DYEING OF SULFONATION AND CROSSLINKED COTTON FABRIC

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Abstract:

Cotton fabrics were modified by different methods such as oxidation, sulfonation and crosslinking processes. The modified and unmodified fabrics were subjected to weight measurements, water absorbency and strength tests. In SEM analysis, modified fabrics showed improved woven pattern with less protruding fibres in x 75 magnification and swollen smooth rod like appearances in x 1500 magnification than in unmodified fabrics. Modified fabrics were dyed with Reactive Red 120 and Direct Blue 86 under alkaline condition with low salt content. The modified fabrics showed improved dye uptake than unmodified fabric. Crosslinking modification was found to be very effective than sulfonation modification. Dye uptake and wet fastness properties were improved for modified fabrics. For a 0.5% dye concentration study, the dye uptake obtained for modifications is ranked as UM < 1W < 2W < 4W < 3W in reactive dyeing and UM < 1W < 4W <2W <3W in direct dyeing.

Key words:

Cotton, modification, oxidation, sulfonation, crosslinking, dyeing, fastness

Introduction

As the textile industry has grown, modification of individual fibre types has been developed to broaden uses. Modified fibres can be produced by chemical alteration of the polymer fibre or fabric or by the use of non-reacting additives. Improved dyeability is usually effected by use of a suitable co-monomer. The introduction of permanent - press treatment of polyester-cotton staple fibre blends in fabric form was a major factor in the growth of polyester usage. Wash and wear characteristics can be imparted to fabrics by treatment with suitable thermo-setting (cross-linking) resin system but an accompanying strength loss made this approach unsuitable for non-cellulosic fibres such as cotton or rayon.

Recent studies have been revealed that chemically modified cotton fabrics exhibit improved dyeing behavior when compared to unmodified cotton. Modification by partially acetylated, carbamylethylated and grafted cellulose [1-3], the susceptibility of various oxidized cellulose to dyeing [4-6] and modification by sulfonation of cotton fabric using sodium bisulfite have been reported [7,8] in literature. Pretreatment of cotton fabric with cationic agents has been reported to diminish or eliminate the amount of electrolyte required and improve the wet fastness of direct dyes [9-10]. Modification of cotton with sodium benzoylthioglycollate for disperse dyeing [11-14], formaldehyde free crosslinking agents [15], a durable press finishing process [16], a trifunctional crosslinker on cotton via a cold pad process have also been studied [17].

In this investigation, it was planned to modify the cotton fabric by two different methods namely sulfonation using sodium bisulfite reagent and crosslinking using citric acid reagent. Citric acid crosslinking comes under the non-formaldehyde category. The dyeability of the modified cotton was also aimed at. Based on the performance of trisodium citrate as an exhausting agent in dyeing investigations done in different parts of study, the same was used in this investigation also. Importance was given to citric acid and trisodium citrate due to their eco-friendly nature.

Materials and methods

Plain woven bleached cotton fabric (ends per inch = 60, picks per inch = 52, count = 10s) was used. Sodium metaperiodate was used for oxidation modification of cotton. Sodium bisulfite was used for sulfonation modification of the oxidized cotton. Citric acid, magnesium chloride, ethylene glycol were used for crosslinking of cotton. CI Reactive Red 120 and CI Direct Blue 86 dyes were used for dyeing. Trisodium citrate was used as an exhausting agent. Sodium carbonate, acetic acid and Sandozin NIE (wetting agent) were used as dyeing auxiliaries.

The sequences of modifications employed in this study were numbered as 1, 2, 3 and 4 for convenience. Similarly, the wash and unwashed processes were designated as W and UW respectively.

Modification1 = Oxidation-wash-sulfonation-Wash (1W) &Unwash (1UW)
Modification2 = Crosslinking- Wash (2W) & Unwash (2UW)
Modification3 = Oxidation-wash-sulfonation-wash-crosslinking- Wash (3W) & Unwash (3UW)
Modification4 = Crosslinked-wash-oxidation-wash-sulfonation-wash (4W) &Unwash (4UW)

Sulfonation (1W & 1UW): The bleached cotton fabrics were used for modification by different procedures. Before sulfonation, the cotton fabric was oxidized with 0.05M sodium metaperiodate at a pH 4.6, MLR 1:35 at 20(C for one hour and washed with water. The oxidized fabric was sulphonated with 5% (owf) sodium bisulfite, pH 4.2, MLR 1:20 at 60(C for 3 hours. After sulfonation, one part of fabric was washed (designated as A) with water and other part of the fabric was unwashed (designated as B) and dried.

Crosslinking (2W & 2UW): The bleached cotton fabric was treated with 2% owf citric acid by padding twice to about 85% wet pickup in presence of 1% owf ethylene glycol and 0.2% magnesium chloride as catalyst. Padded fabric was dried at 85(C for 5 min and cured at 180(C for 3 min. After curing, one part of fabric was washed and other part of the fabric was unwashed and dried.

