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Effect of ultrasonication and enzyme activity on dye uptake of cationised cotton fabric

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To eliminate the usage of salt, salt-free reactive dyeing using CHPTAC (3-Chloro-2-hydroxypropyl trimethylammonium chloride) has been proposed. Studies have shown promising results, such as better dye shade attainment and less effluent load compared to conventional methods. In this work, to improve the effective utilisation of CHPTAC, the cotton fabric has been treated with cellulase enzyme and the application of CHPTAC is carried out using the ultrasonication technique. The samples are then characterised for colour parameters and it is found that the enzymatic treatment and ultrasonication lead to improve the dye uptake, as the interaction of CHPTAC with the fabric becomes better.

Keywords: 3-Chloro-2-hydroxypropyl trimethylammonium chloride, Cotton fabrics, Colour strength, Dyeing, Ultrasonication

1 Introduction

The colouration of textile materials is necessary for improving the aesthetic performance of the garments. The majority of cotton-based hosiery fabrics are dyed with reactive dyes and the dyeing is carried out in two stages, such as exhaustion and fixation of dye molecules onto the structure. The exhaustion stage of dyeing involves the addition of salt to overcome the negative zeta potential of the cotton fabric. Depending on shade (%), 10 - 80 gpL of salt is added to the dyebath. The effluent let out after reactive dyeing is laden with salt and unfixed dyes. Even though standard treatments are available for colour removal, dissolved salt poses a serious challenge in processing. The processors are looking for an alternate way where the usage of salt can be avoided[1-3]. Surface modification of cotton using CHPTAC is one of the effective methods for salt-free reactive dyeing[4,5]. The attempts for less or salt-free reactive dyeing is well documented in the literature[6]. The challenge now faced by the industry is the effective utilisation of CHPTAC agent for effective dyeing. The challenge lies in ensuring the maximum interaction of the cationising agent with the cotton fabric.

This can be achieved by either making the cotton substrate more receptive to the cationising agent or by ensuring maximum interaction of the cationic agent with the cotton substrate using agitation [7-9]. It is well mentioned in the literature that the amorphous cellulosic structure of cotton absorbs better chemicals as compared to the crystalline structure. Decrystallisation of cotton using chemicals or enzymes would make the substrate more receptive for interaction with CHPTAC [10]. In this work, the enzyme cellulase was chosen as it was found that the enzyme hydrolyses the crystalline region of cellulose by the combined action of endoglucanases and cellobiohydrolases [11]. Moreover, usage of ultrasonic waves ensures proper agitation of the bath resulting in better interaction of CHPTAC with the cotton substrate [12, 13]. Thus, CHPTAC has been applied on an enzymatically modified cotton substrate with and without agitation using ultrasonic waves. The colour strength parameters of the dyed fabrics are analysed and reported.

2 Materials and Methods

2.1 Materials

Single jersey cotton knit fabric [ready to dye fabric (RTD)] of 180 gsm was purchased from White House Processing Unit, Andhra Pradesh. 3-Chloro-2-hydroxypropyl trimethylammonium chloride (CHPTAC) with a concentration of 65 % was purchased from Dow Chemical Pvt Ltd, Tiruppur. Reactive dye (Yellow GD3R) was obtained from Colourtex Industries Ltd, Tiruppur. Cellulase NB was procured from Laxmi Exim Corporation, Tiruppur. Sodium hydroxide, sodium

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sulphate, sodium carbonate and acetic acid, all analytical grade, were purchased from SRL Chemicals, Mumbai.

2.2 Methods

2.2.1 Colouration of Cotton Fabric

The dyeing process of the knitted fabric samples was carried out using the conventional and salt-free reactive dyeing process. In the case of salt-free reactive dyeing, CHPTAC was used to eliminate the usage of salt during the exhaustion stage of dyeing. To improve the interaction of CHPTAC with the cotton fabric, ultrasonication was employed before the dyeing process. On the other hand, the cellulase enzyme was used to increase the amorphous content of the cotton fabric, which, in turn, offers a higher reactive site for cationising agent.

