



Keywords

Cotton,
Soya Protein,
Extracted Amino Acids,
Pre Oxidation,
Cationization

Received: June 26, 2015

Revised: July 3, 2015

Accepted: July 4, 2015

Cationization of Periodate Oxidized Cotton Cellulose of Muslin Fabric Using Natural Amino Acid Extract from Soya Bean Seed Waste and Its Eco-Friendly Dyeing

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Citation

Ashis Kumar Samanta, Tapas Ranjan Kar, Asis Mukhopadhyay, Debashis Shome, Adwaita Konar. Cationization of Periodate Oxidized Cotton Cellulose of Muslin Fabric Using Natural Amino Acid Extract from Soya Bean Seed Waste and its Eco-Friendly Dyeing. *Journal of Materials Sciences and Applications*. Vol. 1, No. 4, 2015, pp. 142-154.

Abstract

Bleached cotton fabric pre-oxidized with NaIO_4 (oxy-cotton) was chemically modified with natural amino acids extracted from soyabean seed waste by pad-dry-calendering process to investigate the changes in textile properties and its dyeability with reactive dye. This soya protein modified cotton (soya-cotton) incorporates new functional groups producing- NH_3^+ or NH^+ -ion (cationic groups) in acid bath to obtain cationized cotton rendering it to salt free reactive dyeing with acceptable shade depth and mechanical properties. Bi-functional High exhaustion reactive dye shows better dye uptake than mono-functional cold brand as well as hot brand reactive dye. Moreover, application of dye fixing agent further improves surface color depth (K/S) of the soya modified cotton fabric. Study of surface morphology of said chemically modified cotton substrate indicate surface anchorage of treated amino acids on the oxy-cotton fabric surface than control cotton fabric. Corresponding reaction mechanism for such modifications were analyzed with FTIR spectroscopy. Finally it is revealed that oxidized cotton treated with soyabean seed waste extract provide a new route of acid bath salt free reactive dyeing showing higher dye uptake.

1. Introduction

Cotton muslin fabric is an ancient heritage of India. Handspun finer cotton yarns of special characteristics are used to produce cotton muslin fabrics having 35 to 75 g/m² areal density and that are being made locally in three or four locations in West Bengal, Tamil Nadu and Kerala in the Indian subcontinent and Dhaka, Sonargaon, Dhamrai, Teetbady, Junglebary and Bijitpurin Bangladesh as the availability of fine variety cotton like SUVIN variety is rare. The special characteristics of the muslin fabric are its light weight, transparent appearance, low cover factor¹, high drape and elegant look creating its special export potential to the weight, transparent appearance, low cover factor¹, high drape and elegant look creating its special export potential to the other countries from

India and Bangladesh, as a eco-friendly handspun special type of finest cotton fabric available in the world. Such variety of cow-dung bleached cotton muslin fabrics are generally used as dhoti, saree, finest transparent decorative and home furnishing, other diversified uses etc. and has noteworthy economic and social importance along with significant role in self-employed occupation.

This SUVIN cotton of higher staple length (approx. 38 mm) is grown in Attur, Salem district of Tamil Nadu in India or sometimes it is imported from Somalia or Egypt.² This cotton muslin fabric has a monopolistic business opportunity to the artisans of specific area in India (West Bengal, Kerala, Tamil Nadu) and Dhaka. In India, particularly in West Bengal, artisans and producers of such yarn and fabrics, purchase this SUVIN cotton to make the 2.3 to 2.7 tex cotton yarn. The special characteristics of "Suvin" cotton fibre used in making cotton muslin fabric are its high staple length, high fineness and micronaire value for which cotton muslin fabric shows lighter dyeing shades due to the higher specific surface area of the finest Suvin cotton fibre. The dye adsorption on the fibre surface is higher due to higher surface area, whilst, in comparison available internal volume is low. Hence, it is envisaged that as dyeing proceeds, there is a limit to the amount of dye that could be accommodated within the comparatively lower internal volume of the substrate resulting less diffusion which in turn limits the rate of dye uptake and therefore the extent of dye bath exhaustion.³ Due to delicate fine warp and weft yarns, the strength of cotton muslin fabric is lower than the normal cotton fabric. Although export potential is high for this eco-friendly fabric for its finest/light weight, transparent appearance, high drape and elegant look, but due to its light shades, low tensile strength it is less used in ready-made garment sectors. So it is thought that, if its functional and dyeing properties can be improved without loss of its mechanical properties, the usage of this natural soya modified cotton fabric could be in ready-made dress making etc. For fulfilling the said objectives, cotton muslin fabrics have to be modified with suitable chemical treatment for achieving required dyeing and finishing criteria without much loss of its textile related properties for diversifying its usage in garment sector in some of the dress making, finest decorative and sheeting of house hold items. Many works on chemical modification for cotton textiles are reported in literature⁴⁻⁶, but such work on a finest variety of cotton muslin fabric are rare and scanty. Now-a-days, recent trend is to carryout eco-friendly chemical processing using natural product, if possible for a need to strike a balance of its textile properties and dye ability. Hence in the present work an attempt has been made to modify bleached cotton muslin fabric with natural soya seed extract (mixture of amino acids) to optimize/balance the overall textile related properties and dye ability.

Presently researchers are finding way out for eco-friendly salt-free reactive dyeing of cotton cellulose with reactive dyes in acid bath after its pre-cationisation with different agents with or without pre-oxidation. Recently cationization

of cotton cellulose with choline chloride has got attention which paves the way of oxidation of the cotton cellulose for dyeing purpose⁶. Considering the above facts, in the present work, it is thought use full to study the effect of cationising cotton muslin fabric by natural soyabean seed extracted amino acid and also with glycine as a model single amino acid in presence of acidic catalyst by pad-dry-heat (iron) process to observe the effect of such treatment on important textile related mechanical properties and dye ability with reactive dye comparing the results in conventional alkali bath with the dyeing results in salt-free acidic bath of untreated and treated soya-cotton cellulose.

2. Material and Methods

2.1. Material

Desized, scoured and bleached plain woven cotton muslin fabric (as basic cellulose material) available in the local market, made from 2.7 tex hand spun cotton yarns as warp and 2.7 tex hand spun cotton yarns as weft, 47 ends per cm and 62 picks per cm, fabric are areal density 38g/m² has been used in the present work. This finest and very delicate cotton muslin fabric was bleached by standardized cow dung bleaching⁷⁻⁸ process.

Hot brand reactive dye Colron Red HE7B (C.I. Reactive Red 141), Reactive Blue H5G (C.I. Reactive Blue 25) and cold brand Procion Red M8B (C.I. Reactive Red 11), Cationic quaternary ammonium compound based Dye fixer agent i.e. "Optifix WE.IN" obtained from M/s Archroma India Pvt. Ltd. formerly M/s Clariant Chemicals (India) Ltd, UV absorber based on hydroxy-benzotriazole compound obtained from Loba chem. (India), Magnesium Chloride (MgCl₂) as a catalyst from M/s Thermo fisher scientific India Pvt Ltd, Laboratory grade sodium carbonate (Na₂CO₃), Hydrochloric acid (35% Conc.) sodium chloride (NaCl) and commercial grade sodium hydroxide (NaOH), Hydrated calcium hydroxide (Ca(OH)₂) have been used in the present work. Sodium meta periodate (NaIO₄) as oxidizing agent from M/s Loba-chem, soyabean seed waste purchased from local market have been used.

2.2. Methods

2.2.1. Bleaching

The bleaching of very delicate cotton muslin fabric was carried out by treating the fabric in filtered cow dung solution (pH 7-8) for one and half hour followed by steaming at 100°C for 30 minutes and then washing and drying to get uniform bleached cotton muslin fabric by this eco-friendly bio-pre-treatment.

2.2.2. Extraction of Amino Acids from Soya Seed Waste

200gm of soyabean seed waste purchased from the local market has been treated with 10% hydrochloric acid for 24 hours at room temperature (27±3°C). The solution is then

filtered and the pH of the solution was brought to 5.7 to 6.0 by addition of dilute caustic soda (NaOH) solution. The solution is then filtered to remove any solid on precipitated salts and the filtrate was taken as soya bean seed extracted amino acid solution-A.

