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Surface Modification of Cotton Using Slaughterhouse Wastes

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***Abstract*—**Cotton dyeing using reactive dyes is one of the major water polluter; this is due to large amount of dye and salt remaining in effluent. Recent adverse climate change and its associated effect to human life have lead 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 there are proteinous products which are rich in amino and ammonium salts which can be carefully harnessed to be used as cationizing agent for cotton. The hoofs and horns have successfully been used to cationize cotton so as to improve cotton affinity to the 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 and untreated salt free dyed fabric. UV-VIS absorption results showed better dye absorption (62.5% and 50% dye bath exhaustion percentage for cationized and untreated respectively) while K/S values of treated samples were similar to conventional sample.

***Keywords*—**Cationization, cotton, proteinous products, reactive dyes.

I. 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 cheap, versatile in 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 and its colorant of choice, 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 [3], [4], [10]. 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 [3], [7], [10].

Presence of much amount of salt in the wastewater leads to; impairing the delicate biochemistry of aquatic life, destructive attack on pipes due to the formation of alumino-sulhato complexes which swell and crack concretes, hydrogen sulphide gas liberation under anaerobic conditions when sodium sulphate is used as electrolyte, dissolution of such sulfides and subsequent bacterial oxidation causes harmful sulphuric acid and higher Biological Oxygen Demand, Chemical Oxygen Demand, and Absorbable Oxygen Halides [11], [12]. Finally, if the effluent must be treated, i.e. desalinated, the additional cost of this processing step makes the 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 to add value [19], [20], [24]. 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 [11], [13]-[22].

For decades, no one really understood or appreciated 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 as well as for the environmental impact 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

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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.

In a continuing evolution in more sustainable anionic dye 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. There are many existing modification method, but there is no available constant classification yet. The suitable classification method is based on changes in fiber composition (chemical modification) or changes in fiber structure (physical modification) [5], [21]. Chemical modification techniques can include surface patterning, photo-bleaching, plasma treatments and cationization; the earlier three methods need high initial investment [9].

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, best route to overcoming the lack of affinity for cotton of 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 [1], [13].

A number of processes have been proposed from early 1930s, till date to improve the substantivity of anionic dyes towards cellulosic fibres 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 [3]. 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 [15] 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 trifluridеetherate 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 they have reported (Wu and Chen) [15] 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, viz. bis(N-methylol-2-cabamoylethyl)butylamine, N-(N,N0-dimethylol- 2-cabamoylethyl) diethylamine and N-(N, N0-dimethylol-2-cabamoylethyl) dimethylamine on acid dyeability has been investigated by El-kharadly et al [3].

Currently, there is a growing interest in the development of biodegradable cationizing agent in keeping with the requests of people for environmental protection. In terms of environmental friendly, cost, and ease of application, using bio product cationizing agent, is without a doubt the method of best choice for cationization of cellulose being biodegradable and renewable. Thus, this study has focused on cationization of cotton using bio products; cattle hoof and horn keratin hydrolysate. The figurative illustration of cattle hoof and horn is given in Fig. 1.

Fig. 1 Cattle Hoof and Horn

Cattle hoof and horn have 93.3% crude protein, Keratin [25], which is a poly peptide (Fig. 2). 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 [23]. 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 [14], [23]. 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) [16], [23].

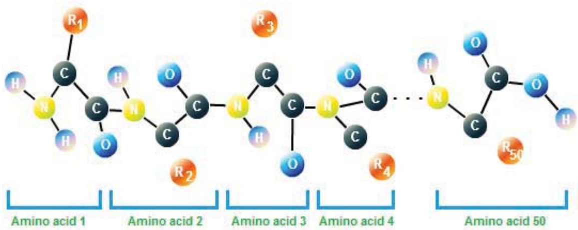

Fig. 2 Primary structure of peptides

Ethiopia is believed to have the largest livestock population in Africa. The estimates of the total cattle (Fig. 3), sheep, goat, donkey, horse, camel and mule population for the country are estimated to be about 53.99, 25.5, 24.06, 6.75, 1.91, 0.92, and 0.35 million respectively [6]. Livestock is a significant contributor to economic and social development in Ethiopia at the household and national level.

Fig. 3 Cattle in Ethiopia

The byproduct of these animals is 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 [2], [8], [18]. Moreover, hoof and horns are hard keratin which has very slow decomposition, apart from that anything does not it hoof and horn even hyena, so that it pollutes the environment for long period of time releasing bad smell.

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 the waste. However, no one has been conducted to study the hoof and horn protein-based as dyeing auxiliary.

Cattle hoof and horn keratin will have good reactive properties and dyeing ability due to the presence of a large number of reactive amino hydrophilic polar groups (nucleophilic groups) within its molecular structures, so it is possible to synthesize a kind of protein derivative agent, and this kind of agent can be applied to cotton as a salt-free dyeing auxiliary for reactive dyes.

Using locally available bio products such as animal hoof and horn as source of keratin hydrolysate to cationize cotton for salt free dyeing has dual advantage on the green economy by protecting the environment from the accumulation of the slaughterhouse wastes and by cutting the electrolyte in dyeing in effluent and wastewater.

