ECO PRINTING OF COTTON WITH REACTIVE DYES

Geeta Mahale

Abstract: There have been a number of options developed to overcome the polluted effluent problem of dyeing cotton fabric with reactive dyes. This paper reviews the options to improve sustainability of the dyeing process through development of reactive dyes, modification of dyeing machinery and processes, chemical modification of cotton brief prior to dyeing, use of biodegradable organic compounds in dye bath formulation.

Most cotton fabrics are dyed with reactive dyes because they produce a full range of bright fashion colours with a high degree of wash fastness. Application of these dyes, however, causes high and undesirable levels of dissolved solids and oxygen demand in the effluent. This is due to the use of considerable quantities of inorganic salt and alkali to ensure efficient utilization and fixation of the reactive dyes. Dye that is unfixed on cotton also contributes to effluent pollution. There are two approaches to deal with the effluent problem:

1. alternative dyeing techniques and technology;
2. Effluent treatment after dyeing. The effluent treatment requires additional capital investment and high treatment and maintenance costs.

Therefore, the first approach is always preferable. There have been a number of options developed to overcome the polluted effluent problem of dyeing cotton fabric with reactive dyes. This paper reviews the options to improve sustainability of the dyeing process through development of reactive dyes, modification of dyeing machinery and processes, chemical modification of cotton brief prior to dyeing, use of biodegradable organic compounds in dye bath formulation. Printing of cellulosic fabrics with reactive dyes produce brilliant shades with very good colour fastness and leveling properties. It is conventional to use urea with sodium alginate, a biocompatible natural polymer as the thickening agent for reactive dye print pastes.

Use of biodegradable organic compounds in dye bath formulation and the use of alternative biodegradable non-toxic dyes and chemicals for dyeing is a direct approach of reducing the effluent pollution. Urea reduction or elimination in reactive dye print pastes is of ecological interest. Use of urea poses ecological problems associated with the high nitrogen content of the printing effluent. Different approaches have been reported on the elimination or replacement of urea in cellulose printing. Use of selected organic compounds has been shown to be an effective alternative to inorganic salt (Rucker and Guthrie,1997).Such compounds reduce effluent load, as most of these tend to be biodegradable. Betaine, an organic compound, has been reported to reduce the amount of inorganic salt (Liu and Yao, 2009). Organic cationic surfactants have also been studied as inorganic salt substitutes (Rucker and Guthrie, 1997). The use of a mixture of magnesium-based organic compounds in the dyeing of cotton with direct or reactive dyes has been patented (Moore, 1993). The mixture is claimed to substitute inorganic sodium chloride or sodium sulphate that prevents the discharge of untreatable toxic effluent. However, this could not be commercialised because magnesium ions cause water hardness and create problems with colour matching and dyeing process control (Jain and Mehta,1991). The sodium salts of organic acids have been explored as alternatives to sodium chloride and sodium sulphate. Prabu and Sundrajan (2002). have demonstrated the use of trisodium citrate as an alternative to traditional inorganic salts for exhaust dyeing of cotton with reactive, direct and solubilised vat dyes. Salts of polycarboxylic acids have also been shown to be the most effective alternatives to inorganic salts (Guan et al.2007). The tetrasodium ethylene diamine tetra-acetate, an alkaline polycarboxylic sodium salt, has been reported as an alternative to inorganic salt and alkali in exhaust (Ahmed, 2005) and continuous pad-steam dyeing (Khatri, 2011) of cotton with reactive dyes. The use of other alkaline polycarboxylic salts (Khatri et al., 2010), such as trisodium nitrilotriacetate.

(Khatri et al., 2013) and tetrasodium N,N-bis(carboxylatomethyl)-L-glutamate (Khatri and Peerzada, 2012), has also been shown to effectively substitute the inorganic salt and alkali in continuous pad-steam reactive dyeing of cotton. This development led to reducing effluent TDS and improve dye fixation efficiency. In the continuous pad-dry-bake reactive dyeing method, where urea is used, the process conditions result in some decomposition of the urea. That causes an increase in the residual nitrogen content and to some extent reduces the yield of dye-fibre reaction. Using reduced amount of urea with a dicyandiamide in the dyebath has been proposed to reduce the environmental impact (Phillips,1996).

Different factors that may affect the printability of cotton, such as the concentrations of thickener, urea, dye, absence or presence of alkali and steaming time in the prints with respect to the dye fixation, colour strength. dye penetration, leveling and the fastness properties. The aim of this study is to examine the use of an environmentally-safe and non-toxic biodegradable organic salt, as a substitute for urea-in the conventional reactive dye print pastes and its viability for dye-fibre fixation.

Objectives

1. To find out the suitability of Reactive printing dyes ,thickeners and urea substitute on Cotton
2. To assess the printability of cotton with respect to dye fixation, colour strength and fastness properties
3. To estimate Cost of production of eco-printed Cotton.