It is observed in LCMS⁹ that amino acid content in this hydrolyzed soya bean seed waste was 19.72% which constitutes total 17 types of amino acids out of which glutamic acid and arginine contents are higher.

2.2.3. Pre-Oxidation of Cotton Muslin

This bleached cotton fabric (S1) was treated with varying concentration of 1%, 2%, 3% and 4% aqueous solution of NaIO₄ at room temperature (27±3°C) for a period of 30 minutes to 2 hours in an increasing duration steps of 30 minutes for each concentration (S2 to S17 respectively*) with M:L ratio 1:20. The NaIO₄ treated fabric was then washed and dried in air at room temperature in each case to obtain a low degree of oxidized cotton muslin fabric (Oxy-cotton). However, before disposal of residual liquor of oxidation bath, sodium thiosulphate (Na₂S₂O₃) is required to be added and then to be neutralized with soda ash or sulphuric acid as needed for discharging it to large excess water. The Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) after 5 days at 20°C along with the pH value of 1% solution of NaIO₄ neutralized residual solution is measured as per IS:3025-Part 58:2006 and IS:3025-Part 44:1993 respectively and depicted in Table 1.

Table 1. The chemical analysis of NaIO₄ neutralized residual solution.

pH	COD(mg/liter)	BOD(mg/liter)
7-8	8.0	3.0

2.2.4. Cationization of Cotton and Oxy-Cotton Cellulose by Treatment with Soya Seed Extract

Bleached cotton oxidized fabric samples (S2 to S17) were padded with aqueous amino extracted solution-A (as mentioned above) in presence of specified concentration (1/5th of the content of amino acid) of MgCl₂ using two-bowl laboratory padding mangle (2 dips and 2 nips) at 100% wet pick up. The treated fabric was then subjected to drying at 100°C for 10 min in hot air oven and further cured at low temperature of 110°C by calendaring (ironing) twice for 4 minutes i.e. total 8 minutes. After this, the fabric sample (termed as Soya-cotton) was dried in air before it was dyed with reactive dyes (ST2 to ST17*) to obtain a balance between dye ability and other textile related properties. The residual soya bean seed waste extracted amino acid solution was then added with hydrated lime (CaOH₂) and polyelectrolyte to bring the pH to neutral and then disposed with large quantities of water.

*The description of samples S2 to S17 are given below the foot note of Table 3 mentioned later. Samples ST2 to ST17 are the corresponding soya bean seed waste extracted amino acid treated sample so fS2 to S17.

2.2.5. Dyeing with Reactive Dye (by Conventional and Nonconventional Salt Free Acid Bath Process)

Bleached oxidized cotton fabric samples were dyed with a Cold brand Procion Red M8B (C.I.ReactiveRed11) in a conventional alkali bath cold brand reactive dyeing process¹⁰⁻¹¹ and hot brand Colron Reactive blue H5G (C.I.Reactive Blue 25) as well as high exhaustive hot brand reactive Colron Red HE7B (C.I.Reactive Red 141) dye by conventional alkali bath hot brand reactive dyeing process¹⁰⁻¹¹

Additionally a non-conventional process of reactive dyeing in acid bath was carried out via salt free acid bath dyeing of the preoxidized and cationized (chemically modified) cotton fabric (with all three types of reactive dyes (cold brand, hot brand and high exhaustive brand) as mentioned above at room temperature for cold brand reactive dye and at 85°C for both hot brand and HE brands reactive dye for 120 mins; at material to liquor ratio 1:20, Concentration of dye 2% (owf) and pH 5 to 5.5 by addition of acetic acid¹⁰.

There active dye bath at acidic condition was initially set at pH 5 to 5.5 with addition of 1% aqueous acetic acid with or without addition of 1% aqueous hydrochloric acid solution as per need in the absence of any salt/electrolyte i.e. sodium chloride. The other conditions and procedure so f dyeing with reactive dye remain same as above; omitting the need of adding salt and soda¹¹. Finally the dyed fabrics was washed with cold water and then soaped d with 2 gpl soap solution at 60°C for 20 min, washed in running water and then dried in air. In another experiment before soaping the dyed fabric was treated with 2.3gpl solution of the mentioned cationic dye fixing agent for 30 minutes at room temperature for improving fastness.

Testing methods

Before carrying out any physical testing, all the fabric samples were conditioned for 48 hours at 65% (±5%) relative humidity and 27°C (±2°C) temperature as per IS:6359-1971 method¹².

The warp-way bending length (C₁) of untreated and selectively treated cotton fabrics were measured as per IS:6490-1971 (cantilever test) method¹³ using a SASMIRA stiffness tester with a specimen size of 200mmX25mm. The total (warp-way plus weft-way) crease recovery angle (CRA) of untreated and selectively treated cotton fabric samples was measured in degree as per IS:4681-1968 method¹⁴ allowing 5min loading (using 1000g standard load) and 5min recovery time using a SASMIRA Crease Recovery Tester as per standard method.

Degree of polymerization of the oxidized and controlled cotton samples were studied by standard cupramonium fluidity test as per IS244:2006 method¹⁵. Nitrogen content of chemically modified cotton was determined by Kjeldahl method following IS-5194-1969 (reaffirmed 2002) standard¹⁶. XPS analysis was carried out on PHI5000 VersaProbe II and UV (340nm wavelength) exposure was carried out at standard atmospheric condition with 0.35w/m² irradiance¹⁷.

Fourier Transform Infrared Spectroscopy (FTIR) of Cotton muslin fabric (finely crushed) samples were examined in a

FTIR spectrophotometer (Model–PerkinElmer spectrum version 10.03.09) using KBr disc technique.¹⁰⁻¹¹

K/S values of dyed cotton fabrics were determined by using a computer aided color eye XTH reflectance spectrophotometer followed by calculating the K/S values using Kubelka Munk¹⁸ equation with the help of relevant software taking standard white tile as a reference material for calibration. Whiteness index was calculated as CIE standard¹⁸⁻¹⁹.

Color fastness to washing of the dyed fabric samples was determined as per IS:764-1979 method¹³ using a Paramount launder-O-meter. The wash fastness rating was assessed using grey scale as per ISO:05-AO2-1993 (loss of shade depth) and ISO:105-AO3-1993 (extent of staining).

Color Fastness to rubbing (dry and wet) was assessed as per IS: 766-1988 method¹³ using hand operated crock meter from Presto and using grayscale as per ISO-105-AO3-1993 (extent of staining). Light fastness of the samples were tested in daylight as per IS 686:1957 method¹³.

However, the wave length scan of UV-VIS Spectra of 0.1% aqueous solution of three reactive dyes (Figure 6) have been studied using Specord 200 of Analytik Jena AG UV-VIS-absorbance-spectrophotometer following standard practice¹⁴.

3. Results and Discussion

The present paper focuses on the effect of chemical modification on dyeability for bleached cotton fabric using natural amino acid mixture extracted from soyabean seed waste to obtain a new route of salt free dyeing of modified cotton with reactive dyes. An attempt was made to incorporate nucleophilic amine/aldimine functional groups or to generate cationized quaternary ammonium groups in the cotton cellulose for generating higher affinity to anionic reactive dye which may lead to simultaneous changes/improvement in some of the important textile related properties like surface morphology, bending length, crease recovery with/without loss of tensile strength. The present paper discusses on the observed changes in these textile properties for selective chemical modification of cotton muslin fabric through application of soya extracted mixed amino acids on bleached cotton muslin fabric.

Effect of preoxidation followed by cationization

Relevant results on textile related properties of untreated (control) and differently treated (modified) cotton muslin fabric are shown in Table 2.