2.2.2 Conventional Dyeing of Cotton Fabric

The RFD knit fabric was dyed using an Infra-Red Dyer machine (R B Electronics, Mumbai) with material-to- liquor ratio of 1:60. The fabric sample was dyed with the reactive dye of 1 % shade and immersed in dye liquor. To promote the exhaustion of dye towards the fabric, 30gpL of sodium sulphate (Glauber's salt) was added to the bath and maintained at 60 ℃ for 20 min. Following the exhaustion process, the fixation of dye on the fabric samples was achieved by the addition of 10 gpL of sodium carbonate and the dyeing was carried out at 80 ℃ for 30 min. The dyed fabric was after treated with acetic acid (0.5gpL) at 90 ℃ for 10 min, washed and dried to vaporise the residual moisture.

2.2.3 Salt-free Reactive Dyeing and Effect of Ultrasonication Time

The fabric was subjected to the cationisation process using CHPTAC as a cationising agent. The cotton fabric was modified by treating with sodium hydroxide (24 gpL) at room temperature (35 ℃) for 15 min followed by the addition of CHPTAC (80 gpl) by increasing the bath temperature to 80 ℃ for 45 min to fix the cationic agent into the cotton fabric. The material to liquor ratio (MLR) was fixed as 1:60. The material was subjected to after treatment which involves hot and cold wash followed by acidic wash (1 % acetic acid) further following aqueous wash. In order to improve the dyeing efficiency by enhancing the interaction with CHPTAC, the fabric sample was sonicated using a Probe sonicator (Sonics, VCX 500) with a frequency of 20 kHz. The RFD fabric samples were cationised in presence of ultrasonic waves for different duration such as 10, 20, 30 and 40 min. The sonicated samples were then dyed using the salt-free dyeing technique. Based on the CHN analysis, the Nitrogen (%) content on the fabric was estimated as 0.24 %, as the procedure stated in literature [6].

2.2.4 Effect of Enzyme Treatment

The RFD knitted fabric was subjected to enzyme treatment with MLR ratio of 1:60 using bio-polishing cellulase enzymes to de-crystallise the cotton fabric. In this method, the fabric was treated with Cellshine NB enzyme with a 2 wt % concentration at 50 ℃ for 40 min to reduce the crystallinity of the cellulosic material. The weight loss percentage of enzyme treated fabrics was found in the range of 1-2 %. The deactivation of the enzyme was achieved by raising the temperature to 80 ℃ for 10 min and dried at room temperature (35 ℃). The obtained enzyme-treated sample was then conventionally dyed using salt. To study the interaction of enzyme-treated fabric with CHPTAC, the fabric was surface modified using cationising agent and dyed using a salt-free reactive dyeing technique. The effect of ultrasonication on enzyme-treated fabric was studied by carrying out the cationisation process in the presence of ultrasonic waves and dyed with salt-free reactive dyeing technique.

2.3 Determination of Colour Parameters of the Fabric

The colour strength and reflectance spectra were measured for the dyed fabric using UV-Visible Spectrophotometer (R B Electronics, Mumbai). The colour strength (*K/S*), relative colour strength (%) and chromaticity coordinates (L^*, a^* & b^*) for the dyed fabrics were evaluated as cited in the literature [7].

The surface morphology of the fabrics treated with enzyme and cationising agent was studied using Surface Electron Microscope (SEM, HITACHI S-3400). The interaction between the cationising agent and cotton fabric was analysed using Fourier Transform Infrared (FTIR, Bruker Alpha FTIR) spectrometer in the wavelength range 4000 - 400 cm^{-1} with scanning speed of 3mm/s. The cationised and enzyme treated fabric were tested for wash and rub fastness according to ISO 105-C06-C2S and ISO 105 X 12 standards. The change in colour was rated according to the appropriate gray scale value. Light colour fastness was tested according to ISO 105 B02 standard, and the fading degree was assessed as per the Society of Dyers and Colourist blue wool scales.