Sulfonation - Crosslinking (3W & 3UW): 1W, 1UW experiments were done first. The modified fabrics were then subjected to 2W, 2UW step experiments.

Crosslinking - sulfonation (4W & 4UW): 2W, 2UW experiments were done first. The modified fabrics were then subjected to 1W, 1UW step experiments.

Assessment of the modified fabrics by the above said procedures were subjected to the following measurements for the assessment of the efficiency modification. The modified and unmodified fabrics were subjected to weight measurements, water absorbency and strength tests. The modified and unmodified fabrics were subjected to SEM measurements at two different magnifications (x75 and x1500). The modified and unmodified cotton fabrics were subjected to reactive and direct dyeing separately. The dye exhaustion and fastness (wash, light and rub) tests were done as per the ISO procedures .

Results and discussion

Experiments carried out in 'W' series of different modifications produced weight gain for individual steps. The sulfonation step consisted of both oxidation and addition reactions. Though there was a possibility of weight loss in oxidation step, SO3Na-addition contributed an overall weight increase of about 4%. Linkage of citrate group led to a weight gain in the crosslinking process to about 6%. A combined process of sulfonation followed by crosslinking produced an additive weight gain of about 11%. Similarly, a combined process of crosslinking followed by sulfonation produced a similar additive weight gain of about 10%. The order of weight gain obtained in different method is ranked 3W > 4W > 2W > 1W. In UW series experiments, the modified (unwashed) fabrics produced weight gain for each step. The order of weight gain obtained is ranked as 4UW > 3UW > 2UW > 1UW (Table1).

The unwashed fabrics showed higher weight gain than washed fabrics. This may be due to the presence of unreacted species in the modification processes. These unreacted materials were leached out by the washing step and hence W series showed lower weight gain values when compared to the values of UW series.

The time for water absorbency was recorded for all modified and unmodified fabrics in both W and UW series of experiments. Series W showed a time of 1 sec for all modifications. 1UW, 2UW, 3UW and 4UW experiments produced the absorbency time of 2, 23, 13 and 22 sec respectively. 1UW method recorded the lowest absorbency time, while 2UW recorded the highest absorbency time. This may be due to the presence of inorganic water-soluble nature of unreacted sodium bisulfite in 1UW and presence of unreacted organic citric acid in 2UW. In 3UW, the inorganic unreacted was washed in the intermediate step while organic unreacted produced in the final effect. Hence, a time of 13 sec was observed. In 4UW, crosslinking was very dominant and effective than sulfonation (Table1).

The strength of the modified fabrics improved for different modification steps. For the wash category, the strength obtained was increased in the order UM < 1W < 2W < 4W < 3W. UW series of unwashed fabrics produced a slight improvement in strength than washed (W series) fabrics did. This may be due to the presence of unreacted species in unwashed conditions (Table1).

Mechanism of sulfonation

When cellulose is oxidized, carbonyl groups are generated. The carbon atom of the carbonyl group is electron deficient and the oxygen atom is electron rich. Therefore the carbonyl group in both aldehydes and ketones is highly reactive. The electron deficient carbon atom can be easily attacked by nucleophiles. In general terms, there are three possible mechanisms for addition of a nucleophile and a proton to give a tetrahedral intermediate in a carbonyl addition reaction.

(i) protonation followed by nucleophilic attack on the protonated carbonyl group,

H+ + = C=O —> = C=O-H

Nu : - + = C=O-H —> Nu-C-O-H

(ii) nucleophilic addition at the carbonyl group followed by protonation

Nu : - + = C=O —> Nu-C-O-

Nu = C-O- + H+ —> Nu-C-OH

(iii) Concerted proton transfer and nucleophilic attack.

Nu: - = C=O H+ —> Nu-C-O-H

Crosslinking of cellulose

Cotton is crosslinked to improve wrinkle resistance and other properties. Crosslinking is carried out by the use of difunctional reagents that react with the numerous hydroxyl groups on the polymer chain. The primary hydroxyl group at C6 is the most reactive group, but other hydroxyl groups also participate in the crosslinking reaction.

Cell-CH2OH + CH2O —> Cell-CH2OCH2OCH2-Cell

A crosslinking scheme using citric acid can be represented as below:

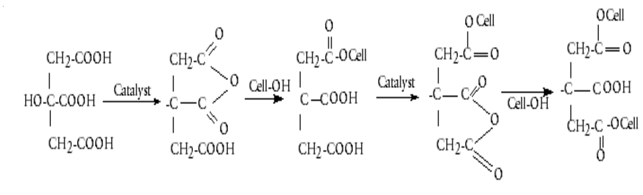

Table 1. Effect of modification and its properties of weight loss, water absorbency and strength results.

