An Eco-friendly Approach for Sodium Chloride Free Cotton Dyeing

T. Umer[1], I. A. Shaikh[2], S. Munir[3], E. Suhail[4], M. Zameer[5], I. Ahmad[6]

[1,2,3,4,5,6]College of Earth and Environmental Sciences, University of the Punjab, Lahore
[4]erham_great@hotmail.com

Abstract-Present study was conducted with an aim to develop an environmental friendly method of dyeing cotton as an alternative to standard reactive dyeing process that requires high level of salt. When dyeing was carried out in the absence of sodium chloride (NaCl), an extremely lighter depth of shade was experienced, and hence this particular research was focused on the reduction of the total colour difference (ΔE*) to a minimum level. Instead of adding any other chemical or any additional process like cationization, salt-free reactive dyeing was carried out by varying three common process parameters (dyes, alkali, and process time) to achieve required depth of shade. The results obtained were compared with those of conventionally dyed fabrics in terms of depth of shade (ΔL*), total colour difference (ΔE*), washing fastness, and rubbing fastness. The results were found to be promising and comparable to those dyed with using NaCl. Moreover, the investigated method showed a significant reduction of Total Dissolved Solids (TDS) and Electrical Conductivity (EC) in the wastewater, and thus proved to be an environment friendly process.

Keywords-Cotton, Reactive Dyes, Salt-free Dying, Colour, Wastewater

I. INTRODUCTION

Industries uses large amount of water and chemicals, and textile industry is no exception. Textile processes consume large amount of water, and in return, produce huge volume of wastewater containing large number of pollutants such as coloured effluent, residual chemicals, high pH, Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), and high amount of Total Suspended Solids (TSS) and Total Dissolved Solids (TDS) [i].

Dyes such as reactive, direct, vat, and sulphur are extensively used in the dyeing of cellulosic materials, however, reactive dyes are high in demand due to its advantageous properties like excellent brightness, wide gamut of colours available, and excellent wash fastness due to the formation of covalent bonds between dye and fibre [ii]. Use of reactive dyes is also proved to be an expensive and time consuming process because it requires high amount of electrolytes (salt and alkali), extensive rinsing and hot washing-off steps after dyeing for the removal of unfixed dyes. All this creates a large volume of wastewater containing elevated amount of salt and alkali [iii].

Electrolytes (NaCl or Na_2CO_3) are required in the process of reactive dyeing to overcome the large repulsive forces (zeta potential) between anionic reactive dye and negatively charged cotton fiber [iv]. Concentration of electrolyte depends upon the required depth of colour and type of dye structure, and can be varied up to 100 grams per liter [v].

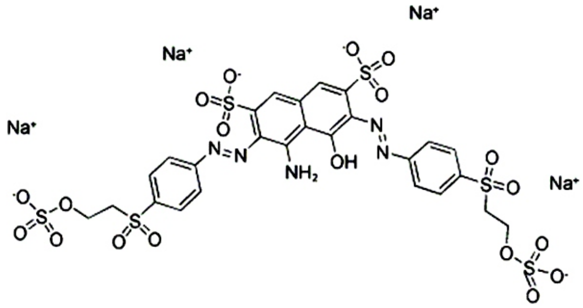
Several researchers reported different methods to achieve salt-free dyeing, including modification of reactive dyes [v], pre-treatment of cotton with chitosan derivatives [vi], polyvinylamine chloride [vii], cationic modification of cotton [viii], dendrimer use to modify the dyeing behavior [ii], NBP-NH2 to graft cotton fiber [ix] and use of organic salt [x].

The aim of the present work was to develop a salt-free dyeing method which can produce similar depth of shade compared to that of standard dyeing method. It was also of interest to find the reduction of the pollution load associated with the excessive usage of electrolytes in standard textile dyeing process. To achieve this goal, numbers of salt-free dyeing were performed by varying only common process parameters (dyes, alkali, and process time).