METHODOLOGY

Printing of Cotton With Reactive Dyes

1. **Procurement of raw materials**

A. **Five Reactive dyes** -Indian dye stock company,Banglore

1. Procion Reactive Black - HE4B
2. Procion Reactive Turquoise blue-S7G
3. Procion Reactive green-SE4G
4. Procion Reactive red-H48B
5. Procion Reactive Yellow- H8B

B. **Substrates – Organic cotton (OC- 29'S) and Khadi Cotton (KC-8'S)**

2. **Materials required for printing ---**

1 Dye
2 Water
3 Urea-30g **substituted with-** Sodium Acetate/ Sodium Formate/ Sodium Editate/Tri sodium acetate
4 Resist salt-LSodium alginate
5 Sodium carbonate($Na_2 CO_3$)-10g

3. **Printing Recipe for**

1	Colour	30g
2	Water	120cc
3	Urea	30g
4	Resist salt-L	10g
5	Sodium alginate	300g
6	Sodium carbonate(Na_2SO_3)	10g
	Total	**500 gms**

4. **Procedure:**

Sodium alginate was soaked over night. Dye paste was made with warm water

Urea/ Sodium Acetate/ Sodium Formate/ Sodium Editate/Tri Sodium Acetate is added to dye solution and stirred. Then, resist salt and sodium carbonate is added and mixed thoroughly. Mixed sodium alginate gum to this prepared dye paste.* Printing was carried out at Khadhi Village Industries Commission, Bengeri, Hubli.

5. **Post treatment**

Printed silk samples of different colours were air dried at room temperature for 24 hours and mounted in a super heated fabric steamer with superheated steam at 110^0 C for five minutes.

1. **<u>The test specimen were assessed</u>** for the –

Colour strength (K/S)
Reflectance (RFL)
Colour coordinate (∆Lab)
Colour difference (∆E)

} *"Minolta CM- 600/700 d",* Colour Spectro Photometer

RESULTS AND DISCUSSION

Except Urea treated Green printed cotton samples (Table 1a), rest all samples indicated greater values of colour strength (K/S). Whereas except Green, other printed samples showed lower values of reflectance (RFL). Blue attained least Total colour difference (Table 1b) for OC and KC (ΔE - 1.210 & 1.174) samples treated with Urea.

Table 1a.

Colour strength (K/S) and Reflectance (RFL) values of reactive printed, <u>urea</u> treated organic and khadi cotton samples

Colour	Organic Cotton		Khadhi Cotton	
	K/S	RFL	K/S	RFL
Black	332.8051	0.881	531.4529	0.627
Blue	297.8924	1.714	436.0327	0.991
Green	111.9366	2.620	167.7104	1.347
Red	312.6870	1.440	483.5266	0.806
Yellow	199.1672	1.390	331.5611	0.724

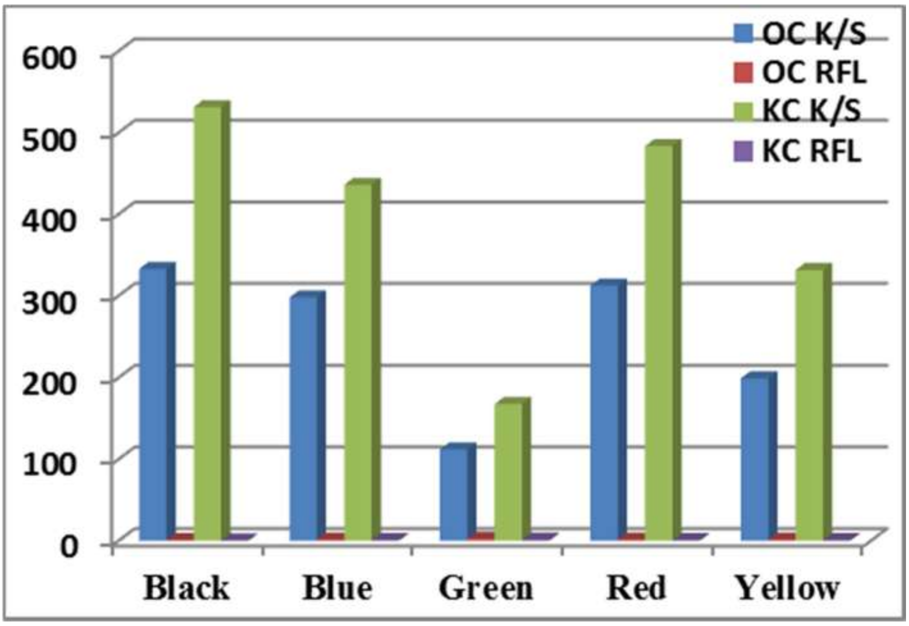

Fig 1a. Colour strength (K/S) and Reflectance (RFL) values of reactive printed, <u>urea</u> treated organic and khadi cotton samples

Table 1b.

