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MODIFICATION OF COTTON FABRICS WITH CHITOSAN FOR IMPROVED DYEABILITY WITH ACID ORANGE 7

AMANDORON M.U. Kristine, MARTÍNEZ-GONZÁLEZ Inés, GISBERT-PAYÁ Jaime, BONET-ARACIL Marilés

Universitat Politècnica de València, Textile and Paper Department, Ferrándiz y Carbonell s/n, 03801, Alcoy, Spain

Corresponding author: Bonet-Aracil, Marilés, E-mail: maboar@txp.upv.es

Abstract: *Cationized cotton fibres, achieved through chemical modification with cationic compounds, have been explored to improve dye uptake while also addressing the concerns about the environmental impact of low exhaustion rates and the use of salts. Chitosan, a green biopolymer, is a potential eco-friendly textile chemical due to its nontoxic, biodegradable, and cost-effective nature. This study investigated the effects of chitosan modification, with and without citric acid crosslinking, on washing and dyeing using an anionic dye, Acid Orange 7. The experimental analysis included fabric preparation, chitosan solution formulation, padding application, curing, washing, and dyeing. Dye exhaustion percentages and colour measurements were analysed. The results demonstrated enhanced dye exhaustion in chitosan-modified cotton fabrics, with optimal results observed at 120°C curing. Chitosan modification led to darker and deeper shades in dyed fabrics. However, adding citric acid for crosslinking did not significantly improve dye exhaustion. In conclusion, chitosan modification improved dye exhaustion and colour intensity, showcasing its potential as an eco-friendly alternative for enhancing dye uptake in cotton fabrics. Further investigations could optimise solution preparation and application methods for optimal results. This study contributes to sustainable practices in the textile industry by highlighting the potential of chitosan as a dyeing enhancer.*

Keywords: *textile; dyeing; mordant; eco-friendly; cotton modification.*

1. INTRODUCTION

Low exhaustion of dyes from the dyeing bath brings economic and environmental concerns [1,2]. Salts have been used to enhance dye exhaustion. However, this approach can also cause the pollution of rivers and streams, which is harmful to aquatic life [3]. In an attempt to improve the dye uptake of fibres from the bath, cationised cotton fibres through chemical modifications with compounds containing cationic groups have been explored [4]. The textile industry continues to look for eco-friendly processes that can substitute for toxic textile chemicals. From this point of view, chitosan is an excellent candidate for the use of eco-friendly textile chemicals [5].

Chitosan, a green biopolymer, possesses multifunctional properties, including nontoxicity, biocompatibility, biodegradability, and low cost. Because of these characteristics, chitosan has been used in the agriculture, biotechnology, medical, textile, cosmetics, and food industries [6-8]. Chitosan is a linear polysaccharide sourced from the full or partial deacetylation of chitin, which consists of a molar fraction of randomly distributed β-(1→4)-linked D-glucosamine (deacetylated unit) and a fraction of N-acetyl-D-glucosamine (acetylated unit) [9].

While chitosan was initially used as a dye-deepening agent in the textile industry, it is also an ideal fixing agent for anionic dyes due to its cationic nature. Salt-free dyeing is possible by using chitosan with the help of some other additives [10]. A possible explanation for the level dyeing effect of chitosan may be explained by the capability of chitosan to form a uniform film on the surface of the fibre. It improves the surface properties of the fibre and reduces the Coulomb repulsion between the fibre and the anionic dyes, significantly improving the dye uptake rate. The deepening effect is also due to the protonation of the free amino group on the chitosan molecule under acidic conditions. When the fabric is immersed in the chitosan solution, the positive charge of the fibre is increased. Thus, the repulsion force between the fibre and the anionic dyes is reduced [11].

The crosslinking of chitosan on cotton fabrics has been considered to improve the durability of the treatment. Moreover, many studies have found that the use of polycarboxylic acids (PCAs) as a crosslinking agent is the best choice. The PCAs lead to the formation of covalent bonds between the chitosan and cellulose [12]. While 1,2,3,4-butane-tetracarboxylic acid (BTCA) appears to be the most promising crosslinker for cellulosic materials, its cost is too high, preventing its application on a commercial scale [13]. An alternative to this is the use of citric acid (CA) as a crosslinker. It has been proven that CA with sodium hypophosphite (SHP) as a catalyst promotes effective crosslinking [12].

This study investigated the effect of chitosan modification with and without citric acid as a crosslinker on the washing and dyeing of cotton fabrics with Acid Orange 7, an anionic azo dye.

2. EXPERIMENTAL

2.1 Materials

The fabric used for this study was 100% bleached cotton with an openwork fabric, plain weave and a density of 46 ends/cm, 36 picks/cm and a grammage of 116 g/m2. It belongs to the Department of Textile Engineering (DITEXPA) of the UPV (Campus Alcoy, Spain). Medium molecular weight chitosan was provided by Sigma Aldrich and was used without any purification. Citric acid was provided by Scharlau, and sodium hypophosphite was provided by Acros Organics. The detergent used for washing was the low foam non-ionic liquid detergent Proindeter ECM supplied by Proindiver S.L. (Barcelona). All chemicals and reagents used in this study were of analytical grade.