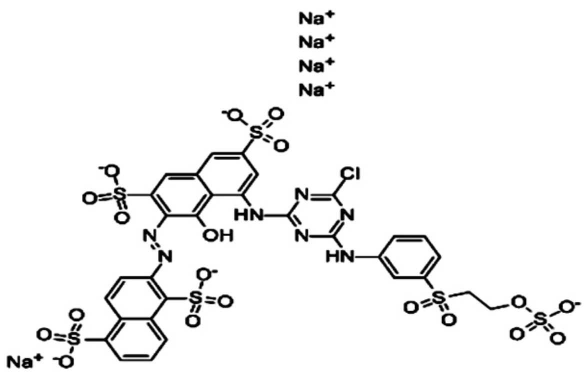
II. MATERIALS AND METHODS

2.1 Materials

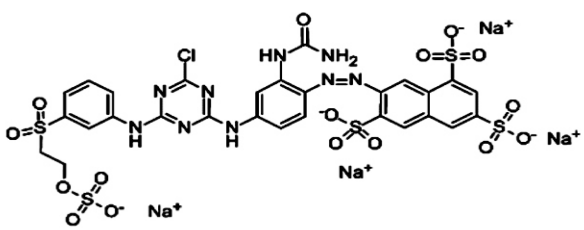
A 100% Cotton knitted fabric (single jersey) made of 30's yarn and having 200 GSM (Grams per Square Meter) was used in the study. The reactive dyes Synozol Black B 150% (CI Reactive Black 5), Synozol Red HF-6BN (CI Reactive Red 195), and Synozol Yellow HF-2GR (CI Reactive Yellow 145) were supplied by KISCO Corporation (Korea). Structural formulas of dyes are given in Fig. 1. Auxiliary chemicals, sodium chloride (NaCl), sodium hydroxide (NaOH), and acetic acid (CH_3COOH), used were of commercial grade and used without any dilution.



a) Reactive Black 5



b) Reactive Red 195



c) Reactive Yellow 145

Fig. 1. Structural formulas of dyes

2.2 Dyeing and wash-off Conditions

10 gram fabric samples were dyed according to exhaust dyeing method (ALL-IN-ONE) for shade depth of 5% o.w.f at a liquor ratio of 1:10. Dyeing was carried out at 60ºC for 60 min with 80g/L sodium chloride and 20g/L sodium carbonate. This dyed fabric was regarded as standard sample. Dyeing trials with 0 g/L salt were carried out the similar way as standard dyeing process. At the completion of dyeing, fabric was subjected to wash-off treatment that involved rinsing, neutralization, warm wash (60°C), hot wash (80°C), soaping/boil off (95°C) and rinsing. Each step was performed for 5 minutes.

Afterwards, fabric samples were removed from laboratory dyeing machine (AHIBA NUANCE, USA), squeezed, dried, and conditioned before evaluating for change of shade and colour fastness properties.

2.3 Measurements

Colour difference values (ΔL*, Δa*, Δb*, ΔC*, ΔH* and ΔE*) [11] were determined using a spectrophotometer (600 PLUS CT, Datacolour, USA) with illuminant D65/10° observer, specular reflectance included, and aperture size 30 mm settings. Colour fastness to washing and crocking were determined using test methods ISO 105-CO6 and ISO 105-X12, respectively, and reported in standard grey scale (marks 1-5, 1=poor, 5=excellent).

III. Results and Discussion

When dyeing was carried out in the absence of salt (0g/l) and compared to standard dyeing, the results were summarized in Fig. 2. The data clearly shows that the values of depth of shade (ΔL*) and total colour difference (ΔE*) were found to be on the higher side. In the case of Black 5, the salt-free dyeing was very light (ΔL*= 3.4) and less saturated (ΔC*= 2.68) compared to standard dyeing, thus resulting into huge total colour difference (ΔE*= 4.41). Salt-free dyeing of Yellow 145 yielded a lighter (ΔL*= 4.45), brighter (ΔC*= 4.52), and an off-shade (ΔE*= 8.63) dyeing. Fabric dyed with Red 195 in the absence of salt was also lighter (ΔL*= 7.33), duller (ΔC*= -6.52), and had a huge total colour difference (ΔE*= 9.81).