3 Results and Discussion

The structure of the cellulose is found swollen by treating with sodium hydroxide as it provides the space for penetration of cationic agent and also this increases reactivity, promoting a higher degree of surface modification. Following the addition of CHPTAC, sodium hydroxide converts the cationising agent into epoxy compound 2, 3-epoxy propyl trimethyl ammonium chloride (EPTAC). The concentration of sodium hydroxide plays a crucial role as the increase in the concentration of NaOH results in hydrolysis of EPTAC into diol (2, 3-dihydroxy propyl trimethyl ammonium chloride) whereas the decrease in concentration results in poor cationisation. On further treatment at 80 °C, EPTAC is further opened due to the alkaline conditions causing an etherification reaction between the primary hydroxyl group of the soda cellulose and EPTAC. The presence of residual EPTAC in the bath on reuse is able to dye lighter shade (%) and it provides a scope to ensure the efficient fixation of CHPTAC on to the fabric.

In this present work, two different approaches are proposed, namely the adoption of ultrasonication and enzyme treatment for effective utilization of CHPTAC. It is well known that ultrasonication produces acoustic cavitation which is the major reason for the enhancement of transport of molecules towards the substrate surface. It also opens up the surface of the substrate for better interaction with the chemicals. The effect can be attributed to the impact of the cavitation bubbles and their collapse which ensures better penetration of the chemicals, as also reported in the literature [14.]

It has been well reported in the literature [15] that the enzyme-cellulose activity would result in the de-crystallization of the cellulose structure. The cellulase enzyme enriched with cellobiohydrolases and endoglucanases is found to attack 1, 4– β – glycosidic bonds of the cellulose molecule resulting in shorter chains. Moreover, the cotton is 65% crystalline and decrystallisation of cotton is likely to produce an increased amorphous region. The higher the amorphous content, higher would be the penetration of CHPTAC.

3.1 Visual Appearance

The knitted cotton fabrics were dyed with reactive dyes to study the effect of ultrasonication and enzyme activity on conventional and cationised cotton dyed samples. The dye uptake of the samples dyed with 1 % shade of reactive dye was seen through visual observation as shown in Fig. 1 which depicts the increment of the depth of the shade (from left to right) in conventional dyed and cationized samples.

The effluents after the dyeing process have been visually compared to analyse the residual dye content in the dye liquor for the understanding of the exhaustion of dye molecules into the fabric. The parent stock solution (1% shade) and the effluent obtained after dyeing are shown in Fig. 2. It can be clearly seen that the intensity of the colour in the samples gradually reduced with the process of cationization, enzyme treatment and sonication techniques. The increase in residual colour indicates the poor exhaustion during the conventional dyeing process whereas in cationised samples, there is no liquor in trays, which suggests the better exhaustion of dye molecules.

Surface morphology of cotton fabrics are shown in Fig. 3. The control fabric is composed of smooth fibres but upon cationisation, the surface of the fibres is found to be rough showing ridges due to the incorporation of quaternary ammonium groups onto

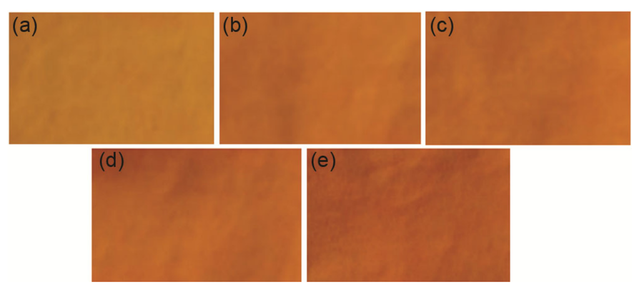

Fig. 1 — Visual observation of dyed sample (a) conventionally dyed, (b) cationised dye, (c) ultrasonicated cationised dyed, (d) enzyme treated and cationised dyed and (e) ultrasonicated enzyme and cationised (combined) dyed