Colour coordinate (∆Lab) and colour difference (∆E) values of reactive printed, Urea treated organic and khadi cotton samples

Colour	Organic Cotton				Khadhi Cotton			
	ΔL	**Δa**	**Δb**	**ΔE**	**ΔL**	**Δa**	**Δb**	**ΔE**
Black	0.174	-0.067	-2.645	2.652	-0.165	0.049	2.343	2.349
Blue	-0.706	0.926	0.329	**1.210**	0.698	-0.870	-0.365	**1.174**
Green	-0.971	2.464	-6.013	**6.570**	0.944	-2.427	5.663	**6.233**
Red	0.633	4.320	-4.520	6.284	-0.620	-4.784	3.992	5.631
Yellow	6.991	-0.987	10.372	**12.547**	-8.239	0.664	-12.483	**14.972**

ΔL- Lightness/darkness (+/-) than standard
Δa - Coordinate axis [+a - red, -a - green]
Δb - Coordinate axis [+b - yellow, -b- blue]
ΔE - Total colour difference

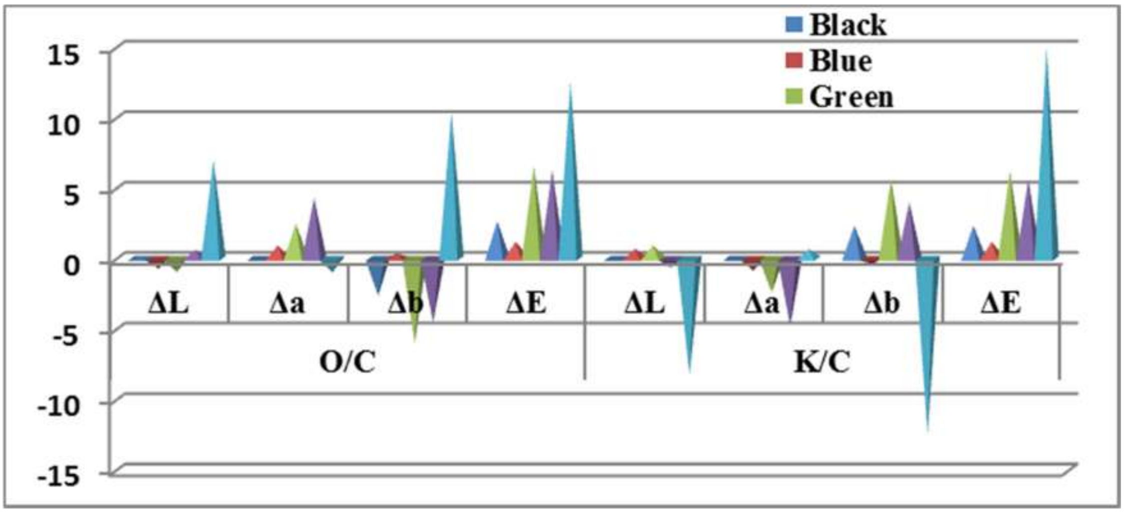

Fig1b. Colour coordinate (∆Lab) and colour difference (∆E) values of reactive printed, Urea treated organic and khadi cotton samples

Increase in colour strength was (Table 2a) seen in Green OC and Blue KC samples treated with Sodium Acetate followed by Black OC Green KC. Red OC and Yellow KC samples exhibited (Table 2a) higher Reflectance (RFL) values (3.923 & 3.741) followed by Black OC and KC (2.342 & 2.517) respectively. Sodium Acetate treated Yellow OC and KC samples (Table2b) indicated (Table 2b) maximum colour difference (ΔE-13.437 & 42.275) value followed by red (ΔE-6.125 &10.046) may be because of breaking of double bond and molecular rearrangement resulting in colour change and hence the maximum colour difference.

Table 2a.

Colour strength (K/S) and Reflectance (RFL) values of reactive printed, Sodium Acetate treated organic and khadi cotton samples

Colour	Organic Cotton		Khadhi Cotton	
	K/S	RFL	K/S	RFL
Black	**258.5188**	**2.342**	249.5132	**2.517**
Blue	230.3920	1.183	**556.8892**	**0.473**
Green	**320.1537**	**1.044**	**297.7540**	1.043
Red	124.6321	**3.923**	273.2122	1.749
Yellow	**85.4940**	3.186	**64.4876**	**3.741**