Many researchers have tried to cationize cotton using synthetic quaternary ammonium salts to solve the limitations of cotton dyeing, but all the chemical they used can to give sustainable solution. Some are expensive, some are complex to synthesize, some chemicals need cross linking agents which in turn facilitate or release toxic chemicals. The agents are not the best greener approach and recommend using bio products but not looked over hoof and horn. Thus, this study fills the gap which is not covered by the many researchers in the globe.

II. Experiment

A. Materials and Chemicals

Full bleached cotton fabric with 21Ne warp and weft count, 58 ends per inch and 50 and picks per inch was taken from EiTEX laboratory. Cattle hoof and horn was collected from Bahir Dar slaughterhouse randomly. Chemicals used for extraction, cationization and/or dyeing; NaOH, NaCO3, H2SO4, NaCl, NaSO4, Acetic acid, and water was used which are available in EiTEX laboratories. Red DCT reactive dye was employed.

B. Equipment/Apparatus

For extraction, cationization as well as dyeing all dyeing accessories; pH indicator, thermometer, beakers, measuring cylinders and pipettes were used, as major and unique equipments the following were functional.

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

Ordinary washing and drying to remove impurities and dirt on the surface of hoof and horn using synthetic detergents and exposure to sunlight and then dryer was the first step and crushing by manual hammering to convert to small pieces.

Hoof and horn keratin itself may not reactive with cellulose. In order for, keratin must be dissolved and converted into the reactive keratin hydrolysate. Keratin protein was hydrolyzed by hydrothermal process; using NaOH at room temperature and 100 ^{0}C for different time intervals. 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 taken place by exhaust method.

Ft-IR of cationized fabric, reflectance, colour strength and K/S of dyed samples were measured using Color eye 1500. The colour absorption was measured using UV/VIS spectrometer.

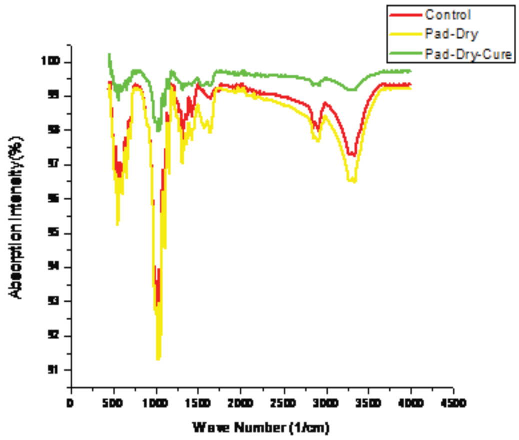

Fig. 4 FT-IR Curve of Cationized and Control (Untreated)

III. Results and Discussion

A. 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 0C for 3-

hour treatment with extraction efficiency 94% and 93% respectively using 20 g/l NaOH at pH>12.

B. 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. 4) showed that there is a change in chemical composition after being cationized, thus the keratin hydrolysate was fixed to the fabric.

C. Dyeing with Dichloro Trazline (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 both samples. The visual observation confirmed that colour yield was higher in the cationized sample as below in Fig.5.

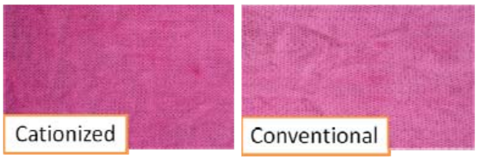

Fig. 5 Dyed samples of Cationized and Conventional (using salt)

The K/S values measure using coloured eye computer colour matching also confirmed the colour yield was better in the cationized fabric as given in Fig. 6.

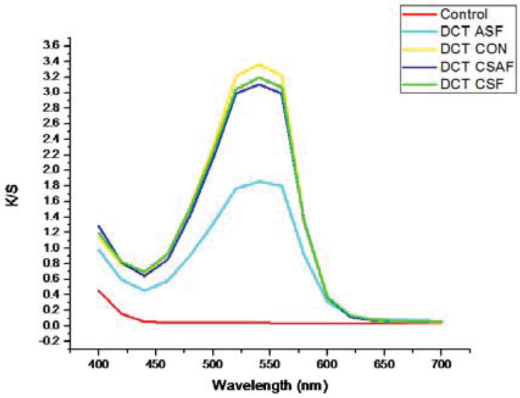

Fig. 6 K/S values of Cationized and Control (Untreated) after dyeing

TABLE I
COLOR EYE COMPUTER COLOUR MATCHING DETAILS FOR D STANDARD 100

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

Table I showed that there was no significant difference in the 'L*' (lightness) and the trichromacity coordinates of the treated and untreated samples. 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.

D. 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. 7.

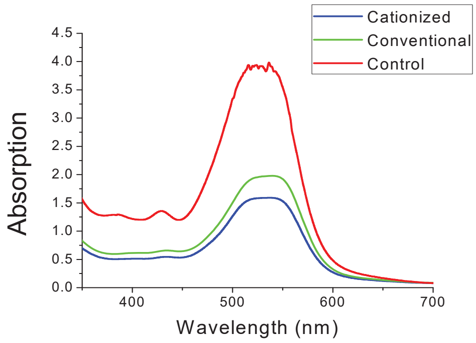

Fig. 7 UV/VIS values

The dye bath exhaustion percentage was calculated using (1) and obtained 62.5% and 50% for cationized and untreated respectively.

$$\%E = (A0-A1)*100/A0 \quad (1)$$

A0 and A1 are the absorbencies at maximum wavelength of dye originally in the dye bath and of residual dye after dyeing respectively.

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