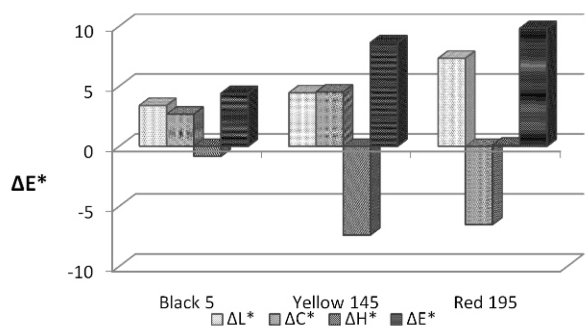


Fig. 2. CIELab Colour differences between standard and 0g/l salt dyeing

To minimize the colour difference between reference dyeing and salt-free dyeing, several dyeings were carried out with increased amount of sodium carbonate (20-40 g/L), and the results are summarized in Table I.

TABLE I
CIELAB VALUES OF SAMPLES WITH VARIED Na_2CO_3 CONCENTRATION

	ΔL*			ΔE*		
Name of dye	20g/l Na_2CO_3	30g/l Na_2CO_3	40g/l Na_2CO_3	20g/l Na_2CO_3	30g/l Na_2CO_3	40g/l Na_2CO_3
Black 5	3.4	1.6	0.47	4.41	1.45	0.49
Yellow 145	4.45	2.8	0.96	8.63	4.38	1.31
Red 195	7.33	4.3	2.28	9.81	6.23	2.92

When the concentration of Na_2CO_3 was limited to 20 g/l (with 0 g/l salt), all three shades were found extremely lighter and different to those of reference dyeing. However, when the concentration of Na_2CO_3 was increased to 30 and 40 g/l (with 0g/l salt), both depth of shade (ΔL*) and total colour difference (ΔE*) was minimized significantly. In case of Black 5, ΔL* and ΔE* were reduced to 0.47 and 0.49, respectively, when the concentration of Na_2CO_3 was increased to 40 g/l. For Yellow 145, both ΔL* and ΔE* were reduced to 0.96 and 1.31, respectively. However, in the case of Red 195, ΔL* was significantly improved from 7.33 to 2.28 and ΔE* from 9.81 to 2.92, but the final colour assessment cannot be regarded as a perfect match due to ΔE* difference greater than 1.0.

Dye concentration influences both dye fixation and the colour strength of the dyed fabric in the dyeing process [12]. Table II clearly demonstrates that colour depth (ΔL*) of the dyed fabric increased with increasing dye concentration, and thus total colour difference (ΔE*) was also reduced and colour fastness was found between 4 to 5. In case of Black 5, the depth of shade (ΔL*) was significantly increased from 3.4 to 0.74 when dye concentration was increased from 5 to 8% owf. Correspondingly, the total colour difference (ΔE*) was also reduced from 4.41 to 1.12. In the dyeing of Yellow 145 and Red 195, an improvement in ΔL* and ΔE* was clearly observed when dye concentration was gradually increased, however the shade difference was still far away from a commercially acceptable match. When the Na_2CO_3 concentration was also increased, from 20 to 40 g/l, along with increased dye concentration, both ΔL* and ΔE* improved significantly. Colour fastness properties of all dyes at all concentrations were almost same.

Table III shows that when the dyeing time was increased from 60 to 120 minutes along with increased dye concentration, an overall improvement in colour difference was observed. In case of Black 5, the lowest colour difference in terms of ΔL* and ΔE* were found to be 0.40 and 0.42, respectively. For Yellow 145, the best results (ΔL*=0.04 and ΔE*= 0.80) were achieved when the depth of shade and dyeing time were increased to 8% o.w.f and 120 minutes, respectively. The dyeing of Red 195 also followed the similar trend. When dyeing time was extended to 120 minutes along with increased dye and Na_2CO_3 concentrations, ΔL*values of -1.18, -0.62, and -0.49 were achieved for Black 5, Yellow 145, and Red 195, respectively. This showed that all samples were darker than those of dyed with zero salt dyeing. Colour fastness properties of all dyes for 2 hours dyeing were not much different from 60 min dyeing and ranges between 4.5 to 5, which are considered excellent colour fastness values.

This study also revealed that the total dissolved solids (TDS) and electrical conductivity (EC) concentration was decreased up to 40 to 50 % when dyeing was carried out in the absence of salt as shown in Table IV.