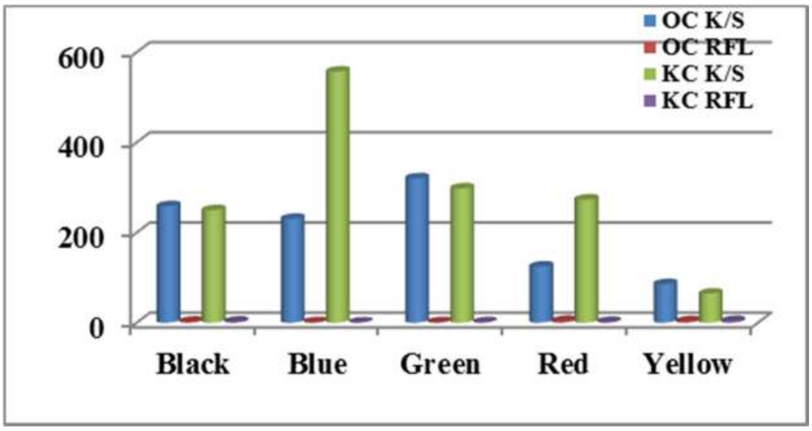

Fig 2a. Colour strength (K/S) and Reflectance (RFL) values of reactive printed, Sodium Acetate treated organic and khadi cotton samples

Table 2b.

Colour coordinate (ΔLab) and colour difference (ΔE) values of reactive printed, Sodium Acetate treated organic and khadi cotton samples

Colour	Organic Cotton				Khadhi Cotton			
	ΔL	Δa	Δb	**ΔE**	ΔL	Δa	Δb	**ΔE**
Black	0.004	0.001	1.321	1.321	-0.095	-0.080	5.552	5.553
Blue	-0.922	0.124	2.079	2.278	2.623	-2.563	-0.136	3.670
Green	1.904	-5.110	1.381	**5.625**	0.803	-1.796	5.408	**5.755**
Red	-0.918	-6.048	0.310	**6.125**	-1.597	-9.068	4.017	**10.046**
Yellow	-6.817	3.110	-11.154	**13.437**	-22.644	7.738	- 34.850	**42.275**

ΔL- Lightness/darkness (+/-) than standard
Δa - Coordinate axis [+a - red, -a - green]
Δb - Coordinate axis [+b - yellow, -b- blue]
ΔE - Total colour difference

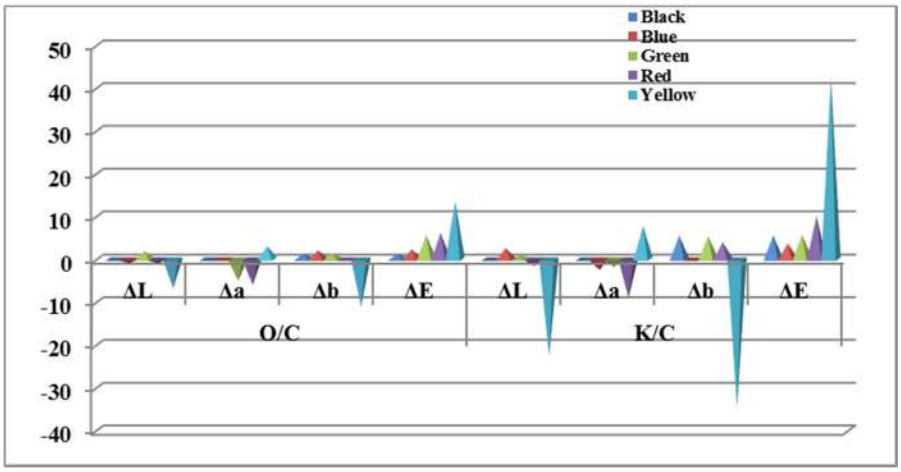

Fig 2b. Colour coordinate (ΔLab) and colour difference (ΔE) values of reactive printed, Sodium Acetate treated organic and khadi cotton samples

Black attained (Table 3a) highest colour strength (K/S) values both in OC and KC (351.3403 &440.6161) samples treated with Sodium Formate, which may be because of Black is a vinyl sulphone type of reactive dye results in low reduction of colour yield. Yellow OC and KC samples treated with Sodium Formate depicted (Table 3b) higher colour difference (ΔE - 9.581 & 27.498) values followed by Green OC and Blue KC (ΔE - 7.451 &8.526) samples.

Table 3a.

Colour strength (K/S) and Reflectance (RFL) values of reactive printed, Sodium Formate treated organic and khadi cotton samples

Colour	Organic Cotton		Khadhi Cotton	
	K/S	RFL	K/S	RFL
Black	351.3403	1.773	440.6161	1.375
Blue	257.4379	**1.074**	210.8716	1.523
Green	266.7195	1.087	134.2498	2.018
Red	243.3004	1.770	413.8322	1.095
Yellow	90.3379	3.178	84.6479	3.107