Table 2 indicates the effect of variation of concentration of NaIO_4 (1-4%) for different duration during preoxidation of bleached cotton substrate on its important textile related properties such as tensile strength, breaking extension, crease recovery angle (CRA) and bending length etc. and the fabric is subsequently treated with different concentration of soya extracted mixed amino acid treatment (the amino acid content in soya seed is analyzed and the composition of mixed amino acid obtained from soya seed extract is given in Table-1 in material and method section) to obtain soya-modified cotton substrate (may be called soya-

cotton). By application of mixture of amino acid extracted from soya bean seed waste (total mixed amino acid content i.e. approx 20% on weight) on bleached oxidized cotton fabric, the total crease recovery values and stiffness have increased to some extent (resulting in higher bending length) with increase of either concentration of NaIO_4 or treatment duration keeping the dose of Soya extracted amino acid treatment same. This result may be viewed as an effect of loss of tenacity due to oxidative chain scission in cellulose by periodate pretreatment as well as weight gain for anchoring/attachment of mixed amino acids for subsequent treatment with soya extraction. Therefore use of NaIO_4 preoxidation above a certain concentration level (more than 2%) and duration (more than 30 mins) is not recommended for this type of finer cotton fabric. The surface appearance of soya-modified cotton (soya-cotton) fabric, obtained either from un-oxidized or pre-oxidized cotton with subsequent soya extracted amino acid treatment, the Whiteness Index (WI) is observed to be decreased significantly for both increase in concentration or treatment duration of NaIO_4 . This may be explained by the fact that soya extracted mixed amino acid treatment on preoxidized cotton substrate at low temperature curing conditions (pad-dry-calendering process) causes some degree of amino acid base yellowing character being added over and above the anchoring of such amino acid deposition which changes/reduces the WI of the said fabric.

Cellulose can be oxidized to generate -CHO group and some -COOH group in it, while -CHO group is more susceptible to react with amines or amino acids (mixed amino acids extracted from soyabean seed) forming aldimine compound with $\text{C}=\text{NH}$ -group which in presence of acid $\text{C}=\text{NH}_3^+$ ion cationizes this modified cotton. NaIO_4 pre-treatment causes controlled degree of oxidation of primary alcohol group (-CH₂OH) of cellulose to aldehyde (-CHO) group and further oxidation causes some chain scission along with ring opening reaction generating mono or di-aldehyde cellulose (DAC) which ultimately affect the tenacity of the said oxy-cotton substrate, but it offers higher degree of reactivity with some other compounds like amines/amides/amino acid. There is reduction in tenacity owing to the above said chain scission and ring opening reaction by NaIO_4 . Chain scission is evident from reduction in DP of cellulose as shown in Table 2.

There may be disorientation of polymer chains in cellulosic matrix caused by infusion of swelling action and oxidative degradation of such oxidative chemical reaction by periodate after such oxidative treatment of cotton (Table 2). The total crease recovery angle is also found to marginally increase initially and then decreases due to such oxidative chain scission, making the elastic property of the cellulosic chains deteriorated by destroying inter-unit linkages and hydrogen bonding etc. in cellulosic matrix which however, gets somewhat further lowered, when such treatment is carried out for more time i.e. for higher pre-oxidation time. However, the initial increase in crease recovery angle for lower percentage of NaIO_4 treatment may

be viewed as an effect of increase of stiffness to some extent due to removal of incrusting wax/fatty matter, before chain scission and degradation starts. The observed result of increase in stiffness to some extent and decrease in flexibility by higher/prolonged oxidative treatment of cotton is probably

due to lowering or partial removal of fats/wax materials from cotton by the said oxidative wash. Hence, there is low scale enhancement in bending length, bending modulus and flexural rigidity on oxy-cotton fabric for such oxidative treatment using 1-4% NaIO₄ (Table-2).

Table 2. Effect of Sodium Periodate oxidative pretreatment of cotton muslin on mechanical and surface properties.

Sample No	Sample State	Degree of Polymerization (Dp)	Warp way tenacity cN/tex and CV%	Warp way Breaking extension%	Total CRA(deg) W+F	Warp way bending length(cm)	Surface Appearance Properties	
							WI	K/S and CV%
S1	Unoxy	1732	1.71(8.4)	9.5	76	1.6	70	0.526(3.4)
1%NaIO ₄								
S2	Oxy	1654	1.18(6.9)	9.7	93	1.9	73.5	0.224(4.5)
S3	Oxy	1632	1.09(5.3)	9.9	90	1.8	73.6	0.264(6.5)
S4	Oxy	1590	1.09(7.3)	9.8	86	1.7	73.6	0.219(5.6)
S5	Oxy	1543	0.95(8.2)	10	84	2.1	75.0	0.250(4.6)
2%NaIO ₄								
S6	Oxy	1456	0.95(8.7)	9.8	90	2.3	74.8	0.252(5.6)
S7	Oxy	1403	0.83(7.3)	9.8	84	2.0	75.0	0.214(7.6)
S8	Oxy	1368	0.77(9.1)	10	71	1.8	75.2	0.268(3.9)
S9	Oxy	1324	0.72(7.9)	9.9	70	1.9	75.0	0.208(7.6)
3%NaIO ₄								
S10	Oxy	1297	0.69(7.6)	9.7	85	1.6	75.0	0.273(4.8)
S11	Oxy	1278	0.69(6.6)	9.9	80	1.7	75.5	0.234(5.9)
S12	Oxy	1234	0.75(8.3)	9.5	72	2.1	76.0	0.255(5.7)
S13	Oxy	1198	0.70(8.7)	9.7	68	1.6	74.0	0.248(6.5)
4%NaIO ₄								
S14	Oxy	1167	0.72(8.4)	10.1	79	1.75	76.0	0.253(5.8)
S15	Oxy	1124	0.69(7.8)	10.3	76	1.45	76.2	0.207(4.8)
S16	Oxy	1079	0.66(7.5)	10.3	70	2.15	75.4	0.247(8.7)
S17	Oxy	1056	0.60(5.3)	10.5	64	1.95	74.2	0.280(8.1)

(Figures in parenthesis are CV% values)

Table 3. Effect of chemical modification of oxy cotton muslin fabric treated with extraction of Soya bean seed waste.

After treating with 20% soya bean seed waste extracted aqueous amino acid solution								
Sample No	Wt gain%	Sample State	N%	Warp way Tenacity (cN/tex) and CV%	Total CRA (deg)W+F	Warp way Bending length (cm)	Surface appearance	
							WI	K/S and CV%
ST2	10.4	Oxy	0.32	1.38 (7.5)	117	1.8	54.7	1.73 (5.5)
ST3	10.7	Oxy	0.32	1.37 (6.7)	119	1.7	53.3	1.73 (3.5)
ST4	10.8	Oxy	0.33	1.36 (9.2)	124	1.9	51.2	1.73 (4.6)
ST5	11.0	Oxy	0.34	1.30 (9.3)	127	2.0	51.0	1.73 (5.6)
ST6	11.8	Oxy	0.35	1.27(7.9)	124	2.1	50.5	1.73 (5.1)
ST7	12.0	Oxy	0.36	1.18 (7.3)	128	2.2	50.4	1.73 (7.3)
ST8	12.8	Oxy	0.37	1.15(5.3)	130	2.2	50.0	1.74 (4.9)
ST9	13.0	Oxy	0.37	1.05 (8.5)	132	2.3	48.6	1.74 (6.6)
ST10	13.2	Oxy	0.37	1.04 (8.2)	130	1.90	48.2	1.74 (5.8)
ST11	13.4	Oxy	0.37	1.01 (8.3)	132	1.90	46.3	1.74 (5.3)
ST12	13.5	Oxy	0.37	1.00 (6.5)	135	2.01	46.1	1.74 (5.2)
ST13	13.7	Oxy	0.37	0.98 (4.9)	141	2.10	45.5	1.75 (4.5)
ST14	13.9	Oxy	0.38	0.99 (7.6)	133	2.01	44.2	1.75 (6.8)
ST15	14.2	Oxy	0.38	0.93 (9.9)	135	2.20	43.1	1.75 (3.8)
ST16	14.3	Oxy	0.39	0.90 (5.8)	140	2.3	42.4	1.75 (5.7)
ST17	14.5	Oxy	0.40	0.85 (8.2)	144	2.4	42.0	1.75 (7.1)