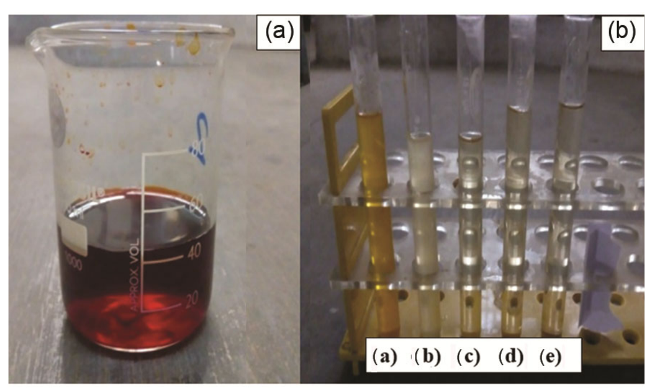

Fig. 2 — (A) Stock solution and (B) effluent after dyeing [(a) conventionally dyed, (b) cationised dye, (c) ultrasonicated cationised dyed, (d) enzyme treated and cationised dyed and (e) ultrasonicated enzyme and cationised (combined) dyed]

the structure. Upon enzyme treatment, the hairiness in the yarn is reduced due to better consolidation of fibres within the yarn.

The cationisation of the cotton fabric is confirmed by FTIR spectrum as shown in Fig. 4. The peak at around 1734 cm^{-1} represents the vibrational stretching of carbonyl groups and the presence of hydroxyl group is confirmed by the stretching of peak at around 3315 cm^{-1}. The cationisation of the cotton fabric is confirmed by the formation of peak at around 1450 cm^{-1} which is due to characteristic vibration of quaternary ammonium group (NH^{3+}) on the cellulose polymer backbone. The peak at around 1200 cm^{-1} represents the stretching of C-N group and at 2900 cm^{-1} due to C-H stretching on the polymer backbone.

3.2 Effect of Ultra Sonication on Colour Parameters

To improve reactivity, the ultrasonication technique is used to study the effect of sound waves on cationised samples and then analysed using various dyeing parameters. The *K/S* and relative colour strength values of conventionally dyed (control) and cationised dyed (CFA treated) fabric are shown in Table 1. It is observed that cationised dyed fabric has higher *K/S* colour strength and RCS value as compared to control fabric, which indicates that the surface modification of substrate shows an affinity for anionic dye molecules. The trials have been extended with the application of sonic waves and the influence of time of ultra Sonication on colour strength is given in Table 1.

An increase in colour parameters is observed when the samples are subjected to ultrasonication treatment. The colour strength (*K/S*) values of the cationised sonicated and dyed samples are found higher, which indicates that the samples are in a darker shade. Meanwhile, the decrease in lightness value from 67.43 (CFA treated) to 64.17 (CFA treated 40) also confirms the same. The relative colour strength of the ultrasonicated cationised dyed sample in comparison with the cationised cotton dyed sample is found to be 40.76%.