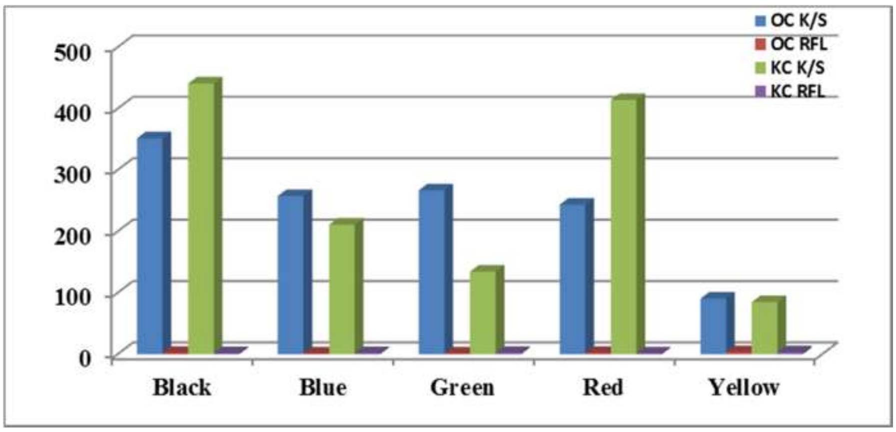

Fig 3a. Colour strength (K/S) and Reflectance (RFL) values of reactive printed, Sodium Formate treated organic and khadi cotton samples

Table 3b.

Colour coordinate (ΔLab) and colour difference (ΔE) values of reactive printed, <u>Sodium Formate</u> treated organic and khadi cotton samples

Colour	O/C				K/C			
	ΔL	Δa	Δb	**ΔE**	ΔL	Δa	Δb	**ΔE**
Black	0.047	-0.182	2.822	2.828	0.012	-0.572	4.683	4.718
Blue	-1.156	0.762	1.310	**1.906**	-5.164	4.683	4.909	**8.526**
Green	2.112	-6.208	-3.538	**7.451**	-1.161	3.149	1.048	**3.516**
Red	0.759	2.942	-0.279	3.051	-1.216	-6.628	4.842	8.298
Yellow	-5.189	0.537	-8.036	**9.581**	-14.980	4.196	-22.674	**27.498**

ΔL- Lightness/darkness (+/-) than standard
Δa - Coordinate axis [+a - red, -a - green]
Δb - Coordinate axis [+b - yellow, -b- blue]
ΔE - Total colour difference

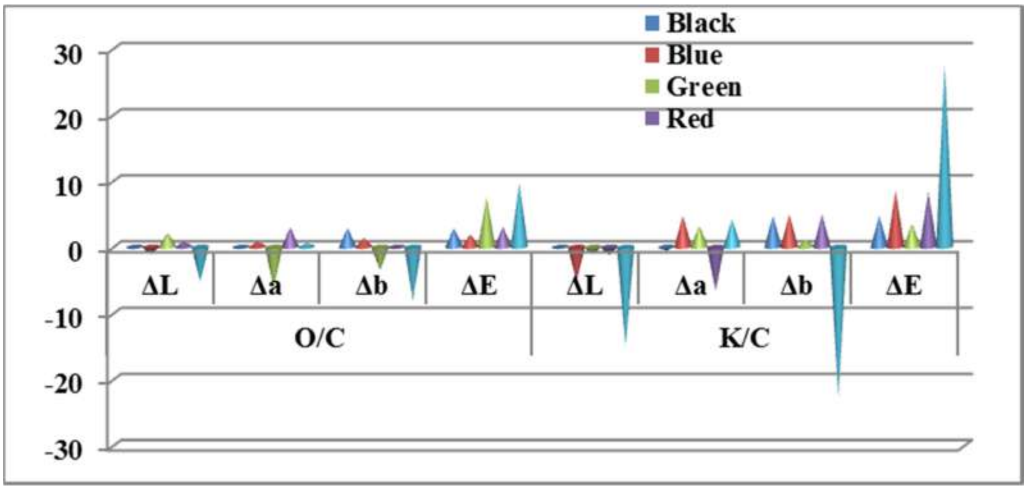

Fig 3b. Colour coordinate (ΔLab) and colour difference (ΔE) values of reactive printed, <u>Sodium Formate</u> treated organic and khadi cotton samples

Maximum colour strength (K/S) was seen (Table 4a) in Sodium Editate treated Red OC (344.4107)and Black KC (423.6336)samples followed by Black OC (336.2522) and Blue KC(225.0867). A high pH actually activates the cellulose fibre, forming a cellulose anion,which can then attack the dye molecule,leading to a reaction that produces a strong,permanent covalent bond.Sodium carbonate is used in the dye paste as one of the ingredient to increase the pH of the dye reaction. Total colour difference was seen highest (Table 4b) in Sodium Editate treated Blue OC and Yelow KC samples (ΔE - 10.527&14.006) followed by Green OC and KC (ΔE - 9.400 &12.555) samples.

Table 4a.

