



Kinetics of Reactive Dyed Pretreated Cotton Fabrics With and without using Salt

B. Venkatesh, Govardhanrao Ch, Md. Vaseem Chavhan, M Siva Jagadish Kumar

Abstract: Most of the cotton fabrics at present are dyeing using reactive dyes which requires large quantities of salt, further produce large amount of effluent load to the environment in the form of more salinity in the effluent water along with other pollutants. In order to reduce the salinity in the waste water lot of investigations were carried out. Cotton fabrics pretreated with chitosan were dyed with reactive dyes. Pretreated samples were dyed without using salt as an electrolyte. The influence of pretreatment on kinetics in dye bath i.e rate of dye particle movement towards the fabric, wash fastness, rubbing fastness was determined. The results of this study shows that the pretreatment of cotton with chitosan increases dye uptake and shows good fastness to washing and rubbing same as that of conventional way of dyed samples. It was determined that chitosan was effective cross linking agent in salt-free dyeing of cotton fabrics.

Index Terms: Reactive dyes, Chitosan, Dye uptake, K/S values

I. INTRODUCTION

Cotton is the most widely used fiber among all the natural textile fibers for apparel purpose. This fiber is having good wet strength and provides good comfort to the wearer, moisture absorption and wicking properties. Now a day's most of the cotton fabrics are dyed with reactive dyes due to their excellent fastness properties but due to the ecological problems associated with the use of high volume of salt content in the effluent water now major concern is about reducing salt content in the dyeing process. Since cotton fiber has only moderate affinity for most of the reactive dyes, large quantity of salt is required to make the dye particles to move towards the fiber. Generally NaCl or Na₂SO₄ are commonly used electrolytes. Even then the dye bath exhaustion and fixation can still low as 50-60% for some dyes most of the time the wastewater contains salinity due to the high quantity of salt, leading to serious environmental problems [1].

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It has been found that pretreatment of cotton with different crosslinking agents before the dyeing is effective in improving dye-fiber affinity in the fiber and makes the way for reduction in the electrolyte usage. Most of the studies have found that chitosan as crosslinking agents. Earlier studies have shown that a variety of compounds may be effective in chemical modification of Cellulosic [2]. Salts plays important role in reactive dyeing by accelerating the dye particle movement toward the fiber and also reduces the solubility of dye in the water. Color intensity increased by the combined contribution of both salt and cationic agent on adsorption and fixation of reactive dyes on cotton. On comparison with the untreated fabric, cationized fabric have higher color uniformity and good fastness properties. This indicates that the cationic groups have a role in reactive dye absorption and the dye fixation is due to the covalent bonding with cotton hydroxyl groups [3]. The kinetics of the dyeing of a dichlorotriazinyl-reactive dye, Procion Blue MX-R, with knitted cotton fabrics have been studied using spectro-chemical channel flow cell. Dyeing experiments were performed over a wide range of dye and electrolyte concentrations and the kinetic parameters were reported. Atomic force microscopic studies proved that the mercerization as a pre-treatment improved the bean shaped fiber surface to circular shape which may offer additional sites in the fiber for dye uptake [4][8]. The investigation on adsorption kinetics of lac dye on cotton fabric was found to follow the pseudo second-order kinetic model and the rate constant indicated a faster adsorption rate than that for lac dye on silk [5]. Finally it was concluded that the activation energy for the adsorption process on cotton was found to be 42.4 kJ/mol [6]. The use of bio-surfactants was reported to be very much effective in the remediation of oil pollution which is more advantageous in biodegradability and reduced toxicity [7]. The present work is concentrates on the effectiveness of chitosan as a crosslinking agent in the pre-treatment of cotton fabrics in improving its dye ability with reactive dyes. Also to determine the kinetics of dye particles in the dye bath in varying concentrations of the chitosan and finally to assess the fastness properties like wash fastness and rubbing fastness after the treatment.

II. MATERIAL AND METHOD

The pretreated cotton fabrics were used in this study to carry out the dyeing and kinetics study. Chitosan powder was purchased from the local suppliers. A reactive dye used in this study was supplied by Color Tex Industries, Mumbai.

