

Surface Modification of Cotton Using Slaughterhouse Wastes

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Abstract: Cotton dyeing using reactive dyes is one of the major water pollutants, due to large amounts of dye and salt discharged in the water effluent. Recent adverse climate change and its associated effect to human life have led to search for more sustainable industrial production. Cationization of cotton to improve its affinity for reactive dye has been earmarked as a major solution for dyeing of cotton with no or less salt. Synthetic cationizing agents of ammonium salt have already been commercialized. However, in nature we have proteinous products which are rich in amino and ammonium salts which can be harnessed to be used as cationizing agent for cotton. This research paper reports the use of cattle hoofs and horns to cationize cotton so as to improve cotton affinity to the reactive dye. The cationization action of the hoof and horn extract on cotton was confirmed by dyeing the pretreated fabric without salt and comparing it with conventionally dyed sample. Using UV-VIS spectrophotometer better absorption (62.5% and 50% for dye bath exhaustion percentage for cationized and untreated respectively) were recorded for the cationized fabric, while K/S values of treated samples were similar to conventional sample.

Keywords: Slaughterhouse waste; cationization; cotton; reactive dyes; proteinous products

1. INTRODUCTION

Dyeing is one of the essential processes of materials for value addition. Among the industrial sector, Textile industry has been one of the largest dye intensive industries in the world. Cotton is the world's most widely used natural fiber being versatile in its application and easily available. For cotton dyeing, anionic dyes have been used very often and they are, by consumption, the most important textile dyes.

The coloration of cotton involving anionic dyes, require vast amounts of salt for efficient dye utilization and fastness requirements. As a result, large amount of salt is discharged in the dye bath effluent (Chattopadhyay et al., 2007; Montazer et al., 2007). Therefore, an alternative approach to cut on salt consumption and improve dye utilization is important. Processes that consume less dye and salt are more sustainable and less polluting. Many academic researchers and industry professionals have developed alternative methods for more sustainable coloration practices of cotton. However, many of these

improvements have not been commercialized and may require large capital investments, and/or increased processing costs. Additionally, none of these innovations provide a fully sustainable method for the coloration of cotton goods. Cationized cotton had presented itself as one of the most viable and sustainable alternatives to conventional reactive dye applications to cotton. However, cationization using synthetic agents is not also sustainable alternate as the chemicals are non- biodegradable, toxic and expensive (Chattopadhyay et al., 2007; Montazer et al., 2007; Knudsen et al., 1996). Higher electrolyte concentration in the effluent causes worst effect such as; impairing the delicate biochemistry of aquatic organism, destructive attack on pipes if sodium sulphate is used as electrolyte due to the formation of alumino-sulphate complexes which swell and crack concretes with considerable alumina content. This may lead to emission of hydrogen sulphide gas under anaerobic conditions, dissolution of such sulfides and subsequent bacterial oxidation, which may form the corrosive sulphuric acid. The aforementioned process will lead to higher Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and Absorbable Oxygen Halides (AOX) (Sabramarian, 2006). Finally, if the effluent must be treated, i.e. desalinated, the additional cost of the process renders desalination unattractive just from an economical point of view.

Even with all the environmental drawbacks of utilizing fiber anionic dyes on cellulose, their use is unparalleled for cotton dyeing (Saleh et al., 2013; Ali et al., 2009). To

present a viable sustainable alternative to anionic dyes requires that similar colors and similar fastness properties be maintained while improving the ecological aspects of cellulosic coloration.

At an academic level, several improvements and technological advancements have been made and suggested, however, the practicality of many of these improvements is questionable.

In coming years, the textile industry must implement sustainable technologies and develop environmentally safer and efficient methods for textiles processing to remain competitive. Thus, seeking environmentally safer options to cut or reduce salt and improve dye utilization is important. The options to reduce salt are; process improvements, recycling the salt contaminated dye bath after dyeing, molecular engineering of anionic dye to have higher affinity and good wash off properties and, molecular modification of fiber to have greater affinity and attraction towards anionic dyes (Sabramarian, 2006; Wang et al., 2014; Ristic et al., 2012; Biswas et al., 2010)

For decades, very little research was undertaken on the effects of the bath ratio of batch textile dyeing equipment because water, dye, and chemical use were of little concern. The liquor ratio, the mass or volume of water compared to the mass or volume of the fabric is now recognized as a very important and critical variable for processing of reactive dyed cellulose. Traditionally, liquor ratios ranged upward of 1:20 to 1:40 because color yield and salt utilization were not important. Typically, the

amount of salt and alkali required for batch reactive dyeing are based on a concentration, therefore in order to maintain that concentration at higher liquor ratios requires much more salt and alkali than the same process run at a lower liquor ratio.