Colour strength (K/S) and Reflectance (RFL) values of reactive printed, Sodium Editate treated organic and khadi cotton samples

Colour	OC		KC	
	K/S	RFL	K/S	RFL
Black	336.2522	2.298	423.6336	1.374
Blue	193.8484	1.552	225.0867	1.396
Green	115.6020	3.259	105.2575	4.025
Red	344.4107	1.353	225.0519	1.763
Yellow	178.9060	1.743	195.2163	1.622

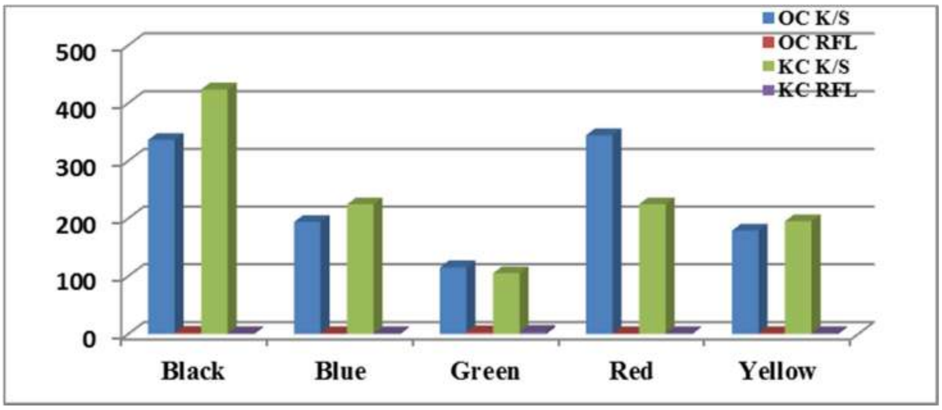

Fig 4a. Colour strength (K/S) and Reflectance (RFL) values of reactive printed, Sodium Editate treated organic and khadi cotton samples

Table 4b.

Colour coordinate (∆Lab) and colour difference (∆E) values of reactive printed, Sodium Editate treated organic and khadi cotton samples

Colour	O/C				K/C			
	∆L	∆a	∆b	**∆E**	∆L	∆a	∆b	**∆E**
Black	1.107	-2.241	1.650	2.995	-0.070	-0.218	3.357	3.365
Blue	-4.963	0.475	9.271	10.527	-4.116	3.007	4.364	6.710
Green	0.941	2.929	8.882	9.400	0.965	2.381	12.289	12.555
Red	0.301	0.649	1.574	1.729	1.002	2.268	6.048	6.537
Yellow	-0.090	-1.741	0.401	1.789	-7.814	-0.846	-11.593	14.006

∆L- Lightness/darkness (+/-) than standard **∆a** - Coordinate axis [+a - red, -a - green]
∆b - Coordinate axis [+b - yellow, -b- blue] **∆E** - Total colour difference

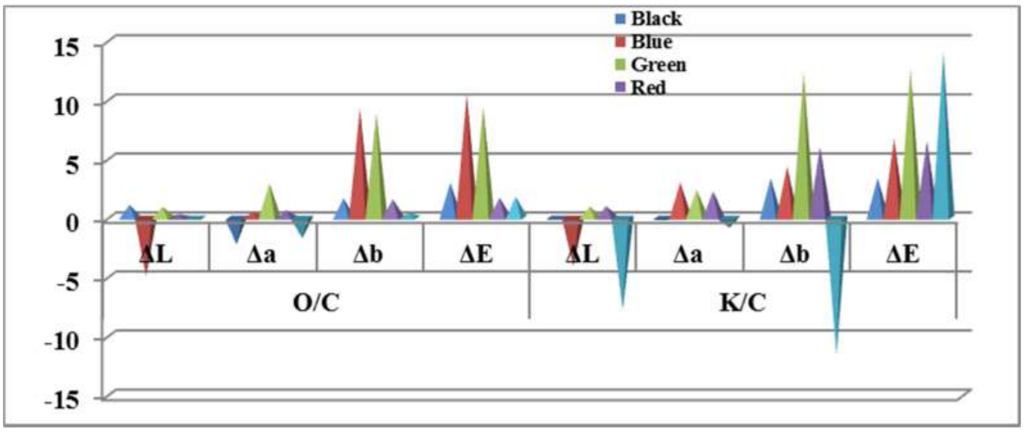

Fig4b. Colour coordinate (ΔLab) and colour difference (ΔE) values of reactive printed,Sodium Editate treated organic and khadi cotton samples

Black attained (Table 5a) highest colour strength (K/S)values both in OC and KC (385.2854& 395.6286) samples treated with Tri sodium Citrate followed by Red OC and KC (224.9509& 308.1982). Tri Sodium Citrate treated (Table 5b) Blue OC and Yellow KC samples indicated maximum Total colour difference (ΔE - 13.465 &24.840) values followed by Yellow OC and Blue KC (ΔE-9.798& 12.962) respectively.