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Acetic acid and Sodium carbonate was purchased from National Scientifics, Guntur. The bleached cotton fabrics were treated with varying concentration of Chitosan i.e 3%, 5% and 7% by using pad, dry and cure method. Acetic acid was used to dissolve the Chitosan[9]. Then the dyeing was carried out on to untreated cotton fabrics using salt and without using salt for the Chitosan treated fabrics. The treated fabrics were evaluated for its color value and fastness properties.

III. RESULT AND DISCUSSION

The treatment of untreated and treated cotton fabrics with reactive dyes were carried out in IR Beaker dyeing machine. In this process the cotton fabrics initially dyed with conventional way of dyeing with reactive dyes and then with three different concentrations of chitosan i.e 3%, 5% & 7%. Kinetics of dye liquors at different time intervals have been taken for all the combinations of the dyes. The color values of dye liquors collected in different time Intervals of 3% chitosan treated dye liquor were shown in table 1. It clearly shows that there is a considerable change in the color difference values[10]. It may be due to the transfer of color when the temperature and time increases in the presence of chitosan. A plot of Transmission versus Wavelength has been drawn which is again clear that the high transmission values were obtained for the dye liquors consists of chitosan shown in Fig. 1.

Table 1: Color values of 3% Chitosan treated dye liquors

	Standard	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6	Batch 7	Batch 8	Batch 9	Batch 10
X	53.101	53.186	52.430	54.069	46.726	39.418	40.925	43.903	39.423	20.384	21.890
Y	40.328	40.749	40.416	41.822	34.733	29.915	30.164	32.641	28.900	14.958	15.991
Z	0.163	0.176	0.185	0.177	0.136	0.126	0.100	0.150	0.108	0.075	0.059
L*	69.703	70.000	69.765	70.748	65.541	61.581	61.795	63.869	60.693	45.576	46.963
a*	42.786	41.727	40.774	40.770	43.522	38.819	42.594	42.608	42.662	34.155	35.380
b*	117.814	118.141	117.600	119.414	111.029	104.349	105.087	107.941	103.077	77.491	80.111
C*	125.343	125.293	124.468	126.182	119.254	111.336	113.391	116.046	111.557	84.684	87.576
H*	70.013	70.519	70.849	71.121	68.568	69.566	67.909	68.432	67.489	66.187	66.145
dE*	-----	1.147	2.024	2.778	7.994	16.218	14.985	11.469	17.274	47.776	44.648
DL*	-----	0.297	0.062	1.045	-4.162	-8.122	-7.908	-5.834	-9.010	-24.127	-22.740
Da*	-----	-1.059	-2.012	-2.016	0.736	-3.967	-0.192	-0.178	-0.124	-8.631	-7.406
Db*	-----	0.327	-0.214	1.600	-6.785	-13.465	-12.727	-9.873	-14.737	-40.323	-37.703
DC*	-----	-0.049	-0.875	0.839	-6.088	-14.007	-11.952	-9.297	-13.786	-40.658	-37.767
DH*	-----	1.107	1.825	2.433	-3.084	-0.921	-4.379	-3.329	-5.210	-6.880	-7.073

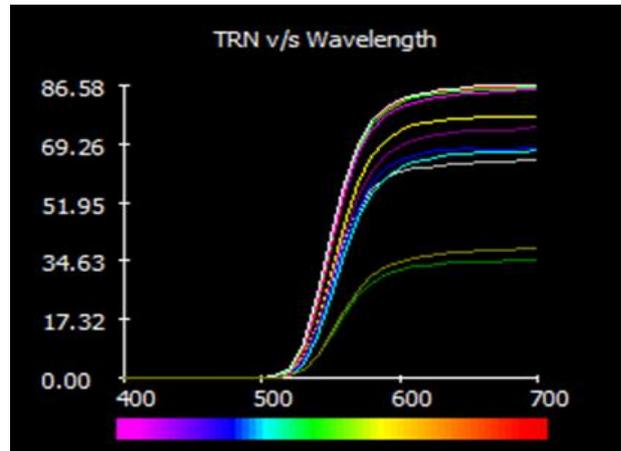


Fig 1: Transmission vs Wavelength curves of 3% Chitosan treated dye liquors

Table 2 shows the kinetics of dye liquors collected and examined at different time intervals of 5% chitosan used in the dyeing process. It was clear from the table and the plot of transmission versus wavelength from the fig 2 shows that the color values were in the increasing pattern when compared with the 3% chitosan treated samples. It may be due to the reason that the concentration of chitosan is increasing.

