAC, showed very good washing fastness, rating 4.5 to 5 for all the shade percentages. The fabric cationized with 40 g/L of cationic agent also showed a good rating, as compared to the uncationized fabric. This can be explained by the fact that the dye is anionic in nature and gets attached to positively charged fabric *via* the electrostatic force of attraction and hence is difficult to remove. The washing fastness to staining was also checked using a multifiber strip and no staining was observed on the multifiber

strip. Hence, the washing fastness to color change and staining of the cationized fabric was better than that of the uncationized fabric.

Light fastness

The light fastness of all the samples was assessed according to ISO 105 B02 standard and the results are shown in Figure 7. A little change in the light fastness of cationized and uncationized fabric was observed. From Figure 7, it is obvious that light fastness was improved as the concentration of cationizing agent was increased from 0 to 60 g/L. The reason for the increase in light fastness with increasing cationization can be assumed to lie in the fact that the positive charge on cotton increases with the increase in CHPTAC application. The amount of dyestuff per unit area of fabric increases quantitatively due to the chemical potential difference. Therefore, the number of faded dye

molecules remains the same, irrespective of the shade depth, as the light falls on a constant surface area. Hence, the light fastness of fabric cationized with a higher number of molecules (because of higher surface cationization) increases.

Rubbing fastness

Figure 8 shows the results for dry rubbing fastness of dyed cationized and uncationized samples, which were assessed according to ISO105 X12 standard. It was observed that the cationized samples exhibited high rating of dry rubbing fastness, as compared to the uncationized fabric. As the concentration of the cationic agent increased, the rubbing fastness also increased. It can be attributed to the fact that cationization creates more reactive sites on cotton fiber and hence promotes the bonding of dyes. The more strongly the dye is bonded, the higher the rubbing fastness, as well as the washing fastness. Figure 9 illustrates the wet rubbing fastness of the dyed cationized samples. As commonly known, the dry rubbing fastness is better than the wet rubbing

fastness in the case of both cationized and uncationized fabrics. The best rating with regard to dry rubbing fastness is 5, according to the grey scale, and for wet rubbing fastness, the best rating is 4. It was also observed that the dry and wet rubbing decreased with the increase in shade depth, which is quite understandable. As the amount of dye molecules (with increased color depth) increases, there is a higher chance for the dye molecules to rub off from the surface of the fabric, despite their attachment to the fabric. Figures 8 and 9 illustrate this phenomenon, as the shade depth increases.

Color strength (K/S values)

Figure 10 presents the color strength (shade depth) of all the dyed cationized and uncationized samples. It was observed that shade depth increases as the concentration of the cationic agent rises. This may be explained by the fact that a more cationic nature of fabric will help the exhaustion of anionic dye molecules towards it, which contributes to higher K/S values of the fabric, enhancing its color strength.

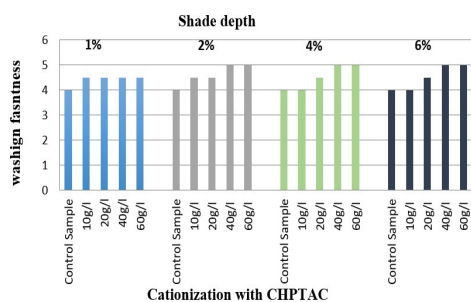


Figure 6: Washing fastness rating of dyed cationized and uncationized cotton samples

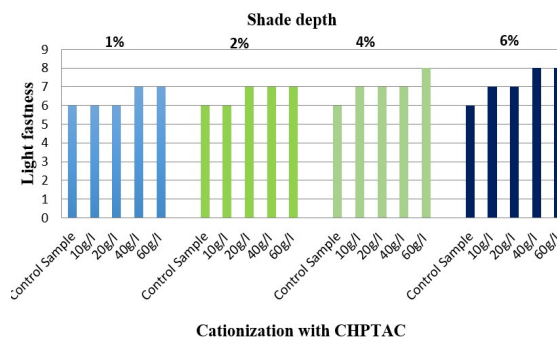


Figure 7: Light fastness rating of dyed cationized and uncationized cotton samples

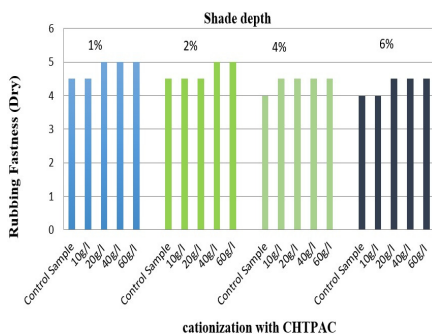


Figure 8: Dry rubbing fastness of dyed cationized and uncationized cotton samples

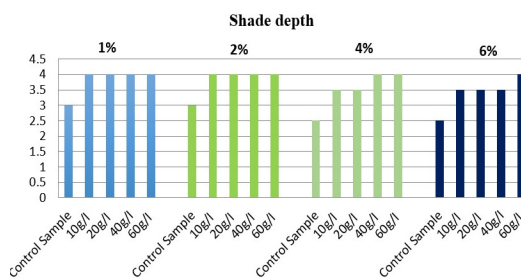


Figure 9: Wet rubbing fastness of dyed cationized and uncationized cotton samples

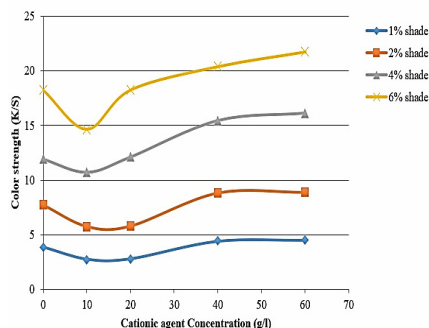


Figure 10: Color strength measurements of dyed uncationized and cationized samples

A further explanation of the increase in color strength is illustrated in Figure 11. The cationized fibers bearing positive charges due to quaternary amines will have higher affinity for the reduced sulphur dye molecules and will have enhanced buildup. The K/S values for the dyed cationized cotton are higher, compared to those of the conventionally dyed fabric, in the case of a higher amount of CHPTAC. However, with a lower amount of CHPTAC, the K/S values are lower than those for the untreated cotton, as salt was added in the conventional dyeing procedure, which led to higher dye uptake.