Table 5a.

Colour strength (K/S) and Reflectance (RFL) values of reactive printed, Tri Sodium Citrate treated organic and khadi cotton samples

Colour	OC		KC	
	K/S	RFL	K/S	RFL
Black	385.2854	1.710	395.6286	1.593
Blue	179.4180	1.973	169.8739	1.950
Green	138.1519	2.838	105.3188	3.980
Red	224.9509	2.113	308.1982	1.530
Yellow	89.7870	3.194	113.3335	2.483

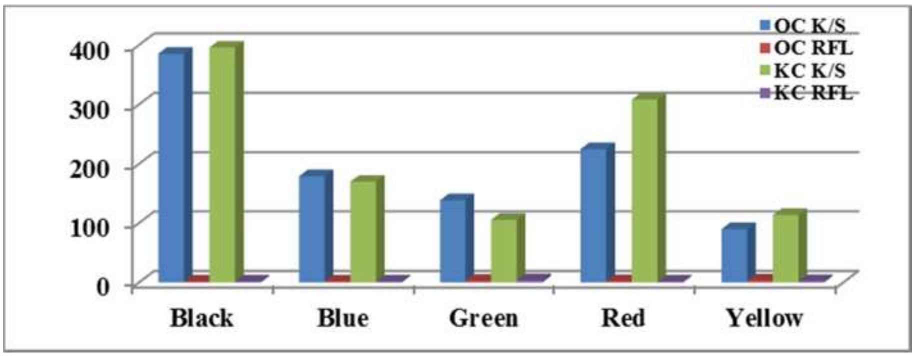

Fig 5a. Colour strength (K/S) and Reflectance (RFL) values of reactive printed, Tri Sodium Citrate treated organic and khadi cotton samples

Table 5b.

Colour coordinate (∆Lab) and colour difference (∆E) values of reactive printed, Tri Sodium Citrate treated organic and khadi cotton samples

Colour	O/C				K/C			
	∆L	∆a	∆b	**∆E**	∆L	∆a	∆b	**∆E**
Black	-0.133	1.108	3.234	3.421	-0.191	0.620	5.239	5.279
Blue	-7.478	4.866	10.085	13.465	-7.239	6.158	8.814	12.962
Green	-1.503	6.570	2.421	7.161	-1.679	8.605	7.051	11.251
Red	-0.231	-2.420	1.210	2.715	-1.300	-6.941	4.119	8.175
Yellow	-5.296	0.176	-8.242	9.798	-13.679	4.389	-20.264	24.840

∆L- Lightness/darkness (+/-) than standard **∆a** - Coordinate axis [+a - red, -a - green]
∆b - Coordinate axis [+b - yellow, -b- blue] **∆E** - Total colour difference

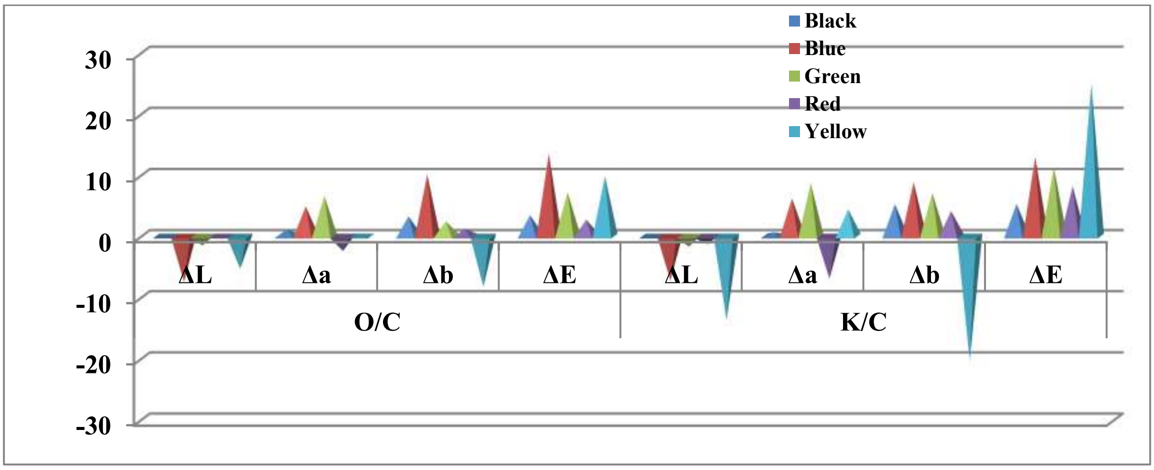

Fig 5b. Colour coordinate (∆Lab) and colour difference (∆E) values of reactive printed, Tri Sodium Citrate treated organic and khadi cotton samples

Table 6.