Parameter	UM	1W	1UW	2W	2UW	3W	3UW	4W	4UW
Weight gain (%)	-	4.37	5.87	6.07	7.46	11.44	13.43	10.31	13.58
Absorbency time (sec)	1	1	2	1	23	1	13	1	22
Strength (Kg)	10	11	12	13	14	16	18	15	18

Table 2. Dye uptake in reactive and direct dyeing (for W series).

Parameter	Range studied	Reactive Dyeing					Direct Dyeing				
		UM	1W	2W	3W	4W	UM	1W	2W	3W	4W
Dye conc. (%)	0.5	50.14	61.74	78.74	82.45	80.21	45.43	48.90	60.47	65.24	49.80
	1.0	52.33	63.46	79.57	84.03	80.43	45.75	50.55	65.24	66.20	51.45
	1.5	54.46	65.33	80.37	87.94	80.66	46.08	54.37	70.33	66.78	51.77
	2.0	56.28	66.61	82.31	88.00	80.95	46.37	58.33	70.74	67.82	58.55
	2.5	57.31	69.23	84.68	88.68	81.28	50.21	60.52	71.05	68.84	61.47
Exhausting agent conc. (%)	2	50.48	55.08	74.49	80.16	70.41	45.47	49.60	64.21	64.00	52.53
	4	50.73	55.98	77.49	83.00	73.65	48.21	56.74	65.27	65.18	58.27
	6	53.45	61.24	80.24	84.43	80.51	50.34	57.40	70.15	66.74	60.16
	8	56.28	63.92	81.24	86.43	80.96	52.32	59.21	74.23	67.31	61.72
	10	59.18	65.30	86.87	88.61	81.68	54.87	64.40	76.46	68.84	63.23
Dyeing time (min)	30	50.00	42.99	69.87	80.00	49.40	46.21	47.28	58.37	62.12	47.48
	45	50.43	54.07	71.82	81.04	50.66	47.32	50.49	64.40	64.49	49.52
	60	51.05	69.91	73.46	82.63	68.47	49.67	61.49	70.41	65.66	61.33
	75	51.77	71.49	74.03	83.48	74.46	50.51	63.74	73.33	66.21	64.77
	90	52.65	72.00	77.42	87.14	81.58	53.47	66.49	74.71	66.78	67.46
Dyeing temperature (°C)	60	50.41	52.40	62.49	81.66	66.46	48.22	54.44	57.20	60.00	54.56
	70	51.54	54.07	69.99	83.48	75.38	49.05	56.42	59.32	61.74	57.43
	80	52.31	69.91	73.74	85.51	80.18	60.14	57.31	63.30	62.21	58.48
	90	53.46	71.49	75.62	87.43	80.76	61.72	64.10	63.74	64.31	65.31
	100	55.27	74.62	79.47	89.00	81.47	61.85	66.22	64.22	66.72	67.28
Dyeing pH	10.0	50.49	42.21	66.87	80.11	80.00	44.32	49.40	55.20	60.24	49.47
	10.5	54.46	44.67	69.92	82.03	80.16	45.35	50.11	55.78	62.35	48.56
	11.0	55.00	46.45	71.87	83.64	80.46	48.72	52.15	56.31	64.72	52.33
	11.5	55.05	49.37	73.22	87.05	80.58	50.41	56.72	55.34	65.32	55.74
	12.0	55.27	50.21	77.47	88.00	80.76	51.22	57.24	58.21	66.21	57.75

Only the modifications in W series fabrics were subjected to SEM measurements. Owing to the uneven nature of unwashed (UW series) fabrics, the SEM measurement was not performed for UW series fabrics. Unmodified and modified cotton fabrics were SEM photographed with a magnification factor (x 75) to look for the woven pattern and they were also SEM photographed with a magnification factor (x 1500) to view the fibre surface nature. Unmodified fabric showed fuzzy woven pattern in x 75 magnification and rough fibre surface in x 1500. Modified fabrics showed improved woven pattern with less protruding fibres in x 75 magnification and swollen smooth rod like appearances in x 1500 magnification. Regular and uniformity in fibre surfaces were noticed in crosslinking modification (2W) than in sulfonation modification (1W). Between the combined modification methods, 3W processed fabric produced better modification effect than 4W processed. It was noticed from this investigation that processes ending with crosslinking showed better modification effect than processes ending with sulfonation (Figure 1).

Effect of variables in dyeing for W & UW series method

As the dye concentration was increased from 0.5 to 2.5%, the uptake increased for unmodified and various modified fabrics. Reactive dyeing showed better dyeing effect than direct dyeing. For a 0.5% dye concentration study, the dye uptake obtained for modifications is ranked as UM < 1W < 2W < 4W < 3W in reactive dyeing and UM < 1W < 4W <2W <3W in direct dyeing. For a 2.5% dye concentration study, dye uptake obtained for modifications is ranked as UM < 1W < 4W < 2W < 3W in reactive dyeing and UM < 1W < 4W <3W <2W in direct dyeing (Table 2).