(Figures in parenthesis are CV% values)

S1-Untreated controlled bleached cotton fabric, S2toS5-After treating with 1% NaIO₄ for (30mins to2hrs in a increasing duration step of 30mins), S6toS9-After treating with 2%NaIO₄ for (30mins to2hrs in a increasing duration

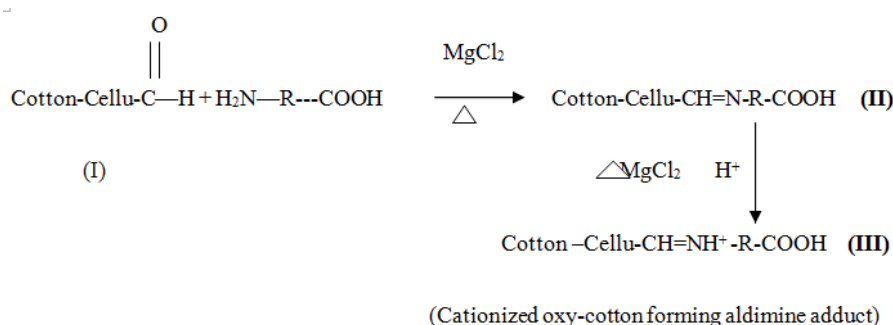
step of 30mins, S10toS13-After treatingwith3% NaIO₄ for (30mins to2hrs in a increasing duration step of 30mins), S14 toS17-AfterTreating with 4% NaIO₄ for (30mins to2 hrs in a increasing duration step of 30mins)

Data in Table 3 indicate the result of textile related important property parameters after treatment of different degree of pre-oxidized cotton muslin fabric (oxy-cotton) with natural mixed amino acids (extracted from soya protein seeds by acid hydrolysis containing approx 20% mixed amino acids content).

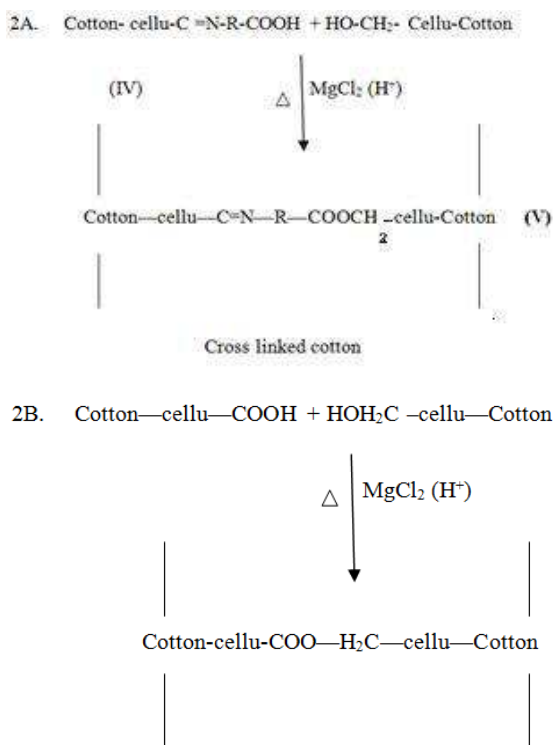
This chemical modification of oxy-cotton with amino acid extract of soya protein show marginal loss in tenacity but some improvement in crease recovery angle, as well as generates marginally higher stiffness. This marginal loss in tenacity for amino acid treatment on oxy cotton is probably due to acidic degradation caused by the catalyst (MgCl_2) under heat, while the marginal but measurable increase in stiffness may be viewed as cross linking reaction between some acid group generated in cotton cellulose (by higher degree of oxidation) and normal cotton cellulosic chain with $\text{CH}_2\text{-OH}$ group by esterification reaction (corresponding reaction scheme is shown later). The increase in crease recovery angle to a limited extent may be explained by the

above possibility of cross linking.

After incorporation of amino acids from soya protein on oxy-cotton, there is a little or marginal change in K/S value, while there is a measurable reduction in whiteness index. This change in WI may be considered as an effect of change in surface character by finer deposition of anchored amino acid on cellulosic surface. It is better understood by comparing corresponding scanning electron micrograph (SEM) of a) untreated unoxidized cotton b) oxy cotton (NaIO_4 treated) c) oxy cotton treated with soyabean extracted amino acids as shown in Figure 1. SEM photograph in Figure 1(a) clearly indicate that the surface of untreated cotton is smooth enough, while Figure 1(b) indicate that the surface of periodate treated oxy cotton has some striations and pothole damage due to oxidative damage while Figure 1(c) indicate that surface of amino acid post treated oxy cotton show some finer granular depositions of anchored amino acids reducing the regular reflection decreasing the whiteness index results.



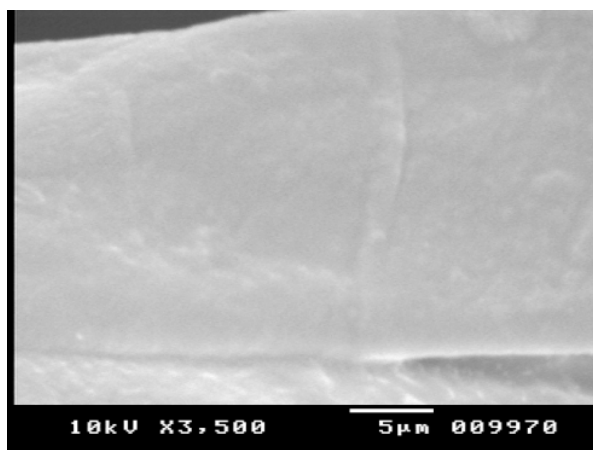
Reaction Scheme 1. (Formation of aldimine).



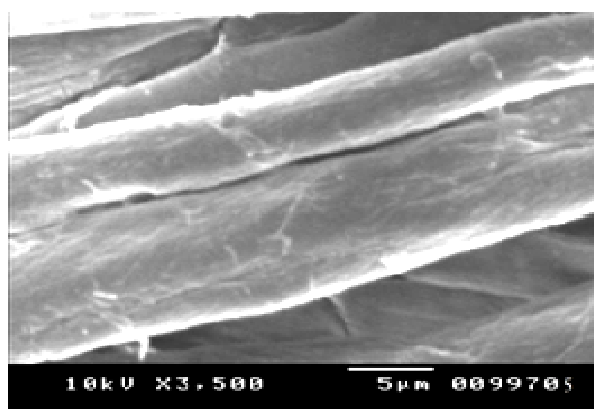
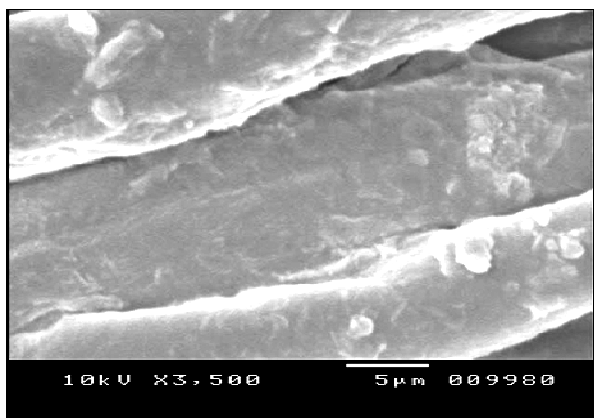
Reaction Scheme 2. (cross linking.)