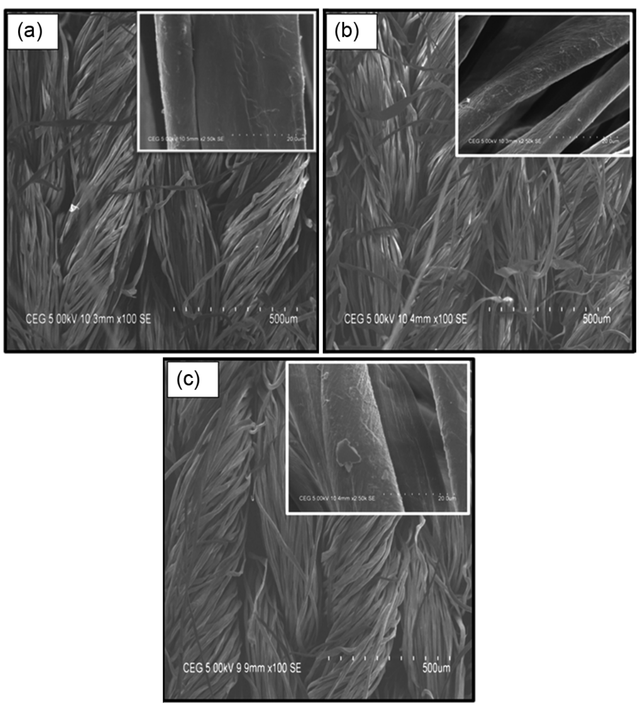

Fig. 3 — SEM of (a) control, (b) cationised samples and (c) enzyme treated cationised samples (500 µm) (inset 20µm)

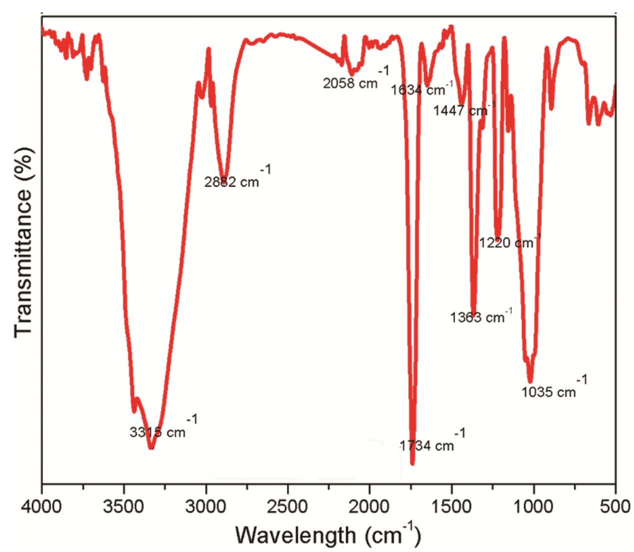

Fig. 4 — FTIR of cationised cotton sample

Table 1 — *K/S* and relative colour strength of ultrasonicated samples

Samples	*K/S*	*L**	*a**	*b**	RCS%	Dye exhaustion, %
Conventional dyed (Control)	4.26	75.62	27.18	65.50	100.00	73
Cationised cotton dyed (CFA treated)	15.81	67.43	42.05	79.20	371.18	82
Cationised ultra sonicated and dyed (CFA-ultrasonic)						
10 min	17.06	66.67	41.71	79.00	400.41	85
20 min	19.33	63.98	43.96	77.23	453.75	84
30 min	21.73	64.00	41.88	79.70	510.08	88
40 min	22.26	64.17	38.67	77.16	522.49	86

Table 2 — *K/S* and relative colour strength of enzyme treated samples

Samples	*K/S*	*L**	*a**	*b**	RCS%	Dye exhaustion, %
Conventional (Control)	4.26	75.62	27.18	65.50	100.00	73
Enzyme control (ENZ treated)	9.33	70.40	28.92	73.78	219.00	84
Enzyme treated and cationised in IR (ENZ + CFA treated)	11.77	67.76	40.82	73.84	276.29	82
Enzyme treated and cationised in US (ENZ + CFA treated-ultrasonic)	17.06	64.23	38.29	75.47	400.41	86

Table 3 — Fastness property of dyed fabrics

Samples	Wash fastness		Rub fastness		Light fastness
	Colour change	Staining	Dry	Wet	
Conventional dyed (Control)	4-5	4-5	4-5	4-5	5
Cationised cotton dyed (CFA treated)	4-5	5	4-5	4-5	5
Cationised ultra sonicated and dyed (CFA-ultrasonic)					
10 min	4-5	5	5	4-5	5
20 min	4-5	5	5	4-5	5
30 min	4-5	5	5	4-5	5
40 min	4-5	5	5	4-5	5
Enzyme control (ENZ treated)	4-5	4-5	4-5	4-5	5
Enzyme treated and cationised in IR (ENZ + CFA treated)	4-5	5	5	4-5	5
Enzyme treated and cationised in US (ENZ + CFA treated-ultrasonic)	4-5	5	5	4-5	5

It can be seen that the value shifts to darker sides with an increase in ultrasonication time. The tone of the fabric is not altered. No significant changes occur on dyed fabrics with cationisation process. However, better exhaustion of dyes is achieved by the cationisation process compared to that of control.