One approach of working towards sustainable anionic dyeing practices of cotton, many researchers have recognized that the greatest efficiency and utilization of dyestuffs can be obtained by modifying cotton itself at a molecular level to contain a cationized charge and to utilize existing anionic dyestuffs. Several surface modification techniques can be used to alter the surface charge on a substrate. In spite of the great number of existing modification methods no consistent classification is available as yet. Some authors divide the methods into two groups depending on whether they involve changes in fiber composition (chemical modification) or changes in fiber structure (physical modification) (Matthew et al., 2012; Shahid, et al., 2013). Chemical modification techniques can include surface patterning, photo-bleaching, plasma treatments and cationization, with the first three methods needing higher initial investment (Hyde et al., 2007).

The process of modifying cotton by developing cation site on its surface without affecting its bulk property is called cationization. Modifying the cotton fibre to increase dye-fibre interactions is thus one of the routes to overcoming the lack of affinity for cotton for commercial reactive dyes, so that it can be dyed without salt. It was found that during cationization of

cotton, etherification of primary hydroxyl groups on cellulose takes place (Ristic, et al., 2012, Chaiyapat, et al., 2002).

A number of processes have been proposed from early 1930s, till date to improve the substantivity of anionic dyes towards cellulosic fibers by introducing cationic sites on the fibres. Schlack was the first to report improved affinity of acid dyes towards cellulose modified through the introduction of aminated epoxy groups and then Rupin and Rupin studied the dyeability of cellulose towards direct and reactive dyes after pretreatment with glycidyltrimethyl ammonium chloride (Chattopadhyay et al., 2007). It was reported that the Glytac pretreatment improved the dyeability of cotton with reactive dyes in the presence of alkali and salt. Wu and Chen (Hauser et al., 2001) treated cotton with polyepichlorohydrin (PECH) dimethylamine which was manufactured by initial polymerization of epichlorohydrin, followed by amination with dimethylamine. The epichlorohydrin was polymerized in carbon tetrachloride using boron trifluoride etherate as catalyst. The dyeability of treated cotton towards direct dyes was investigated and it was found that PECH-amine could improve the direct dyeability of modified cotton. In another work Wu and Chen (Hauser et al., 2001) reported the effect of PECH-amine treatment on the reactive dyeability of cotton. It was found that the modified cotton can be dyed with selected low reactivity dyes under neutral condition using limited salt concentrations or with selected high reactivity dyes without salt. The effect of modification of cotton using various N-ethylolacrylamide derivatives has also been

investigated by El-kharadly et al (Chattopadhyay et al., 2007).

Currently, there is a growing interest in the development of biodegradable cationizing agent in keeping with the ever-growing environmental awareness. In terms of environmentally friendly, cost, and ease of application, using bio product cationizing agent, is without a doubt one of the methods for cationization of cellulose, which may provide a viable salt-free cotton dyeing method. Thus, this study has focused on cationization of cotton using cattle hoof and horn keratin hydrolysate. Cattle hoof and horn have 93.3% crude protein, Keratin, which is a poly peptide. Although it has been known for many years that these keratins differ markedly in amino acid composition, it has been shown only recently that this variability in composition is due to variations in their content of three constituent protein groups which have vastly different compositions. The keratins appear to be built to the same plan with filaments (microfibrils), often aligned, of about 7•0 nm diameter embedded in a non-filamentous matrix (Mokrejš et al., 2011). The filaments appear to be composed of proteins (low sulphur) which are lower in sulphur content than the parent keratin, whilst the matrix contains two groups of proteins-one group is rich in cystine (high-sulphur proteins) and the other is rich in glycine and tyrosine (high-tyrosine proteins) (Karthikeyan et al., 2007).

Ethiopia is believed to have the largest livestock population in Africa. The estimates of the total cattle population are 53.99 million (Fig. 1). Livestock is a significant

contributor to economic and social development in Ethiopia at the household and national level. The cattle horns and hoofs are simply disposed to the nearby environment without any treatment. Keratins are difficult to degrade by the common proteolytic enzymes and their disposal leads to environmental problems (Omole & Ogbiye, 2013). Moreover, hoof and horns are hard keratin material which have very slow decomposition rate.