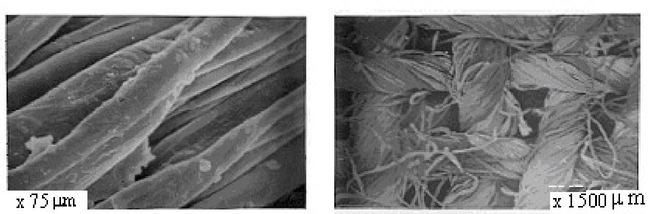

Figure 1a. Unmodified fabrics for x 75 and x 1,500 mm.

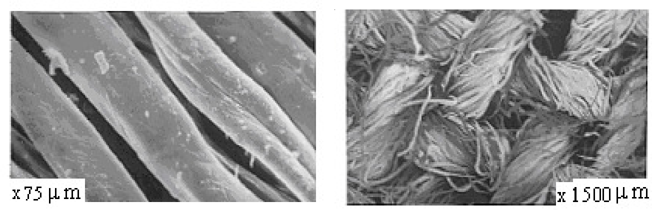

Figure 1b. Sulfonated fabrics for x 75 and x 1,500 mm.

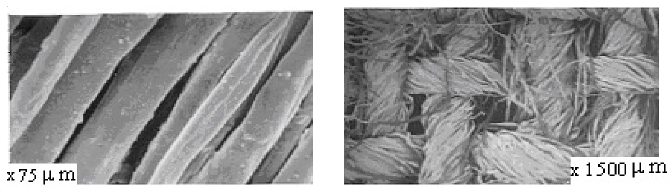

Figure 1c. Crosslinked fabrics for x 75 and x 1,500 mm.

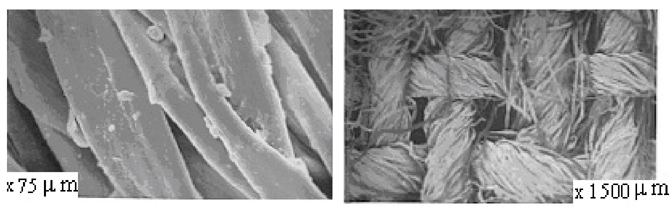

Figure 1d. Sulfonated and crosslinked fabrics for x 75 and x 1,500 mm.

Table 3. Dye uptake in reactive and direct dyeing (for W series).

Fastness	Reactive Dyeing					Direct Dyeing				
	UM	1W	2W	3W	4W	UM	1W	2W	3W	4W
Wash	3	4	4	4	4	2	3	3	3	3
Rub	2	3	3	4	3	2	2	2	3	2
Light	5	6	6	6	6	4	5	5	5	5

The processes ending with crosslinking showed higher dye uptake than others did. When the exhausting agent concentration was changed from 2 to 10%, the dye uptake increased for all modifications studied. For a concentration change from 2 to 10%, a dye uptake difference of about 10 and 15 % were observed for reactive and direct dyeing respectively. As the dyeing time was increased from 30 to 90 min, the dye uptake increased linearly. Higher dyeing time favored better dye uptake for all modified fabrics. The modification by 3W method produced maximum dye uptake in both reactive and direct dyeing methods. As the dyeing temperature was increased from 60 to 100(C, the dye uptake also increased. Here also, fabrics modified by 3W method produced maximum dye uptake in both reactive and direct dyeing methods. Dye bath pH influenced the dye uptake. For the range studied, higher alkaline pH favored better dye uptake. For UW series of experiments, as the study parameter values increased, improvement in dye uptake was noticed for majority of the cases studied. Particularly in dye concentration, in exhausting agent concentration and in dyeing time studies, 2UW modified fabrics produced the maximum dye uptake values. For studies in temperature and pH, mixed responses in dye uptake were noticed (Table3).

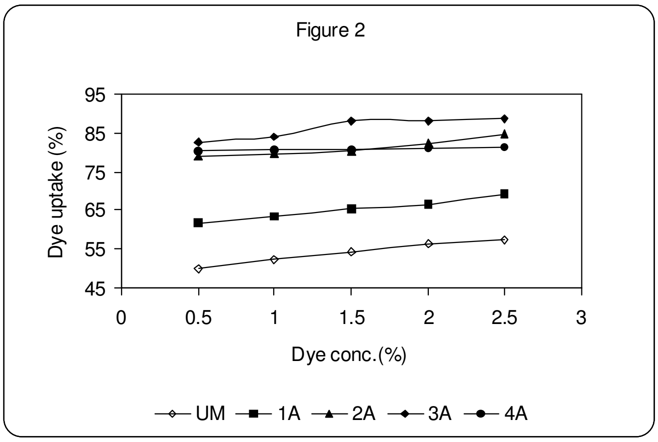

Figure 2. Effect of dye concentration on dye uptake in reactive dyeing (series A).