As a whole the effects will be better understood, if the possible reaction mechanisms are given below (reaction schemes 1 and 2). The possible reaction mechanism is shown in reaction scheme 1 where periodate treated oxy-cotton with mono-aldehyde cellulose moieties or di-aldehyde cellulose moieties in presence of MgCl_2 and mild heat at 110°C for 8 minutes by calendaring ironing), is when admixed with mixed amino acid from soya protein, may form aldimine adduct between oxy-cotton (aldehyde) and amino acids incorporating -C=N- group in cotton cellulose moieties having -COOH end group, which in presence of acid (from MgCl_2 and mild heat) may be protonated and may form -C=NH^+ functionality producing a form of cationized oxy-cotton cellulose (III), while reaction schemes 2A and 2B show the above said possibility of some cross linking reactions also by two modes.

The FTIR spectra of all the three types of samples (a), (b), (c) in Figure 2 show a doublet observed at $2917\text{-}2927\text{cm}^{-1}$ and at 2850cm^{-1} attributed to -CH_2 asymmetric vibrations. The broader absorption band between 3000cm^{-1} and 3600cm^{-1} is attributed to O-H stretching vibration forming hydrogen bonds in cellulose molecule. This common absorption band is composed of two small vibrations located at $3,285\text{cm}^{-1}$ (attributed to intermolecular hydrogen bonds) and $3,335\text{cm}^{-1}$ (attributed to intra-molecular hydrogen bonds).



a. Untreated Cotton Fabric(unoxidised)

b. OxyCottonfabric(NaIO₄treated).

c. Oxy-cotton treated with soyabean seed waste extracted amino acids

Figure 1. Scanning Electron micrograph of (a) untreated (control) fabric (b) Oxidised fabric (c) Oxy-cotton treated with soyabean seed waste extracted amino acid.

The FTIR peak at 1582 cm⁻¹ indicated that there is formation of amine group in spectra c) while it is absent in spectra a) and b). This FTIR spectra thus evidences the formation of aldimine group (-C=N-) at 1643 with a sharp peak in spectra c) and therefore supports the reaction scheme 1 for formation of aldimine group between the aldehyde group obtained in oxidized cotton cellulose and amino groups of soybean protein. The peak at 1735 shows formation of

aldehyde or ester group in spectra (b) which has been eliminated in spectra (c) due to possible reactions.

The common FTIR peaks for all the three FTIR spectra (a), (b), and (c) is shown in Table 4.

Table 4. FTIR spectra of Cotton showing common specific peaks/trough.

Common FTIR Peak Position in cm ⁻¹	Assignment of reasons for specific peak positions
~ 3335 -3337	v(OH) (free) stretching
~ 2900 -2917	v(C-H) stretching
~ 2850	v(CH ₂) symmetrical stretching
~ 1735	v(C=O) ester group vibration
~ 1635	adsorbed water /moisture
~ 1595	v(C=C) aromatic in-plane stretching
~ 1505	v(C=C) aromatic in-plane stretching
~ 1475	δ(CH ₂) scissoring
~ 1455	δ(C-H); δ(C-OH) primary & secondary alcohol
~ 1420	δ(C-H) stretching
~ 1365	δ(C-H) stretching
~ 1335	δ(CH ₂) wagging
~ 1315	δ(C-H) stretching
~ 1280	δ(CH ₂) twisting
~ 1235	δ(C-OH) out-of-plane bending
~ 1200	δ(C-OH); δ(C-H) stretching
~ 1155	v(C-C) ring breathing, asymmetric
~ 1105	v(C-O-C) glycoside vibration
~ 1050	v(C-OH) secondary alcohol stretching
~ 1025	v(C-OH) primary alcohol stretching
~ 1005	ρ(-CH-) stretching
~ 985	ρ(-CH-) stretching
~ 895	v(C-O-C) in plane, symmetric vibration

Extra Peaks FTIR Position in cm ⁻¹	Assignment of reasons for specific peak positions
~ 1582	(-C-NH ₂) amine group vibration
~ 1643	(-C=N-) aldimine group vibration
~1735	($\begin{smallmatrix} \text{C=O} \\ \\ \text{H} \end{smallmatrix}$) aldehyde or ketone ($\begin{smallmatrix} \\ \text{C=O} \\ \end{smallmatrix}$) group vibration

FTIR outcome is confirmed by derivatization of functional groups by XPS analysis as shown in figure 3. The increase in atomic wt % of oxygen in oxidized cotton cellulose in Figure 3 (b) as compared against Figure 3 (a) confirms formation of aldehyde and acid group on the fabric surface. The presence of nitrogen and chlorine in figure 4(c) depicts the presence of amino groups and residual chlorine on the surface of the oxidized cationized cotton fabric with soya extracted amino acids. Table 5 shows the derivatization of functional groups identified in XP spectrum for aliphatic and aromatic species¹⁹⁻²⁰. The C-H group of untreated and oxidized fabric in Figure 3 (a) has disappeared and converted to C_{arom} at 284.3 (eV) in soyabean seed waste extracted amino acid treated oxidized cotton cellulose. The N1s binding energy (eV) peak at 399 implies the presence of -C=N group supporting reaction scheme 2 along with adjacent formation of NH₃ group at binding energy (eV) peak of 398.8 in Figure 3 (b) supporting both reaction scheme 1 and 2. This NH₃ formation in cellulose may lead to NH₃⁺ in acidic dye bath to attract anionizable reactive dyes and is therefore in tune with the

observed dyeing results.

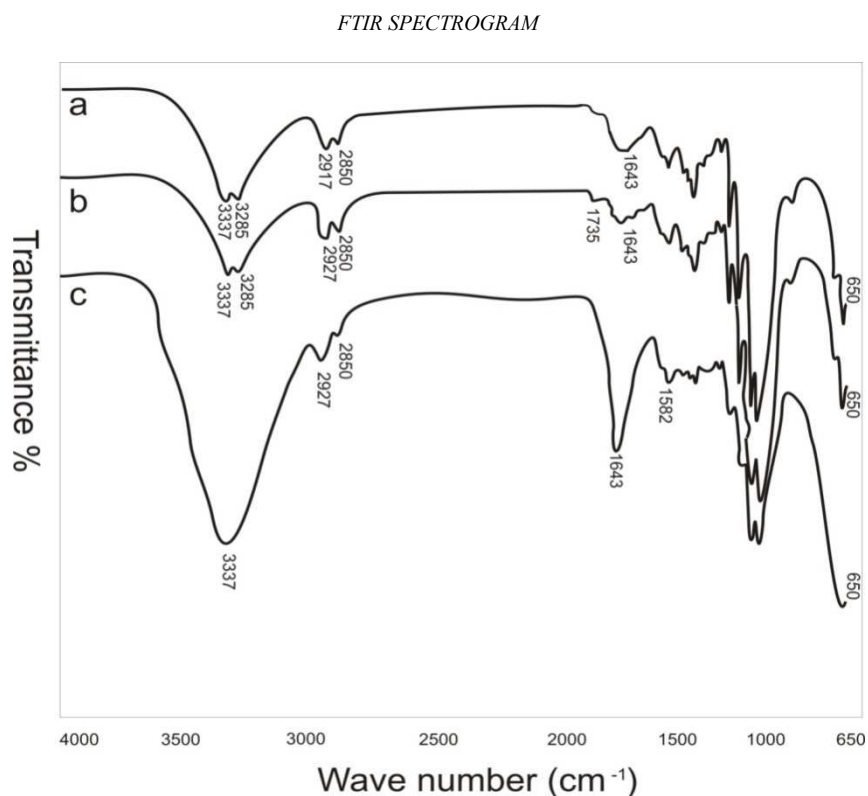


Figure 2. FTIR spectra of a) untreated bleached cotton muslin fabric b) oxidized (2% NaIO_4 for 30 min) cotton muslin fabric c) Soyabean seed waste extracted amino acid treated oxidized cotton muslin fabric.