A 1 L solution of chitosan was prepared (1% w/v) with the addition of acetic acid (0.5% v/v) to aid in the dissolution of the powder. The solution was magnetically stirred for 2 hours to ensure that the chitosan was fully dissolved. Another 1 L solution which contained chitosan (1% w/v), citric acid (7% w/v), non-ionic surfactant Tween 80 (1% v/v), and sodium hypophosphite (1:1 CA-SHP mole ratio) was prepared. The solution was magnetically stirred overnight. This method is based on the study by Grgac et al. (2020) and Chung et al. (1998).

2.2 Application of chitosan on cotton fabric

A roll of cotton fabric was padded with the chitosan solution and the chitosan with a citric acid solution using a small-scale foulard at a controlled pressure of 2 bar. The cotton fabric was allowed to pass through the rollers twice. The wet pick-up of the fabric was obtained. The padded cotton fabric was dried using S.P.E Screen Engineering TD-20 at 80ºC.

The cotton fabrics were cut into smaller parts to weigh approximately 10 g each. Cotton fabrics modified with chitosan (CO_X) and chitosan with citric acid (CO_X_CA) were heated in the oven (Argo Lab TCF 120) for 3 minutes at 120ºC and 150ºC. Pure cotton fabrics (CO) were also heated in the same manner.

2.3 Washing

A solution of Proindeter ECM (0.5 g/L) was prepared for the washing of the cotton fabrics. 500 mL of the solution was placed in each glass tube of the laboratory dyeing equipment (Tint Control Renigal Multi-Mat), which agitated the y-axis of the samples. The washing cycle was done for 30 minutes at 60ºC. The samples were then air-dried overnight.

2.4 Dyeing

A stock solution of Acid Orange 7 dye (1 g/L) was prepared for the dyeing of cotton fabrics (1% o.w.f) with a liquor-to-goods ratio of 1:40 in a laboratory dyeing machine (Paramount Open Bath dyeMaster). The dyeing process was carried out at 25ºC for 6 hours.

2.5 Characterization

2.5.1 Dye Exhaustion

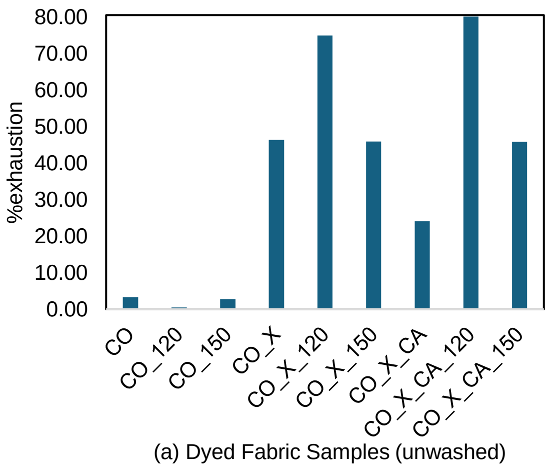
The dye bath exhaustion (%E) was determined from the measurement of the dye solution absorbance before (A_0) and after (A_1) the dyeing process at maximum absorbance wavelength (485 nm) using a UV-Vis spectrophotometer (Thermo Scientific – Helios Epsilon). The dye bath exhaustion (%E) was calculated as in Eq. (1):

$$\%E = \frac{(A_0 - A_1)}{A_0} \times 100 \qquad \textbf{(1)}$$

2.5.2 Color Measurements

The colour yield values of treated and controlled dyed cotton fabric samples were measured under D65/10º illuminant using a Datacolor Spectro 700 spectrophotometer. Samples were measured in three different sites, and the average measurements were recorded.

3. RESULTS



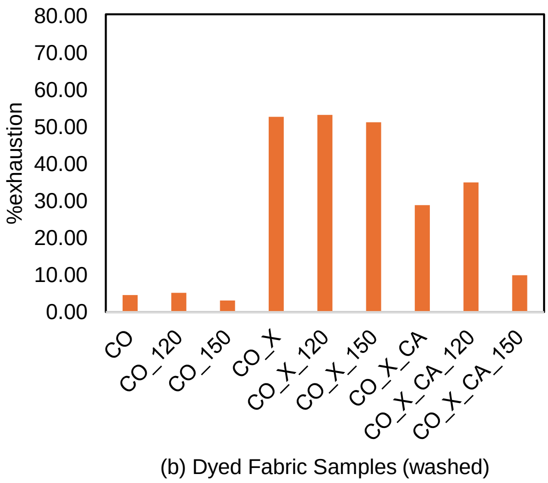


***Fig. 1**: Dye Exhaustion Percentages of (a) unwashed and (b) washed cotton fabric samples*

The data in Figure 1 shows the improved dye exhaustion with the impregnation of chitosan and chitosan with citric acid solutions on the cotton fabric before dying. In Figure 1(a), modified cotton fabrics cured at 120ºC showed higher dye exhaustion percentages compared to the other dyed samples. Meanwhile, in the washed cotton fabric samples in Figure 1(b), cotton fabrics modified with chitosan only showed higher dye exhaustion percentages over those modified with chitosan and citric acid. This could indicate that the cotton fabric has better intermolecular interaction with chitosan alone, and the addition of citric acid was ineffective in improving chitosan attachment to the cotton fabric.