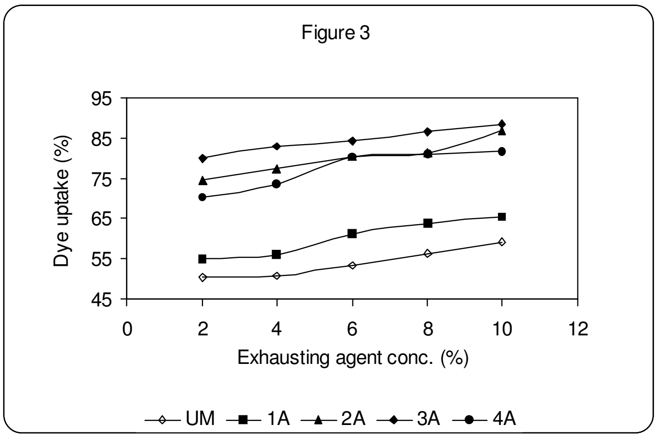

Figure 3. Effect of exhausting agent concentration in reactive dyeing (series A).

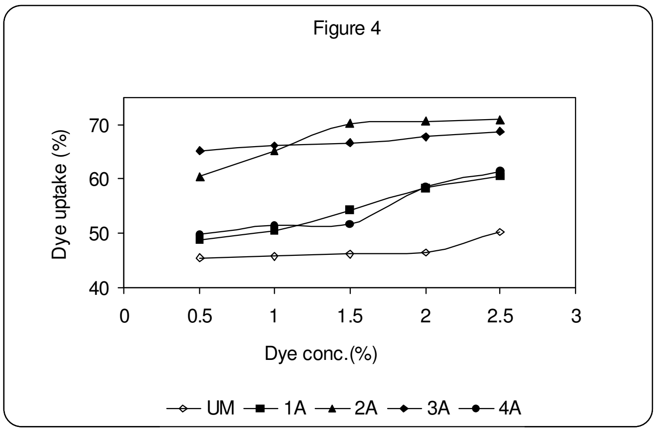

Figure 4. Effect of dye concentration in direct dyeing (series A).

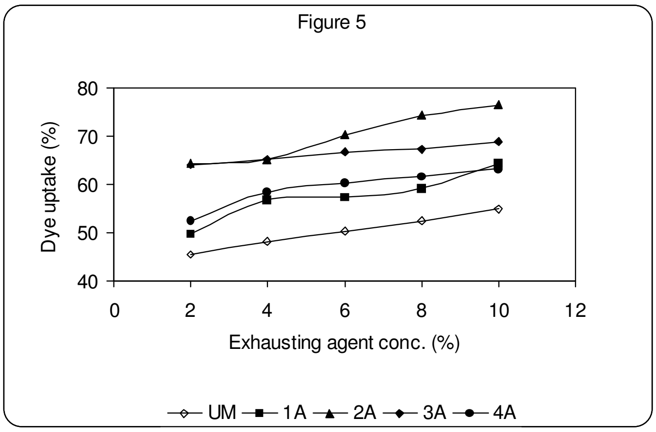

Figure 5. Effect of exhausting agent in direct dyeing (series A).

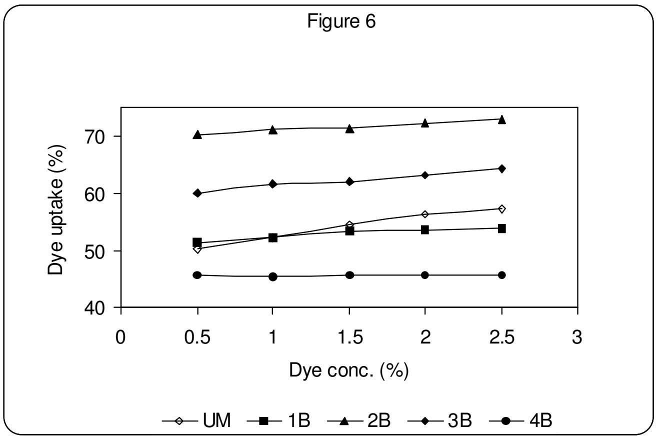

Figure 6. Effect of dye concentration in reactive dyeing (series B).

When the dye concentration was increased, the dye uptake increased for all modification systems studied. Unmodified fabric showed the lowest dye uptake; sulfonation process (1W) improved the dye uptake. Sulfonation and crosslinking (3W) process produced higher dye uptake than either sulfonation

(1W) or crosslinking (2W) process. In general, modifications improved the dye uptake (Figure 2). The exhausting agent concentration also performed similar trends as that were obtained in dye concentration studies (Figure 3).