If the waste could be used as a valuable resource, it could not only turn waste to treasure, but also reduce environmental pollution. This has been reported in many studies in relation to the application of other waste. However, no one has conducted a study on the use of hoof and horn keratin as a dyeing auxiliary. From theoretical considerations cattle hoof and horn keratin will have good reactive properties due to the presence of a large number of reactive amino hydrophilic polar groups (nucleophilic groups) within its molecular structures. If it is possible to synthesize a kind of protein derivative agent, the agent can be applied to cotton, and hence enable salt-free dyeing of cotton using reactive dyes. Such an attempt will lead to use of locally available bio products (animal hoof and horn) as source of keratin hydrolysate to cationize cotton for salt free dyeing. If the experiment is successful there will be dual advantages, one the environment will be protected from accumulation of the slaughterhouse wastes and secondly the dyeing process will be able to reduce electrolytes in the dyeing water effluents. The two advantages will be a welcomed by the advocates of greener production. The

aim of this paper is to study the use of cattle hoof and horn as a sustainable material, which can be used in the cationization of cotton during the dyeing of cotton using reactive dyes.



Figure 1 Cattle in Ethiopia

2. MATERIAL AND METHODS

2.1. Materials and Chemicals

The fabric used for this study was a fully bleached cotton fabric, whose warp and weft count were 21 and 58 ends per inch and 50 picks per inch. Cattle hoof and horn was collected from Bahir Dar slaughterhouse. Chemicals used for extraction, cationization and dyeing included; NaOH, NaCO₃, H₂SO₄, NaCl, NaSO₄, Acetic acid and red DCT reactive dye.

2.2. Equipments/Apparatus

For extraction, cationization as well as dyeing all dyeing accessories; pH indicator, thermometer, beakers, measuring cylinders and pipettes were used, together with;

- i. PerkinElmer UV/VIS Spectrometer Lambda 25 for measuring colour absorption

- ii. Gretag Macbeth COLOR-EYE 3100 for measuring reflectance, K/S and CIE L*a*b*
- iii. FT-IR Spectroscopy PerkinElmer

2.3. Pre-treatment of Cattle Hoofs and Horns

The collected hoofs and horns were washed to remove impurities and dirt on the surface of hoof and horn using synthetic detergents, and then dried before crushing by manual hammering to convert to small pieces.

Hoof and horn keratin itself may not be reactive with cellulose. Therefore, the keratin in the hoof and horn must be dissolved and converted into the reactive keratin hydrolysate. Keratin protein was hydrolyzed by hydrothermal process; using NaOH at various temperatures. Extraction parameters were then optimized. Keratin hydrolysate was applied in the same processing techniques used for conventional dyeing and finishing of textiles. Pad-dry-cure was the technique that was employed to cationize cotton. The dyeing of cationized and untreated cotton was undertaken using exhaust method, and the samples evaluated using FTIR of cationized fabric. The reflectance, colour strength and K/S of dyed samples were measured using Color eye 1500. The colour absorption was measured using UV/VIS spectrometer.

3. RESULTS AND DISCUSSIONS

Extraction of keratin hydrolysate Extraction was done at different temperatures for different time interval in different pH values and optimum extraction was found at room temperature for 3 days and 100 °C for 3-hour treatment with extraction efficiency 94% and 93% respectively using 20 g/l NaOH at 12 pH.

3.1. Cationization

The sample was impregnated in 40 g/l keratin hydrolysate and was subjected to drying and curing at 100 and 135 degree centigrade for

4 and 3 minutes respectively. The peaks in FT-IR curve (Fig. 2) showed that there was a change in chemical composition after being cationized, thus the keratin hydrolysate was fixed to the fabric.

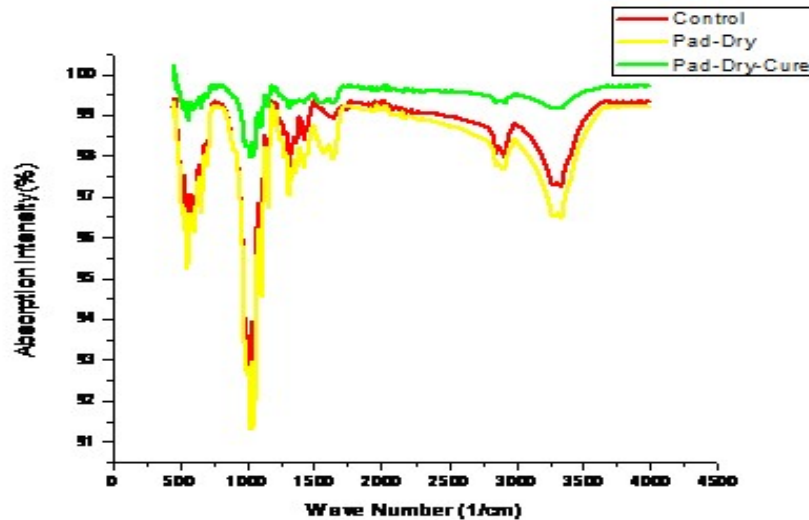


Figure 2 FT-IR Curve of Cationized and Control (Untreated)

3.2. Dyeing with DichloroTrazline (DCT) Red Reactive Dye

Dyeing was carried out as per the conventional dyeing procedures at room temperature for one hour. Washing and soaping was done for the samples. The visual observation confirmed that colour yield was higher in the cationized sample

as in Fig. 3. The K/S values measured using colour eye computer colour matching equipment also confirmed the colour yield was better in the cationized fabric as given in Fig. 4. Table 1 showed that there was no significant difference in the 'L*' (lightness) and the trichromacity coordinates of the treated and untreated samples.