Table 1: Colour measurements of pre-dyed cotton fabrics (unwashed)

Sample	L*	a*	b*	dE*
CO	96.85	3.28	-14.86	
CO_120	96.88	3.24	-14.99	0.15
CO_150	96.84	3.21	-14.78	0.11
CO_X	96.54	2.73	-13.93	
CO_X_120	96.69	2.53	-14.05	0.28
CO_X_150	96.56	2.36	-13.13	0.88
CO_X_CA	97.13	-0.47	-10.17	
CO_X_CA_120	97.07	-0.54	-9.48	0.75
CO_X_CA_150	96.57	-1.06	-7.17	3.12

Table 2: Colour measurements of pre-dyed cotton *fabrics (washed)*

Sample	L*	a*	b*	dE*
CO	97.12	0.32	-11.41	
CO_120	96.85	0.04	-11.1	0.57
CO_150	96.68	0.28	-11.11	0.54
CO_X	96.44	0.53	-11.28	
CO_X_120	96.5	0.5	-11.22	0.11
CO_X_150	96.44	0.46	-10.3	1.06
CO_X_CA	96.69	-0.46	-9.22	
CO_X_CA_120	96.34	-0.23	-9.08	0.44
CO_X_CA_150	96.12	-0.58	-6.14	3.35

Based on the L*a*b values of the pre-dyed cotton fabrics in Tables 1 and 2, fabric samples padded with chitosan slightly reduced the* values compared to plain cotton fabric. There was no significant difference in colour between non-cured cotton fabrics with chitosan and cotton fabrics with chitosan cured at higher temperatures. However, curing at 150ºC increased the colour difference slightly. For cotton fabrics padded with chitosan with a citric acid solution, there was a significant colour difference when the fabric samples were cured at 150ºC, appearing to be more yellowish. After washing, the cotton fabric samples showed a decreasing trend in the* values.

Table 3: *Color measurements of cotton fabrics dyed with Acid Orange 7 (unwashed)*

Sample	L*	a*	b*	dE*
CO_AO7	79.74	27.95	18.88	
CO_120_AO7	80.23	27.49	17.42	1.61
CO_150_AO7	79.86	27.76	18.29	0.63
CO_X_AO7	68.4	38.67	33.32	
CO_X_120_AO7	66.25	44.89	49.72	17.67

CO_X_150_AO7	67.37	38.80	32.86	1.14
CO_X_CA_AO7	65.37	46.09	53.64	
CO_X_CA_120_AO7	69.36	40.59	35.49	19.38
CO_X_CA_150_AO7	73.09	34.52	34.6	23.58

Table 4: *Color measurements of cotton fabrics dyed with Acid Orange 7 (washed)*

Sample	L*	a*	b*	dE*
CO_AO7	79	28.78	21.63	
CO_120_AO7	79.04	28.4	20.51	1.18
CO_150_AO7	79.18	28.71	20.81	0.85
CO_X_AO7	64.98	33.14	33.34	
CO_X_120_AO7	68.41	42.15	39.75	11.57
CO_X_150_AO7	68.32	41.95	39.61	11.31
CO_X_CA_AO7	71.24	40.13	43.66	
CO_X_CA_120_AO7	69.97	40.18	42.73	1.57
CO_X_CA_150_AO7	76.83	31.28	28.56	18.37

As shown in Table 2, the cotton fabrics modified with chitosan and chitosan with citric acid have lower L* values than dyed pure cotton fabrics, showing a darker shade of orange. This shows that the addition of chitosan improves the dyeing of the cotton fabrics and supports the date of improved dye exhaustion when the cotton fabrics were pre-treated with chitosan. Washing the modified cotton fabrics has more effect on the dyeing of the modified cotton fabrics than the pure cotton samples. This indicates that the washing resulted in a reduced amount of chitosan that has been attached to the cotton fabric. The curing of chitosan-modified cotton fabrics also influences the dyeing of the fabrics. There is a considerable colour difference between the cured samples compared to their non-cured counterparts.

4. CONCLUSION

Eco-friendly textile agents have been explored to improve dye exhaustion on textiles while reducing the harmful impact on the environment. Chitosan, a biopolymer sourced from chitin, has multi-functional properties that make it a good candidate for a more sustainable treatment for cotton fabrics to improve dye uptake. The results of this study showed that the dye exhaustion of the cotton fabric was improved by modifying the cotton with chitosan before dyeing. Chitosan improves dyeing with the anionic dye Acid Orange 7 due to its cationic nature. The modification of cotton fabrics with chitosan and citric acid solution for crosslinking did not show substantial improvement with dye exhaustion compared to the modification of cotton fabrics with chitosan only. Further exploration can be done on the solution preparation and padding method to optimise the chitosan pre-treatment of cotton fabrics.

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