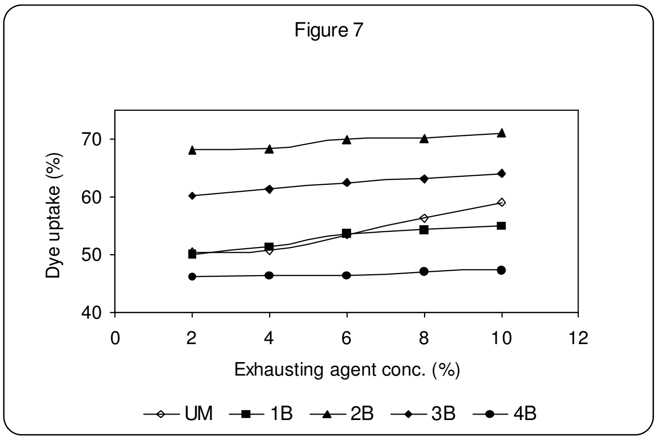

Figure 7. Effect of exhausting agent in reactive dyeing (series B).

When the dye concentration was increased from 0.5 to 2.5%, the dye uptake increased for all modification systems studied. Unmodified fabric showed the lowest dye uptake. Sulfonation process (1W) improved the dye uptake. Processes ending with crosslinking (2W and 3W) produced higher dye uptake than process ending with sulfonation (1W or 4W) process. In general, modifications improved the dye uptake (Figure 4). The exhausting agent concentration also performed similar responses as that were obtained in dye concentration studies (Figure 5). When the dye concentration was increased from 0.5 to 2.5%, the dye uptake increased to a little for all modification systems studied. 1UW and 4UW processes showed lower dye uptake than in unmodified. Thus, washing step is a crucial one in the modification processes. Crosslinking (2UW) process produced the highest dye uptake than others (Figure 6).

The exhausting agent concentration performed similar responses as that were obtained in dye concentration studies (Figure 7). When the dye concentration was increased from 0.5 to 2.5%, the dye uptake increased for all modification systems studied. The dye uptake values were dependent on the dye concentration. Lower dye concentration favored the unmodified fabric, whereas higher dye concentration favored the modified fabrics. Crosslinking (2W) step showed the maximum dyeing effect (Figure 8). The exhausting agent concentration also played a major role. The trends observed for a concentration change from 2 to 6% were in an inverse relation to that of a concentration change from 6 to 10% (Figure 9).

Reactive dyeing showed higher dye uptake than direct dyeing (Figure 10) did. Wash process (W series) showed higher dye uptake than unwash process (UW series) did. Reactive dyeing showed higher dye uptake than direct dyeing (Figure 11) did. Wash process (W series) showed higher dye uptake than unwash process (UW series) did. Reactive dyeing showed higher dye uptake than direct dyeing (Figure 12) did for series W.

Direct dyeing with wash process (W series) showed higher dye uptake than reactive dyeing with unwash process (UW series). Reactive dyeing showed higher dye uptake than direct dyeing (Figure 13) did.

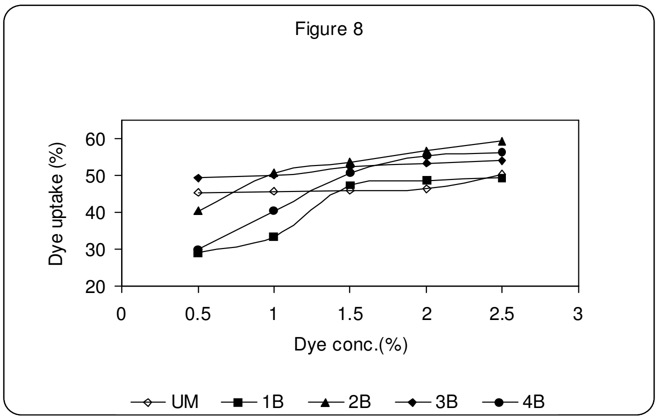

Figure 8. Effect of dye concentration in direct dyeing (series B).

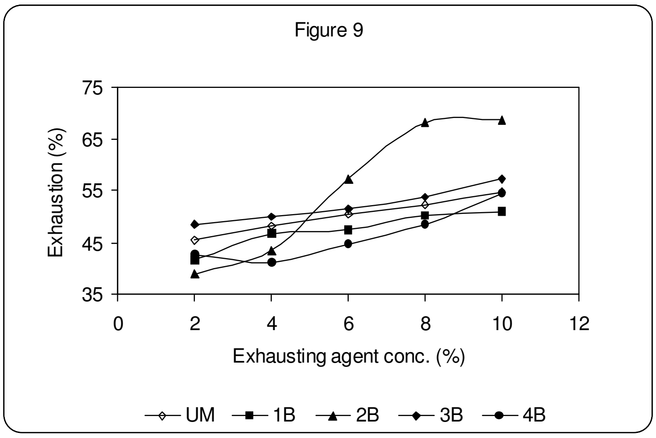

Figure 9. Effect of exhausting agent in direct dyeing (series B).