Table 2: Color values of 5% Chitosan treated dye liquors

	Standard	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6	Batch 7	Batch 8	Batch 9	Batch 10
X	52.168	55.355	55.886	57.035	41.800	54.308	51.870	49.225	44.861	33.819	24.609
Y	40.929	46.026	48.366	48.614	34.814	45.180	42.383	40.247	36.319	26.423	19.370
Z	0.192	0.317	0.471	0.407	0.271	0.324	0.264	0.261	0.229	0.135	0.109
L*	70.126	73.563	75.055	75.211	65.604	73.010	71.134	69.645	66.763	58.436	51.117
a*	38.531	31.901	26.798	28.981	28.850	31.628	33.407	32.751	32.929	33.795	29.683
b*	118.119	122.229	122.574	123.767	109.183	121.175	118.809	116.288	111.786	98.800	86.550
C*	124.245	126.323	125.469	127.115	112.930	125.235	123.416	120.812	116.535	104.420	91.499
H*	71.904	75.342	77.636	76.790	75.168	75.341	74.265	74.241	73.557	71.088	71.042
dE*	-----	8.524	13.484	12.205	13.929	8.081	5.268	6.082	9.099	23.072	37.898
DL*	-----	3.437	4.929	5.085	-4.522	2.884	1.008	-0.481	-3.363	-11.690	-19.009
Da*	-----	-6.630	-11.733	-9.550	-9.681	-6.903	-5.124	-5.780	-5.602	-4.736	-8.848
Db*	-----	4.110	4.455	5.648	-8.936	3.056	0.690	-1.831	-6.333	-19.319	-31.569
DC*	-----	2.079	1.225	2.870	-11.314	0.990	-0.828	-3.433	-7.710	-19.825	-32.746
DH*	-----	7.518	12.490	10.717	6.750	7.484	5.103	4.998	3.472	-1.624	-1.606

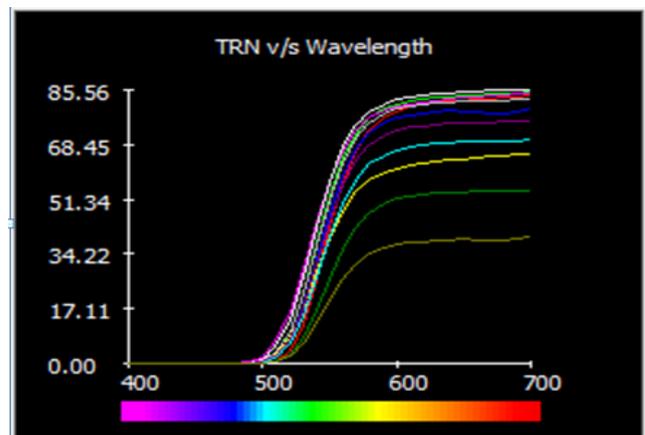


Fig 2: Transmission vs Wavelength curves of 5% Chitosan treated dye liquors

Further to increase the effectiveness of the more dye particle movement towards the fabric 7% of chitosan was added to the dye bath and studied the dyeing kinetics at different time intervals. This was given in the table 3 which shows clearly that the with the increase of dyeing time where there is an incremental pattern in the dye movement. It may be due to the fact that the increase in the chitosan concentration may improve the dye particle movement towards the fabric even though there was no presence of salt.