CONCLUSION

Using salt in the textile dyeing process has a huge impact on the environment. The research work reported here concludes that by cationizing cotton fabric using the CHPTAC cationizing agent prior to dyeing can eliminate the consumption of salt for the exhaustion of anionic dye molecules. Cationic agents have the ability to develop a positive charge on cotton fabric and hence anionic dye molecules develop an affinity towards fabric. Besides the elimination of salts in dyeing, this process also provides dyed fabric with enhanced fastness properties, including washing, light and rubbing fastness. Furthermore, the dyed cationized samples exhibit better color strength values (K/S), as compared to the uncationized one.

REFERENCES

- ¹ J. Bomeman, "Fiber Triology", Textile World, 2005.
- ² S. Acharya, N. Abidi, R. Rajbhandari and F. Meulewaeter, *Cellulose*, **21**, 4693 (2014), <https://doi.org/10.1007/s10570-014-0457-2>
- ³ M. Rupin, *Text. Chem. Color.*, **8**, 54 (1976).

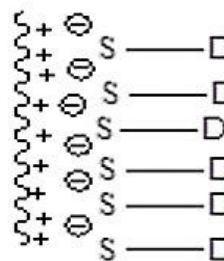


Figure 11: Exhaustion of anionic dye on cationized cotton

- ⁴ M. Montazer, R. M. A. Malek and A. Rahimi, *Fiber Polym.*, **8**, 608 (2007), <https://doi.org/10.1007/BF02875997>
- ⁵ W. E. Wood, *Rev. Prog. Color.*, **7**, 80 (1976).
- ⁶ J. R. Aspland, *Text. Chem. Colour.*, **24**, 22 (1992).
- ⁷ M. A. R. Bhuiyan, A. Shaid and M. A. Khan, *Chem. Mater. Eng.*, **2**, 96 (2014), <https://doi.org/10.13189/cme.2014.020402>
- ⁸ D. P. Chattopadhyay, *Indian J. Fibre Text.*, **26**, 108 (2001), <http://hdl.handle.net/123456789/24920>
- ⁹ B. Xu, P. Gao and C. Yang, US Patent 8038728, 2011.
- ¹⁰ H. Wang and D. M. Lewis, *Color. Technol.*, **118**, 159 (2002), <https://doi.org/10.1111/j.1478-4408.2002.tb00094.x>
- ¹¹ Toyobo Co.'s Viewline, *Jap. Text. News*, **361**, 28 (1984).
- ¹² Cationic cotton fabrics features quick delivery, *Jap. Text. News*, **361**, 26 (1984).
- ¹³ N. F. Ali and R. E. Mohamedy, *Res. J. Text. Appar.*, **14**, 21 (2010).
- ¹⁴ D. M. Lewis and X. P. Lei, in *Procs. AATCC Int. Conference and Exhibition*, Atlanta, Oct. 4-7, 1992, pp. 259-265.
- ¹⁵ S. L. Draper, K. R. Beck, C. B. Smith and P. Hauser, *AATCC Rev.*, **2**, 24 (2002).
- ¹⁶ D. M. Lewis and X. P. Lei, *J. Soc. Dyers Colour.*, **107**, 102 (1991).
- ¹⁷ C. Senior and D. A. Clarke, in "The Dyeing of Cellulosic Fibers", edited by C. Preston, Dyers Company Publications Trust, Bradford, 1986.
- ¹⁸ C. Senior, in "Cellulosic Dyeing", edited by J. Shore, Society of Dyers and Colorists, 1995.
- ¹⁹ A. Johnson, "Theory of Coloration of Textile", Society of Dyers and Colorists, 1995.
- ²⁰ J. N. Chakraborty, "Fundamentals and Practices in Coloration of Textiles", Woodhead Publishing, India Pvt. Ltd., 2010.
- ²¹ J. Shore, "Colorants and Auxiliaries", Society of Dyers and Colorists, 1990.

²² R. M. Christie, R. R. Mather and R. H. Wardman, "The Chemistry of Colour Application", Blackwell Science Ltd., 2001.

²³ W. Ingamells, "Colour for Textiles: A User's Handbook", Society of Dyers and Colourists, 1993.

²⁴ R. B. Chavan, in "Handbook of Textile and Industrial Dyeing", edited by M. Clark, Woodhead Publishing Ltd., UK, 2011.

²⁵ J. Koh, in "Handbook of Textile and Industrial Dyeing", edited by M. Clark, Woodhead Publishing Ltd., UK, 2011.

²⁶ O. Annen, *J. Soc. Dyers Colour.*, **103**, 297 (1987).

²⁷ A. Roessler and X. Jin, *Dyes Pigm.*, **59**, 223 (2003), [https://doi.org/10.1016/S0143-7208\(03\)00108-6](https://doi.org/10.1016/S0143-7208(03)00108-6)

²⁸ S. M. Burkinshaw, in "The Chemistry and Application of Dyes", edited by D. Waring and G. Hallas, Plenum Press, New York, 1991.