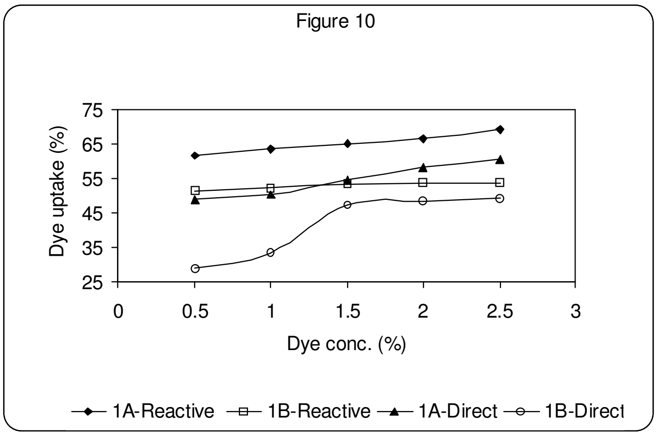

Figure 10. Effect of dye concentration in dyeing of sulfonated fabric.

Direct dyeing with wash process (W series) showed higher dye uptake than reactive dyeing with unwash process (UW series). The affinity of the modified fabric towards dyeing with the mentioned reactive and direct dyes is expected to depend on citric acid concentration. In this study, only a 2% concentration of citric acid was used. Thus, there may be a little change in the acidic property of the modified fabric. In addition, trisodium citrate (3 Na+) contributed higher cationic nature in the dye bath. These could interact well for the good dye uptake for the modified fabric. In both reactive and direct dyeing methods, modification by 3W processed fabric produced good wash, rub and light fastness than unmodified and other modified fabrics. Fabrics modified by UW series of methods produced

Table 4. Dye uptake in reactive and direct dyeing (for W series).

Parameter	Range studied	Reactive Dyeing					Direct Dyeing				
		UM	1UW	2UW	3UW	4UW	UM	1UW	2UW	3UW	4UW
Dye conc. (%)	0.5	50.14	51.41	70.16	60.00	45.68	45.43	28.90	40.44	49.18	29.84
	1.0	52.33	52.33	71.05	61.65	45.44	45.75	33.33	50.75	50.00	40.32
	1.5	54.46	53.41	71.47	62.10	45.65	46.08	47.30	53.56	52.24	50.67
	2.0	56.28	53.72	72.21	63.26	45.66	46.37	48.60	56.64	53.31	55.46
	2.5	57.31	53.81	73.00	64.36	45.75	50.21	49.28	59.24	54.12	56.26
Exhausting agent conc. (%)	2	50.48	50.00	68.12	60.15	46.05	45.47	41.60	38.90	48.52	42.60
	4	50.73	51.27	68.32	61.43	46.28	48.21	46.74	43.33	49.98	41.20
	6	53.45	53.71	69.99	62.43	46.43	50.34	47.40	57.30	51.43	44.72
	8	56.28	54.42	70.21	63.18	47.08	52.32	50.11	68.21	53.71	48.40
	10	59.18	55.00	71.20	64.00	47.17	54.87	51.01	68.75	57.21	54.42
Dyeing time (min)	30	50.00	40.11	58.97	60.00	30.00	46.21	42.33	46.72	48.25	43.22
	45	50.43	43.27	61.78	60.98	40.16	47.32	44.65	48.28	49.26	45.56
	60	51.05	49.28	63.44	61.46	58.47	49.67	50.94	50.35	49.61	50.92
	75	51.77	50.05	65.27	61.51	59.60	50.51	53.92	54.45	50.57	54.31
	90	52.65	52.33	65.93	63.00	60.18	53.47	54.22	56.48	53.23	54.78
Dyeing temperature (°C)	60	50.41	41.40	64.12	60.18	48.43	48.22	44.43	42.91	45.24	46.43
	70	51.54	47.74	65.92	60.78	52.66	49.05	48.28	45.35	46.76	48.33
	80	52.31	49.32	68.73	61.56	60.44	60.14	50.00	47.26	48.56	50.45
	90	53.46	52.05	69.22	62.48	60.73	61.72	54.10	49.47	49.47	54.21
	100	55.27	53.01	70.15	62.56	68.12	61.85	56.22	50.21	50.21	56.27
Dyeing pH	10.0	50.49	40.00	54.21	60.17	60.15	44.32	40.22	54.30	44.78	40.00
	10.5	54.46	43.16	55.48	61.00	60.48	45.35	45.23	54.46	45.10	48.27
	11.0	55.00	43.75	56.30	62.24	63.46	48.72	49.28	54.21	46.71	49.16
	11.5	55.05	53.37	58.21	63.50	63.77	50.41	50.16	54.74	47.32	51.36
	12.0	55.27	54.68	60.37	64.00	64.00	51.22	51.10	55.16	48.22	51.48

Table 5. Dye uptake in reactive and direct dyeing (for W series).