3.3 Effect of Enzyme Treatment on Colour Parameters

To study the effect of enzymes on the fabric absorbency and dyeing parameters, experiments are carried out. The *K/S* and relative colour strength values of enzyme treated fabrics are given in Table 2. On comparison of the dyeing parameters of the enzyme-treated fabric and the control samples, it can be inferred that the colour strength of samples subjected to the enzyme process has increased and a significant change in the colour strength is observed when the ultrasonication process is combined with the enzyme process (17.06).

The high L^* values suggest that the samples are darker in shade and no variations in the a^* and b^* values are observed and thereby suggesting that the tone of the fabric is not altered. The relative colour strength values are twice to that of conventional dyed samples in the normal enzyme treatment whereas with US during cationisation of enzyme treated fabrics the values are quadrupled. It confirms that the enzyme process has played a role in increasing colour parameters in dyeing of the fabric. No siginificant changes in fastness properties is observed for enzyme-treated fabrics as shown in Table 3. However, significant improvement in exhaustion (%) is observed for enzyme-treated cationised fabric.

4 Conclusion

Salt-free dyeing techniques using CHPTAC has been carried out with the aid of enzyme and ultrasonication. The salt-free reactive dyeing supplemented by enzyme treatment and ultrasonication has significantly improved the dye uptake of the cationised cotton. The effluent obtained is found almost colourless and the shade of the dyed samples is much higher as compared to all the samples. The study suggests that the loading of CHPTAC can be reduced by using the enzyme and ultrasonication process. The tone of the fabric is also not altered due to the enzyme and ultrasonication process. Further, the studies are being carried out to reduce the concentration of CHPTAC used for the cationisation process by coupling with enzyme treatment and ultrasonication process.

References

1 Dessiea A & Govindanb N, *J Text Sci Eng*, 08 (2018) 1
2 Sun D, Zhang X, Du H, Fang L & Jiang P, *Fibers Polym,* 18 (2017) 1969.
3 Teklemedhin T B, *Int J Sci Eng Res*, 9 (2018) 907.
4 Arivithamani N & Giri Dev VR, *J Clean Prod*, 183 (2018) 579.
5 Arivithamani N & Giri Dev V R, *J Clean Prod*, 149 (2017) 1188.
6 Nallathambi A & Venkateshwarapuram Rengaswami G D, *Carbohydr Polym,* 174 (2017) 137.

7 Nallathambi A & Venkateshwarapuram Rengaswami G D, *Carbohydr Polym,* 152 (2016) 1.
8 Aktek T & Millat A K M M, *Int J Text Sci*, 6 (2017) 21.
9 Rahman Bhuiyan M A , Shaid A & Khan M A, *Chem Mater Eng*, 2 (2014), 96.
10 Zhang S, Ma W, Ju B, Dang N, Zhang M, Wu S & Yang, J, *Color Technol* , 121 (2005), 183.
11 Patil N B, Dweltz N E & Radhakrishnan T, *Text Res J*, 1 (2015) 517.
12 Cavaco-Paulo A & Almeida L, *Biocatal Biotransformation*, 10 (1994) 353.
13 Thakore K A & Abate B, *Cellul Chem Technol,* 51 (2017) 983.
14 Vaibhav V Nagaje & Ashish A Hulle*, J Basic Appl Eng Res*, 2 (2015) 79.
15 Sarkar A K & Etters J N*, J Cotton Sci*, 8 (2004) 254.