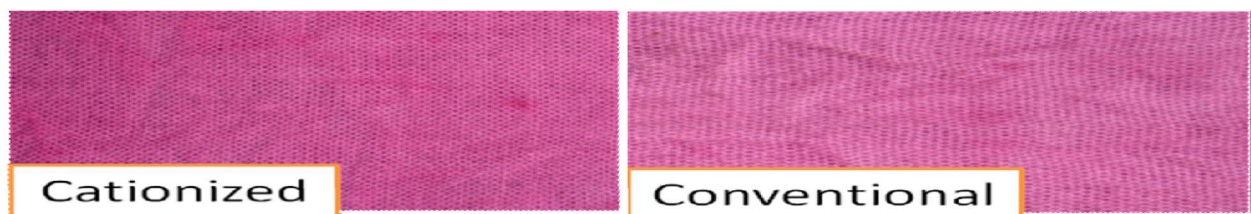


Figure 3 Dyed samples of Cationized and Conventional (using salt)

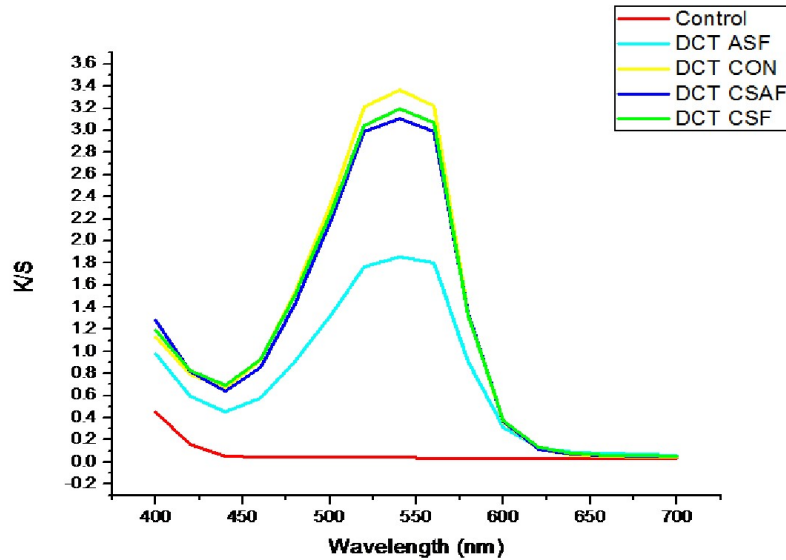


Figure 4 K/S values of Cationized and Control (Untreated) after dyeing

The cationized sample showed lower 'a*' value meaning redder and higher 'b*' value meaning bluer. The yellowness index was lower in the cationized fabric. The whiteness index was lower also which confirmed more dyes are retained in the cationized fabric.

3.3. UV/VIS Spectroscopy Result

The result showed that dye absorption is better in cationized cotton than the conventional method of reactive dyeing as indicated in Fig. 5. The dye bath exhaustion percentage was calculated using equation (1) and obtained 62.5% and 50% for cationized and untreated samples respectively.

$$\%E = (A_0 - A_1) * 100 / A_0 \quad (1)$$

Where A_0 and A_1 are the absorbencies at maximum wavelength of dye originally in the dye bath and of residual dye after dyeing respectively.

Table 1 Color Eye Computer Colour Matching Details for D Standard 10°

Colour Factors	Control Bleached fabric	DCT Conventional	DCT Cationized
L*	89.51	55.39	55.34 a*
-1.09	46.07	43.92 b*	3.78
-8.18	-7.74		
X	70.96	33.65	32.98
Y	75.24	23.31	23.26
Z	76	30.41	30.05
x	0.3194	0.3851	0.3822
y	0.3386	0.2668	0.2695
Yellowness	7.05	38.89	36.97
Whiteness	57.15	74.68	72.29