Fastness	Reactive Dyeing					Direct Dyeing				
	UM	1UW	2UW	3UW	4UW	UM	1UW	2UW	3UW	4UW
Wash	3	2	2	2	2	2	1	1	1	1
Rub	3	2	2	2	2	2	1	1	1	1
Light	5	4	4	4	4	4	3	3	3	3

poor fastness properties. Direct dyed fabrics produced lower fastness properties than reactive dyed fabrics did (Table 4 and Table 5).

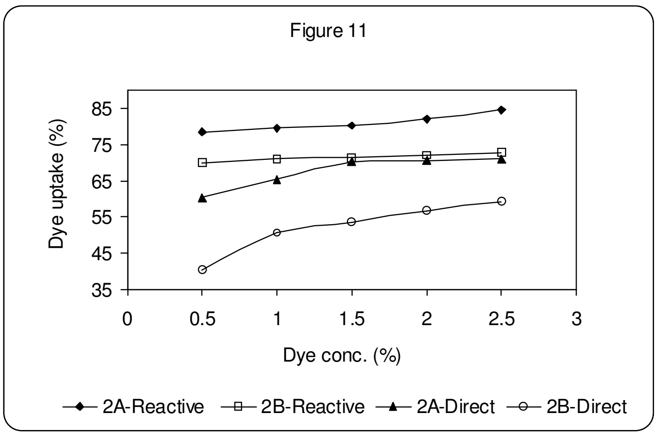

Figure 11. Effect of dye concentration in dyeing of crosslinked fabric.

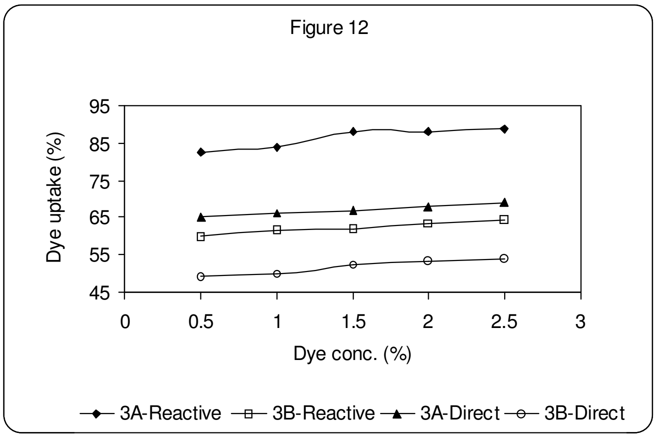

Figure 12. Effect of dye concentration in dyeing of (sulfonated & crosslinked) fabric.

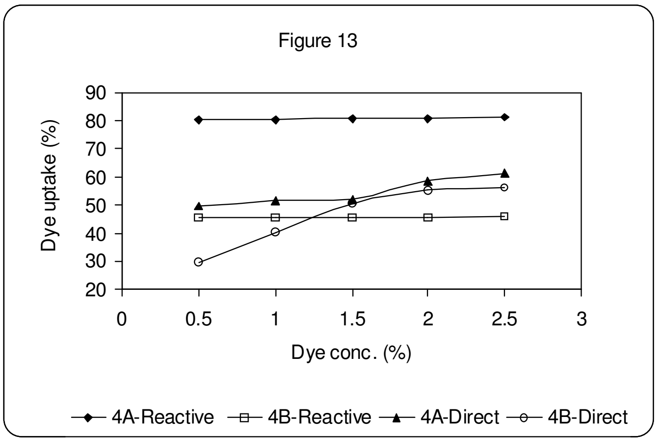

Figure 13. Effect of dye concentration in dyeing of (crosslinked & sulfonated) fabric.

Conclusion

The modified fabrics showed improved dye uptake than unmodified fabric. Crosslinking modification was found to be very effective than sulfonation modification. In direct dyeing, modified fabrics showed higher dye uptake than unmodified fabric. A thorough washing is a very essential step in modification procedures. Non-formaldehyde based citric acid crosslinking modification was found to be very effective for direct and reactive dyeing of cotton. Citric acid based crosslinker is an eco-friendly modifier.

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Acknowledgement

We acknowledge and to certify that the reported work entitled "DYEING OF SULFONATION AND CROSSLINKED COTTON FABRIC" is original. It has not been submitted elsewhere for publication and that the proper citations to the previously reported works have been given.

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