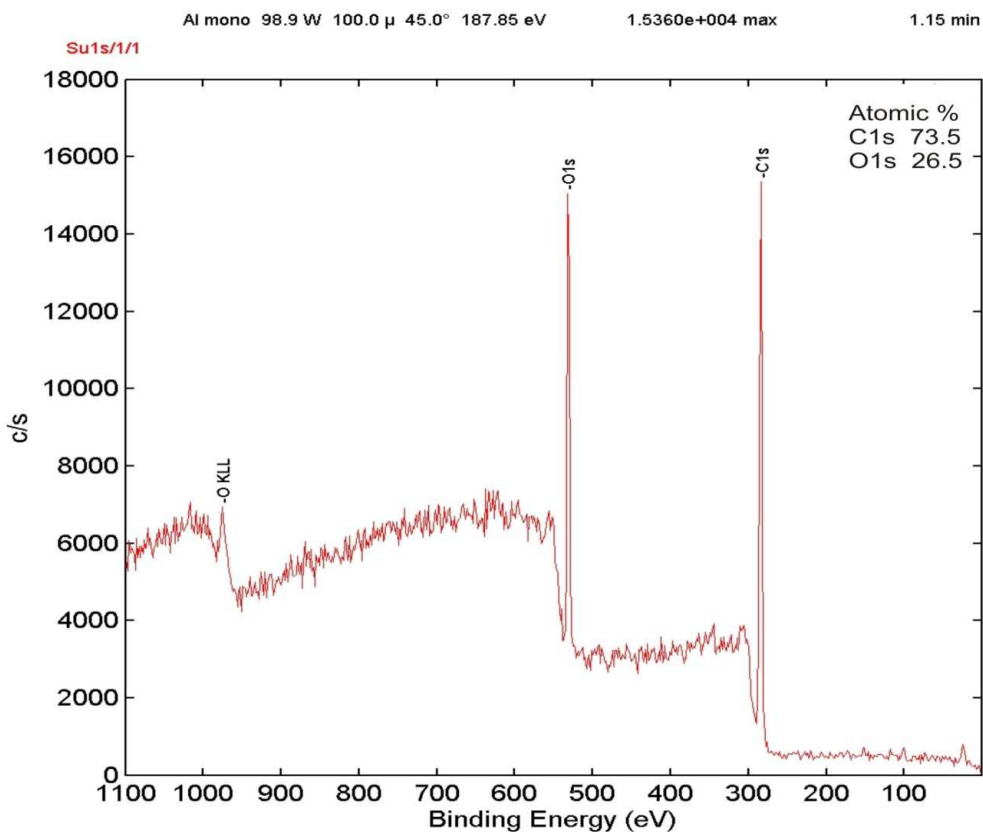


Figure 3 (a). XPS survey scan of untreated bleached cotton fabric.

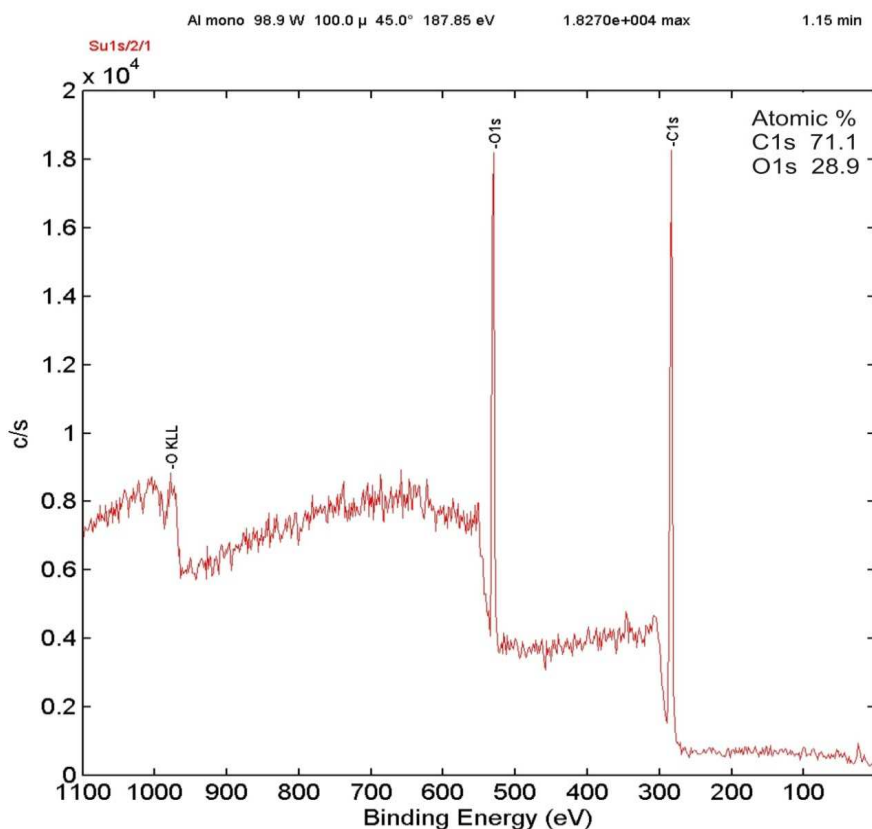


Figure 3 (b). XPS survey Scan of bleached cotton fabric oxidized with 2% NaIO₄ solution for 30 mins.

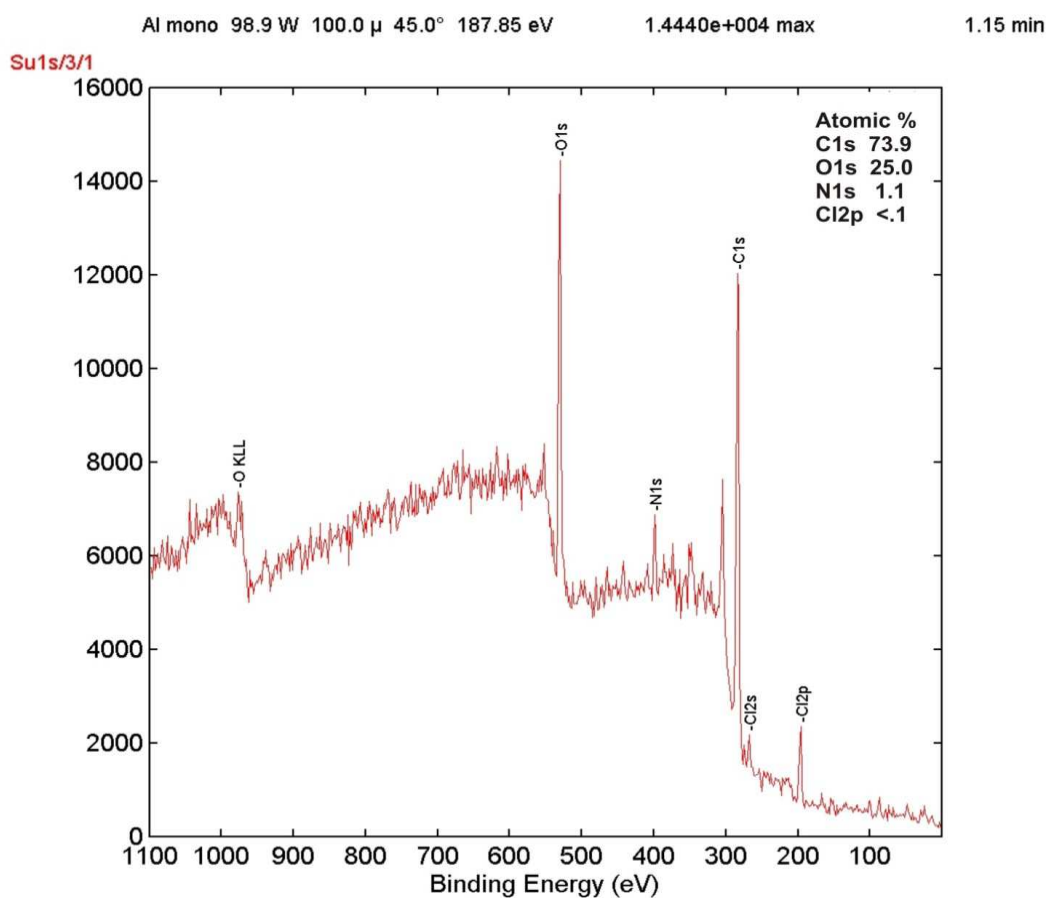


Figure 3 (c). XPS survey scan of soyabean seed waste extracted amino acid treated bleached oxidized cotton fabric.