Table 3: Color values of 7% Chitosan treated dye liquors

Standard	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6	Batch 7	Batch 8	Batch 9	Batch 10	
X	46.032	39.973	43.705	35.394	35.018	59.642	54.244	56.212	60.873	60.589	57.179
Y	39.490	33.198	36.240	32.363	32.046	59.063	51.979	52.502	58.324	58.118	54.133
Z	0.428	0.280	0.284	0.893	0.884	4.394	2.385	1.524	2.626	2.706	2.230
L*	69.105	64.321	66.703	63.642	63.381	81.326	77.268	77.580	80.918	80.804	78.539
a*	26.194	28.753	29.810	16.778	16.622	8.959	13.112	16.728	13.644	13.465	14.991
b*	112.937	106.836	110.879	96.762	96.444	98.869	104.578	112.909	109.038	108.253	108.010
C*	115.935	110.638	114.816	98.206	97.866	99.274	105.397	114.141	109.888	109.087	109.045
H*	76.911	74.907	74.922	80.131	80.189	84.788	82.820	81.540	82.834	82.876	82.065
dE*	8.164	4.804	19.497	19.910	25.383	17.540	12.706	17.671	17.912	15.453
DL*	-4.784	-2.402	-5.463	-5.724	12.221	8.163	8.475	11.813	11.699	9.434
Da*	2.559	3.616	-9.416	-9.572	-17.235	-13.082	-9.466	-12.550	-12.729	-11.203
Db*	-6.101	-2.058	-16.175	-16.493	-14.068	-8.359	-0.028	-3.899	-4.684	-4.927
DC*	-5.297	-1.119	-17.729	-18.069	-16.661	-10.538	-1.793	-6.047	-6.848	-6.889
DH*	-3.963	-4.007	5.998	6.096	14.744	11.400	9.295	11.668	11.708	10.115

Transmission versus wavelength curves shown in the fig 3 also confirms the same pattern of increase in the dye movement with increase in the concentration of chitosan.

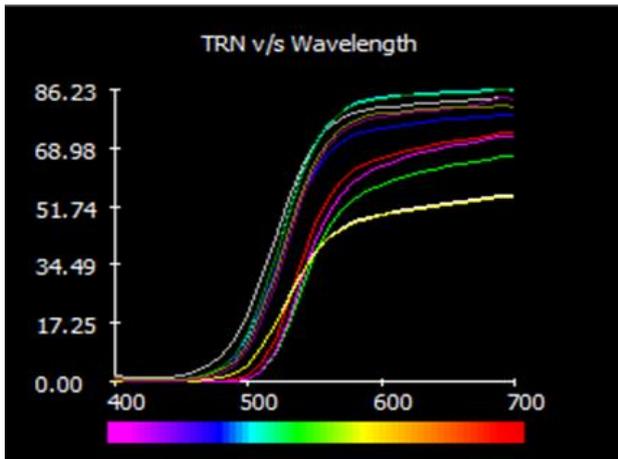


Fig 3: Transmission vs Wavelength curves of 7% Chitosan treated dye liquors

In order to compare the dye movement towards the fabric without using chitosan, the cotton fabrics were also treated by following the conventional way of dyeing and the kinetics were studied at different time intervals same as that previous process. Table no. 4 shows the color values of dye liquor collected from the dye bath at different time intervals and measured through Spectrophotometer.

Table 4: Color values of conventional treated dye liquors

	Standard	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6	Batch 7	Batch 8	Batch 9	Batch 10
X	53.851	54.415	50.968	43.130	37.593	22.644	24.274	29.517	27.864	22.362	27.242
Y	42.773	43.460	40.398	33.803	30.668	17.919	18.810	23.151	22.019	17.922	21.783
Z	0.214	0.223	0.207	0.170	0.203	0.105	0.105	0.118	0.134	0.113	0.124
L*	71.401	71.866	69.752	64.806	62.226	49.398	50.465	55.227	54.048	49.402	53.796
a*	37.397	36.831	36.980	36.284	30.185	28.366	31.044	31.901	30.537	27.057	29.131
b*	120.000	120.668	117.263	109.268	104.340	83.641	85.484	93.503	91.236	83.537	90.944
C*	125.692	126.164	122.956	115.135	108.618	88.320	90.946	98.795	96.211	87.810	95.496
H*	72.662	72.997	72.468	71.602	73.835	71.237	70.013	71.133	71.466	72.024	72.210
dE*	0.991	3.222	12.646	19.530	43.447	40.866	31.526	34.286	43.823	34.964
DL*	0.465	-1.649	-6.595	-9.175	-22.003	-20.936	-16.174	-17.353	-21.999	-17.605
Da*	-0.566	-0.417	-1.113	-7.212	-9.031	-6.353	-5.496	-6.860	-10.340	-8.266
Db*	0.668	-2.737	-10.732	-15.660	-36.359	-34.516	-26.497	-28.764	-36.643	-29.056
DC*	0.472	-2.736	-10.557	-17.074	-37.372	-34.746	-26.897	-29.481	-37.883	-30.197
DH*	0.738	-0.421	-2.226	2.395	-2.620	-4.944	-2.974	-2.296	-1.169	-0.864