TABLE IV
VALUES OF TDS AND EC AT VARIOUS DYEING CONDITIONS

Process type	Dye concentration (%)	Waste water quality parameter	
		TDS(ppm)	EC
Standard dyeing	5	123000	174
Dyeing with 20 g/l Na_2Co_3	5	42000	62
	6	41000	60
	7	42000	63
	8	45000	64
Dyeing with 40 g/l Na_2Co_3	5	70000	73
	6	72000	82
	7	73000	81
	8	75000	81

IV. CONCLUSION

A Salt-free reactive dyeing method aiming a comparable colour yield and having minimum colour differences was investigated. No pre-treatment and no additional chemicals were added, and dyeings were carried out by varying common process parameters like dyes, alkali, and process time only. The optimum dyeing conditions are as follows: for Black 5, 5% owf, 40g/l Na_2CO_3, 60-minute dyeing time; 7% owf, 30 g/l Na_2CO_3, 60-minute dyeing time; 7% owf, 30g/l Na_2CO_3, 120-minute dyeing time; for Yellow 145, 5% owf, 40g/l Na_2CO_3, 60-minute dyeing time; 8% owf, 30g/l Na_2CO_3, 120-minute dyeing time; for Red 195, 7% owf, 40g/l Na_2CO_3, 120-minute dyeing time. At these conditions, a considerable decrease of total dissolved solids (TDS) and electrical conductivity (EC) in the wastewater was observed.

REFERENCES

[i] S. Tubtimhin (2002). *Pollution minimization and energy saving potentials in the cotton dyeing industry,* School of Environmental Resources and Development, Asian Institute of Technology, Thailand.

[ii] S. M. Burkinshaw, M. Mignanelli, P. E. Froehling and M. J. Bide, (2000, Dec). The use of dendrimers to modify the dyeing behaviour of reactive dyes on cotton. *Dyes Pigments*. [Online]. *47(3),* pp. 259-267. Available:http://www.sciencedirect.com/science/article/pii/S014372080000053X

[Iii] C. Zheng, A. Yuan, H. Wang and J. Sun. (2012, Jun). Dyeing properties of novel electrolyte-free reactive dyes on cotton fibre. *Color. Technol.* [Online]. *128(3),* pp. 204-207. Available: http://onlinelibrary.wiley.com/doi/10.1111/j.1478-4408.2012.003

[iv] D. Chattopadhyay, R. Chavan and J. Sharma. (2007, Sep). Salt-free reactive dyeing of cotton. *International J. Cloth. Sci. Tech.* [Online]. *19(2),* pp. 99-108. Available:http://www.emeraldinsight.com/journals.htm?articleid=1593600

[v] K. Srikulkit and P. Santifuengkul. (2000, Dec). Salt-free dyeing of cotton cellulose with a model cationic reactive dye. *Color. Technol.* [Online]. *116(12),* pp. 398-402. Available:http://onlinelibrary.wiley.com/doi/10.1111/j.1478-4408.2000.tb00017.x/pdf

[vi] S. H. Lim and S. H. Hudson. (2004, May). Application of a fibre-reactive chitosan derivative to cotton fabric as a zero-salt dyeing auxiliary. *Color. Technol.* [Online]. *120(3),* pp. 108-113. Available:http://onlinelibrary.wiley.com/doi/10.1111/j.1478-4408.2004.tb00215.x/pdf

[vii] W. Ma, S. Zhang, B. Tang and J. Yang. (2005, Jul). Pretreatment of cotton with poly (vinylamine chloride) for salt-free dyeing with reactive dyes. *Color. Technol.* [Online]. *121(4),* pp. 193-197. Available:http://onlinelibrary.wiley.com/doi/10.1111/j.1478-4408.2005.tb00272.x/pdf

[viii] M. Montazer, R. Malek and A. Rahimi. (2007, Dec). Salt free reactive dyeing of cationized cotton. *Fiber Polym.* [Online]. *8(6),* pp. 608-612. Available:http://link.springer.com/article/10.1007%2FBF02875997