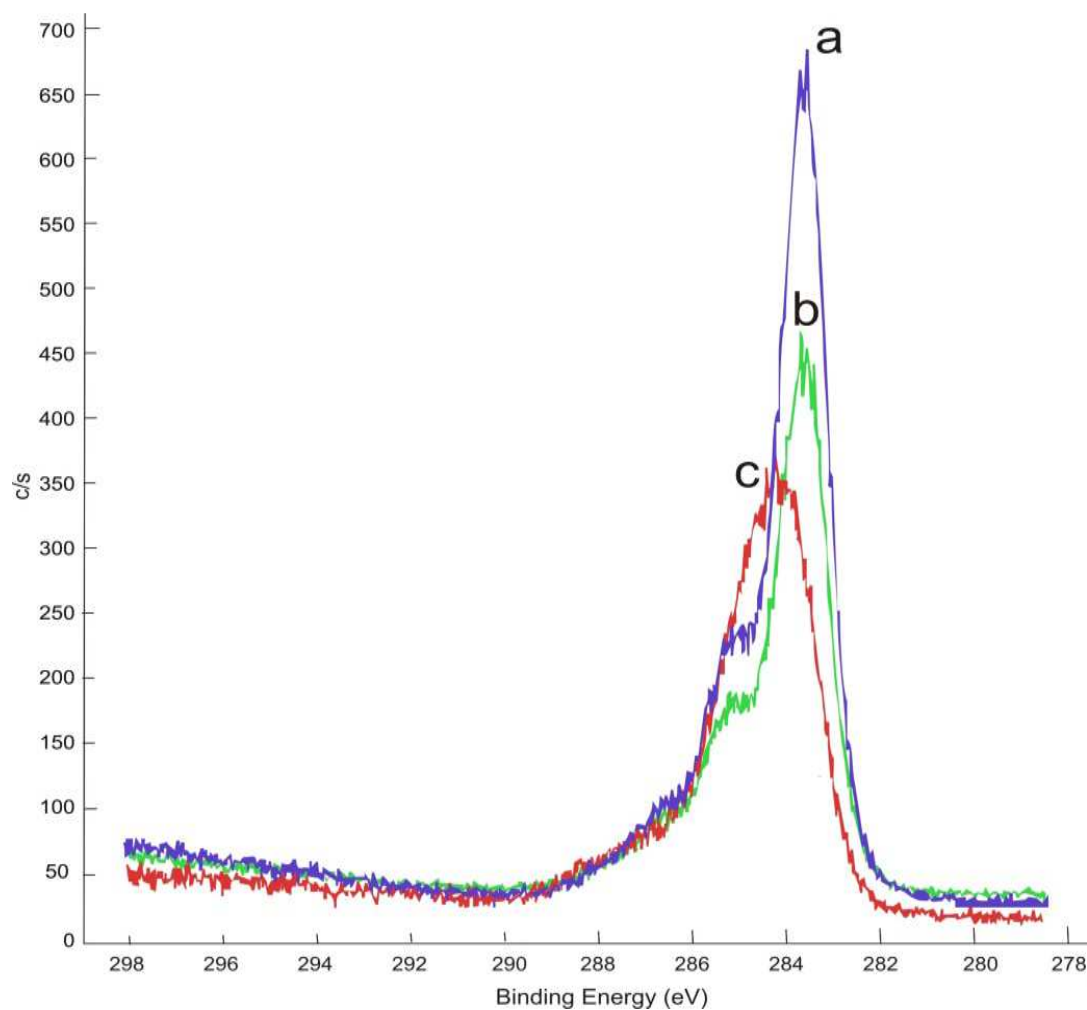


Figure 4 (a). C1s Spectrum of a) untreated cotton fabric b) Oxidized cotton Fabric c) Soyabean seed waste extracted amino acid treated oxidized cotton fabric.

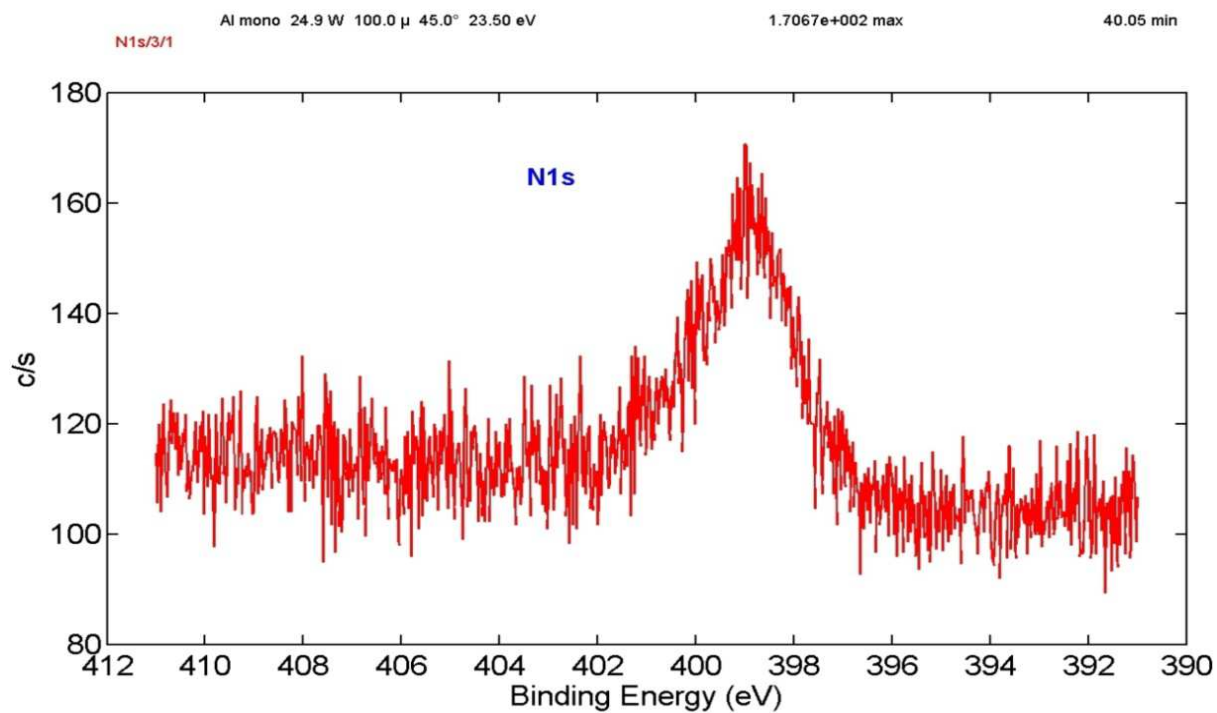


Figure 4 (b). N1s spectrum of soyabean seed waste extracted amino acid treated oxidized cotton fabric.

Table 5. Derivatisation of functional groups for aliphatic and aromatic species in XP spectrum.

Functional Groups	Binding energy
N=C	397.8-399
NH ₂	399.0-399.3
C=O	287.6-287.9.Amide287.9-288.3
COOH	289.3-290.5
	C-N=285.7-286.0
C-N,C-O,C=N/ C≡N	C=N/ C≡N 286.5-286.7
	C-O286.2-286.7
NH ₃	398.8
COOR	289.4
C-C,CH+C _{arom}	285+284.3
C-COOH	285.2

Dyeing with reactive dye

Table 6. Dyeing Results of cotton muslin fabric and oxidized cotton muslin fabric post treated with soyabean extracted amino acid in conventional reactive dyeing process and nonconventional acid bath salt free dyeing process in 2% shade.