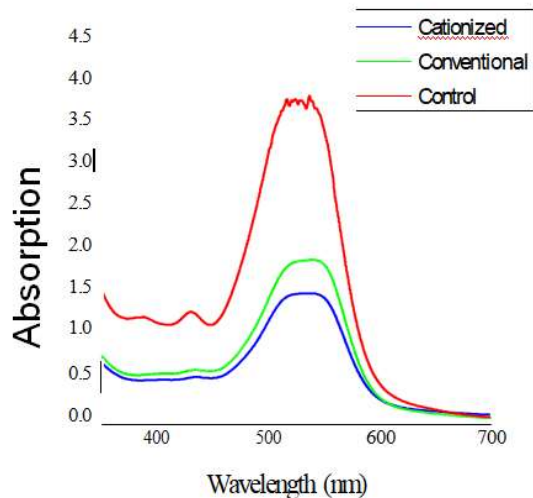


Figure 5 UV/VIS values

4. CONCLUSION

Cationization caused the change of ionic character of the cotton fabric, with 62.5% and 50% dye bath exhaustion percentage was obtained for cationized and untreated respectively. Based on all achieved results, it is evident that alkaline extract of keratin from slaughterhouse wastes imparts cationic character to cotton. Therefore, from the environmental point of view it is a good substitution of cationizing agent. That is providing not only a strategy for reducing risks and pollutants from salt and unutilized dye, but also an opportunity for new markets and new businesses that could be developed in the selling of cattle horn and hoof, which are currently considered as waste in Ethiopia.

Reference

Ali, S., Saleem, S., Umbreen, S., & Hussain, T. (2009). Cationizing efficiency and performance of antimicrobial agent on cotton fabric dyed with vinyl sulfone based reactive blue dye.

Biswas, S., Huang, X., Badger, W. R., & Nantz, M. H. (2010). Nucleophilic cationization reagents. *Tetrahedron letters*, 51(13), 1727-1729.

Chaiyapat, P., Nantaya, Y., & Edgor, A. (2002). Surface modification to improve dyeing of cotton fabric with cationic dye. *Color Tech*, 118(2), 64-68.

Chattopadhyay, D. P., Chavan, R. B., & Sharma, J. K. (2007). Salt-free reactive dyeing of cotton. *International Journal of Clothing Science and Technology*, 19(2), 99-108.

Cook, L. (1994). Increase of cotton's apparel market share has caused salinity in textile effluent streams to become a major issue. *Textile World*, 66(9), 1530-1534.

Hauser, P. J., & Tappa, A. H. (2001). Improving the environmental and economic aspects of cotton dyeing using a cationised cotton. *Coloration Technology*, 117(5), 282-288.

Hyde, K., Dong, H., & Hinestroza, J. P. (2007). Effect of surface cationization on the conformal deposition of polyelectrolytes over cotton fibers. *Cellulose*, 14(6), 615-623.

Karthikeyan, R., Balaji, S., & Sehgal, P. K. (2007). Industrial applications of keratins—A review.

Knudsen, H. H., & Wenzel, H. (1996). Environmentally friendly method in reactive dyeing of cotton. *Water Science and Technology*, 33(6), 17-27.

Matthew, J. F. (2012). Sustainable cotton dyeing. *Fiber and Polymer Science*, 1(1-234).

Mokrejš, P., Krejčí, O., & Svoboda, P. (2011). Producing keratin hydrolysates from sheep wool. *Oriental Journal of Chemistry*.

Montazer, M., Malek, R. M. A., & Rahimi, A. (2007). Salt free reactive dyeing of cationized cotton. *Fibers and polymers*, 8(6), 608-612.

Omole, D. O., & Ogbiye, S. A. (2013). An evaluation of slaughterhouse wastes in south-west Nigeria. *American Journal of Environmental Protection*, 2(3), 85-89

Ristic, N., & Ristic, I. (2012). Cationic modification of cotton fabrics and reactive dyeing characteristics. *Journal of Engineered fibers and fabrics*, 7(4), 155892501200700408.

Sabramarian, M. (2006). Influence of cationization of cotton on reactive dyeing. *Journal of Textile and Apparel Technology and Management*, 5, 1-16.

Saleh, M. S., & El-Badry, H. (2013). Dyeing of cationized cotton fabrics with natural dye extracted from acacia. *International Journal of Textile Science*, 2(2), 21-25.

Shahidi, S., Wiener, J., & Ghoranneviss, M. (2013). Surface modification methods for improving the dyeability of textile fabrics. In *Eco-Friendly Textile Dyeing and Finishing*. IntechOpen.

Wang, X. Y., & Liu, Y. (2014). The dyeing dynamics and structure of modified cotton fabric with cationic chicken feather keratin agent. *Textile Research Journal*, 84(6), 561-571.