[ix] F. Zhang, Y. Chen, H. Lin, H. Wang and B. Zhao. (2008, Oct). HBP-NH2 grafted cotton fiber: Preparation and salt-free dyeing properties. *Carbohydr. Polym.* [Online]. *74(2),* pp. 250-256. Available:http://www.sciencedirect.com/science/article/pii/S0144861708000878

[x] N. S. Ahmed, (2005, Jun). The use of sodium edate in the dyeing of cotton with reactive dyes. *Dyes Pigments*. [Online]. *65(3),* pp. 221-225. Available:http://www.sciencedirect.com/science/article/pii/S0143720804001780

[xi] M. S. Alam, G. A. Khan, S. A. Razzaque, M. J. Hossain, M. Minhaz-ul-Haque and S. Zebsyn, (2008, Mar). Dyeing of cotton fabrics with reactive dyes and their physico-chemical properties. *Indian J. Fibre Text.* [Online]. *33(1),* pp. 66-71. Available:http://nopr.niscair.res.in/handle/123456789/372

[xii] Y. Deng, B. Tang, H. Zhao, J. Xu, J. Xiao, X. Zhang,. . . S. Zhang. (2013, Apr). Dyeing method and properties of polymaleic acid dyes on cotton. *Color. Technol.* [Online]. *129(2),* pp. 144-149. Available:http://onlinelibrary.wiley.com/doi/10.1111/cote.12013/full

TABLE II
CIELAB VALUES OF SAMPLES WITH VARIED DYES AND NA_2CO_3 CONCENTRATION

Dyes	Conc. of dye (%)	ΔL*			ΔE*			Staining of cotton	
		20g/l Na_2CO_3	30g/l Na_2CO_3	40g/l Na_2CO_3	20g/l Na_2CO_3	30g/l Na_2CO_3	40g/l Na_2CO_3	20g/l Na_2CO_3	40g/l Na_2CO_3
Black 5	6	2.17	0.95	-0.05	3.27	0.98	0.15	4	5
	7	0.75	0.45	-0.28	1.34	0.49	0.50	5	5
	8	0.74	0.42	-0.81	1.12	0.45	1.63	4.5	5
Yellow 145	6	4.04	3.22	2.33	7.61	4.50	3.52	5	4.5
	7	2.90	2.60	2.50	6.69	4.63	4.03	5	4
	8	2.78	2.10	1.89	5.42	4.30	3.05	4.5	5
Red 195	6	5.58	3.28	2.48	7.29	4.90	3.68	4.5	5
	7	5.00	3.12	2.99	5.91	4.53	3.87	4	5
	8	3.85	2.74	2.28	4.91	3.67	2.92	5	4.5

TABLE III
CIELAB VALUES OF SAMPLES WITH VARIED DYE AND NA_2CO_3 CONCENTRATION USING 2-HOUR DYEING TIME

Dyes	Conc. Of dye (%)	ΔL*			ΔE*			Staining on cotton	
		20g/l Na_2CO_3	30g/l Na_2CO_3	40g/l Na_2CO_3	20g/l Na_2CO_3	30g/l Na_2CO_3	20g/l Na_2CO_3	20g/l Na_2CO_3	40g/l Na_2CO_3
Black 5	5	3.53	2.19	1.34	4.29	2.58	1.81	4.5	5
	6	1.50	0.56	-0.21	1.82	0.64	0.40	4.5	5
	7	0.45	0.12	-0.40	0.45	0.10	0.73	5	5
	8	0.40	-0.32	-1.18	0.42	0.45	1.63	5	5
Yellow 145	5	1.31	1.10	0.57	2.50	1.39	0.87	4.5	4.5
	6	1.19	0.78	-0.16	2.76	0.83	0.80	5	4.5
	7	1.06	0.54	-0.38	1.93	0.65	0.46	5	5
	8	0.04	0.15	-0.62	0.8	0.45	0.89	4.5	4.5
Red 195	5	4.05	2.99	2.09	5.54	3.10	2.72	5	4.5
	6	3.26	1.86	0.64	4.23	1.79	0.71	5	5
	7	2.75	0.97	0.04	3.53	0.87	0.42	5	5
	8	1.92	0.76	-0.49	2.4	0.49	1.49	4.5	5