Sample	Conventional alkaline dyeing at pH 10						Nonconventional acid bath dyeing at pH 5.5					
	CI Reactive Red 11 (cold brand)		CI Reactive Blue 25 (hot brand)		CI Reactive Red 141 (high exhaustive)		CI Reactive Red 11 (cold brand)		CI Reactive Blue 25 (hot brand)		CI Reactive Red 141 (high exhaustive)	
	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post	Pre	Post
	DF	DF	DF	DF	DF	DF	DF	DF	DF	DF	DF	DF
S1(Control)	2.1 (4.9)	2.1 (4.3)	1.3 (3.2)	1.5 (4.5)	3.1 (4.8)	7.1 (4.7)	0.4 (5.0)	1.7 (4.1)	0.6 (3.2)	0.68 (3.9)	3.7 (4.2)	3.3 (4.5)
S6(Oxy)	1.7 (3.6)	2.2 (4.8)	1.3 (4.6)	1.35 (4.2)	6.8 (5.1)	9.0 (4.2)	0.3 (3.1)	1.3 (4.9)	0.52 (4.7)	0.75 (5.1)	1.3 (5.0)	2.8 (4.3)
ST6(Oxy)	2.1 (4.3)	5.6 (5.0)	3.07 (3.9)	3.07 (4.2)	8.4 (4.9)	11.0 (5.1)	1.9 (5.2)	1.9 (4.2)	0.91 (4.1)	1.4 (3.9)	3.1 (3.4)	6.1 (3.8)

(Figure in parenthesis are CV% values) Pre DF and Post DF means before and after treating with Dye fixing agent after dyeing respectively.

Table 6 indicates dyeing results of oxidized cotton muslin fabric post treated with soya extracted amino acid in conventional alkali bath reactive dyeing process and nonconventional acid bath salt free dyeing process. Data in table 6 indicate that said modification of this oxidized muslin fabrics post treated with 20% mixed amino acid from soya extract show reactive dye uptake at par under conventional alkaline reactive dyeing process, which however show marginal less dye uptake in case of nonconventional acid bath dyeing for cold brand C.I. Reactive Red 11 dye than the dye uptake of bleached controlled cotton fabric dyed under conventional alkaline bath reactive dyeing method, with the same dye (C.I. Reactive Red 11). But for high exhaustion (HE) class of reactive dyes²¹⁻²² such as C.I. Reactive Red 141 (high exhaustion brand) the dye uptake after soya extracted amino acid treatment on pre-oxidized cotton is much improved showing more than double K/S value in conventional alkaline dyeing method, which however further improved to a large extent (depending on the color depth of the shade occur) by use of cationic dye fixing agent in both conventional method of alkaline dyeing and nonconventional method of salt free acid bath dyeing. But this is only true for dye C.I. Reactive Red 141 and not for C.I. Reactive Red 11 or C.I. Reactive Blue 25. The dyeing results of CI Reactive

Blue 25 are also not showing any improvement in colour values (K/S) than that of control fabric.

The reason for much higher dye uptake for HE dyes is probably due to double reactive groups (i.e. two numbers of mono-chlorotriazine homo bi-functional or one di-chlorotriazine and one vinyl sulphone i.e. hetero bi-functional) in it creating much higher potential difference between cationized cotton cellulose and dye molecules attracting more dyes towards cationized cotton fiber. However, this dye uptake is further magnified by application of specific cationic dye fixing agent (Optifix WE.IN) predominantly in case of HE dyes probably due to double complex formed between two reactive groups of one dye molecule and two molecules of dye fixing agent, changing/reducing the scattering coefficient, thereby increasing the K/S value showing further higher depth of shade. The coefficient of variation (CV%) of the K/S values within and around 5% which ensures an uniform dyeing²³.

However, comparing between conventional alkaline method and nonconventional acid bath salt free dyeing for soya treated oxy cotton fabric, the dye uptake is better under conventional alkaline method and obviously it is somewhat less under nonconventional salt free acid bath dyeing method, but the data of color value (K/S) both with or without dye

fixing agent are either at par or marginally higher than the results obtained under conventional method of reactive dyeing for bleached controlled fabric. In pre-oxidized cotton, post treatment with soya extracted amino acids at same dose level offers higher and probably best dye uptake under alkaline dye bath technique which may be due to higher potential difference between reactive dye anion and amino

end group of modified cotton to bring reactive dye attracted towards $\text{he-CH}_2\text{OH}$ group of cotton cellulose. It is therefore clearly indicating that reaction scheme 1 is dominant producing aldimine groups. Thus soya treatment offers an alternative method of dyeing with HE brand of dyes under salt free acid bath.

Table 7. Effect of soya extracted amino acids on color fastness properties of C.I.Reactive141 dyed oxidized bleached cotton muslin fabric.

Sample	Color fastness of C.I.Reactive141							
	Wash (ISO III)		Light (ISO:2454-1984)		Rubbing (ISO:766-1984)			
	C	NC	C	NC	C	NC	Dry	Wet
S1	3-4(4-5)	3-4(4-5)	3-4(3-4)	4(4)	4(4)	3-4(3-4)	4(4)	4(4)
ST6	3-4(4-5)	3-4(4-5)	3-4(3-4)	4(4)	4(4)	3-4(3-4)	4(4)	4(4)

*C–Conventional alkaline bath reactive dyeing **NC Nonconventional acid bath (salt-free) reactive dyeing. Figures in parenthesis are fastness values after treating with dye fixing agent.

Table 8. Cost of the suggested method.

Process	Cost per meter in INR*	
	Conventional reactive dyeing of cotton	Acid bath reactive dyeing of cationized cotton
Cow-dung–bio-bleaching		1.00
Natural H_2O_2 bleaching	3.00	
Pre-oxidation (Na_2IO_4) of cotton		1.00
Extraction of amino acids from soya bean		1.00
Application of amino acid solution on cotton/oxy-cotton by pad–dry–calendering process		3.00
Dyeing with reactive dye		
Using conventional reactive dyeing process	8.00	
Using acid bath salt free reactive dyeing process		5.00
Application of dye fixing agent	1.00	1.00
Cost of dyeing	0.75	0.75
Pollution control measures	1.00	1.25
Total	13.75	14.00

*Indian Rupees

Study of colour fastness to wash, rubbing and light show data in Table 7 indicate that post DF dyed fabrics dyed with 2% C.I. Reactive Red 141 in both alkaline and acid bath dyeing process show washing fastness 4-5, light fastness around 3 to 3-4 and dry and wet rubbing fastness around 3 and 3-4 respectively.

Data in Table 8 shows cost of all pretreatments, dyeing by both conventional and acid bath salt free process etc. wherein it is found that the cost of both the processes are almost same or nearly at par.

4. Conclusions

Soyabean seed waste modified pre-oxidized cotton fabric thus offers an alternative method of salt free dyeing with HE brand of reactive dyes under acid bath conditions giving much higher dye uptake than control bleached cotton muslin fabric, while it shows almost at par dye uptake as compared with control bleached cotton muslin fabric dyed with same reactive dye at conventional alkaline method. However, the surface color strength value (K/S) is further improved to a large extent (depending on the color depth of the shade

occur) after use of cationic dye fixing agent in both conventional method of alkaline dyeing and nonconventional method of acid bath salt free dyeing. This increase of shade depth after treatment with dye fixing agent is much predominant and higher in HE brand of reactive dyes.

Moreover, NaIO_4 based pre-oxidation to get oxy-cotton using recommended level of 2% NaIO_4 at room temperature for subsequent application of soya-based natural amino acid treatment shows superiority in dye uptake but impairs tenacity, overall crystallinity% and orientation, though there is some increase in crease recovery angle (CRA).

Corresponding FTIR spectra supports the chemical reaction between aldehyde group of cellulose and -COOH group of amino acid while aldehyde group of oxy-cotton and amine group of amino acids forms aldimine adduct with the possibility of esterification reaction between CH_2OH group of cotton cellulose and -COOH group of amino acid.

Acknowledgement

Authors acknowledge the help received from Laboratories of BTRA, Textile Committee, Dept. of Jute and Fiber

Technology of Calcutta University for specific testings and analysis of samples. Authors also express special thanks to Director, MGIRI, Wardha, HOD, DJFT, IJT, Calcutta University for all kind of support.

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