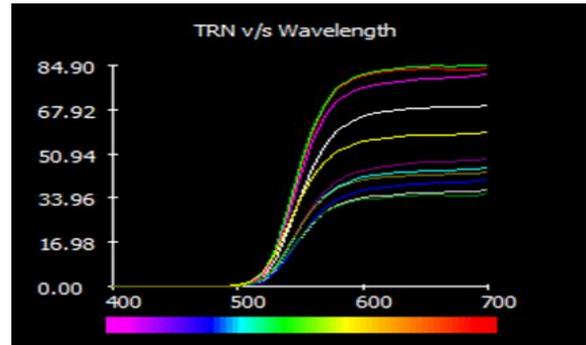


Fig 4: Transmission vs Wavelength curves of conventional dyed samples

With respect to increase in time, the amount of exhaustion in the bath increases in all the shades. We can observe clear peaks in the rise of transmittance values at different wavelengths in Fig 4. The transmittance values of the conventional method were comparatively lower than the transmittance value of pre-treated with 3%chitosan. The transmittance value was found to be less than that of the conventional method when 5, 7% chitosan was used. The maximum transmittance value found with 3% chitosan. As the concentration of chitosan increased above 3%, the transmittance value decreased All the dyed samples after treating with conventional way of dyeing and three different concentrations of chitosan were subjected to fastness testing to assess the properties of dyed samples against rubbing and washing fastness testing. Table 5 shows the rubbing fastness results of all the dyed samples. From the table it was clear that the rubbing fastness ratings of chitosan treated samples were almost similar to the conventional dyed samples even though there was no presence of salt.

Table 5: Rubbing fastness of conventional & chitosan treated samples

Shade %	Dry rub	Wet rub
3% chitosan	5	4/5
5% chitosan	4/5	4
7% chitosan	4	4
conventional	5	4/5

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As compared with conventional dyed, 3% chitosan treated shows inherent rubbing fastness properties in both dry and wet conditions. As compared with conventional dyed, 5, 7% chitosan treated shows poor rubbing fastness properties in both dry and wet conditions. The washing fastness properties of chitosan dyed cotton fabrics were determined using Laundro Meter. The fastness results were compared with conventional dyed fabrics. The washing fastness was found to be good for all the chitosan pretreated dyed sample may be due to the effectiveness of dye fixation due to pretreatment with chitosan. As compared with conventional dyed, 3% chitosan treated shows inherent washing fastness properties. As compared with conventional dyed, 5, 7% chitosan treated shows poor washing fastness properties as shown in Table 6.

Table 6: Washing fastness of conventional & chitosan treated samples

Shade %	Shading	Fading
3% chitosan	5	5
5% chitosan	4	4
7% chitosan	4	4
conventional	4/5	4/5

IV. CONCLUSION

Cotton fabrics were pretreated with chitosan before dyeing which increases the reactivity of dyes on to the fibers. The cotton fabrics treated with chitosan was found to be harsh in feel. The chitosan treated fabrics with 3%, 5%, 7% chitosan shown more dye ability, more exhaustion, good fastness properties. The dye particle movement in the dye bath with respect to time also increased when compared to the untreated cotton fabrics. Wash fastness and rubbing fastness of pretreated sample at 3% is showing better results than that for the conventionally dyed sample.

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