Summarised values of Colour Strength of treated organic and khadi cotton samples

Colour	Colour strength (K/S)values									
	Urea		Sodium Acetate		Sodium Formate		Sodium Editate		Tri Sodium Citrate	
	OC	KC	OC	KC	OC	KC	OC	KC	OC	KC
Black	332.8051	531.4529	258.5188	249.5132	351.3403	440.6161	336.2522	423.6336	385.2854	395.6286
Blue	297.8924	436.0327	230.3920	556.8892	257.4379	210.8716	193.8484	225.0867	179.4180	169.8739
Green	111.9366	167.7104	320.1537	297.7540	266.7195	134.2498	115.6020	105.2575	138.1519	105.3188
Red	312.6870	483.5266	124.6321	273.2122	243.3004	413.8322	344.4107	225.0519	224.9509	308.1982
Yellow	199.1672	331.5611	85.4940	64.4876	90.3379	84.6479	178.9060	195.2163	89.7870	113.3335

Irrespective of alkalies substituted with urea, all (Table 6) selected Reactive dyes exhibited good Stability and colour strength. Yellow color depicted lower values of colour strength treated with Sodium Acetate and Sodium Formate. Whereas Black colour attained greater values of colour strength for all alkalies substituted with urea.hence elimination or replacement of urea in cellulose printing can be done.

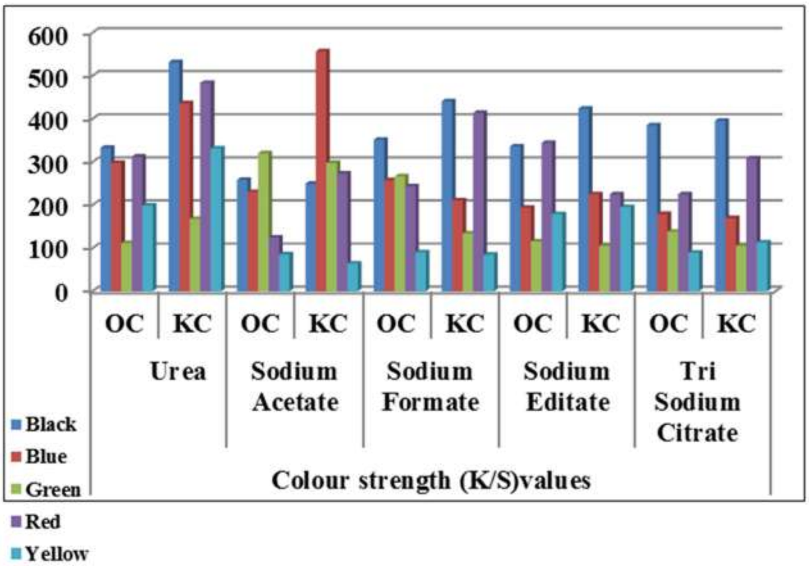

Fig 6. Summarised values of Colour Strength of treated organic and khadi cotton samples

Cost Estimation of printing (per meter)

Table 7.

Cost Estimation of printing (per meter)

Sl no	Materials	Qty	Rate/Unit Rs	Amount Rs
1	Colour	0.5g	480/kg	0.24
2	Water	10ml	-	-
3	Urea and alkalies	2.5g	370/kg	0.92
4	Resist salt-L	0.8g	220/kg	0.18
5	Sodium alginate	1.25g	300/kg	0.38
6	Sodium carbonate	0.5g	310/kg	0.16
7	Electricity	5 min	2.70/unit/hr	0.12
8	Labour charge	One meter	5/meter	5.00
9	Cotton material	One meter	80/meter	80.00
	Total			**87.00**

Conclusion

- Use of an environmentally-safe and non-toxic biodegradable organic salt, as a substitute for urea in the reactive dye print pastes and are viable for dye-fibre fixation. Loss of colour strength was maximum in Black. Higher the colour strength lower the reflectance value which indicates the reflection angle of incident light.
- Use of an environmentally-safe and non-toxic biodegradable organic salt,as a substitute for urea in the reactive dye print pastes and are viable for dye-fibre fixation. Loss of colour strength was maximum in Black. It is clear that the average colour differences (**Δ** E), calculated from the CIE *L*a*b** coordinates) of the printed fabrics showed good levelling properties in all cases.
- The result indicates that organic salts/ alkali printing shows the best results compared with urea/alkali conventional printing. Besides the low cost of organic salts and its use in printing of cotton with reactive dyes, the prints obtained have good levelness, outline sharpness, low penetration with considerable dyestuff savings and thus low demands on the print back cloth washing process leading to a reduction of the wastewater load. This work is a step forward for cleaner production within the textile industry.
- Because of the high nitrogen concentration in urea, it is very important to achieve an even spread. is an organic compound with the chemical formula $CO(NH_2)_2$. The molecule has two — NH_2 groups joined by acarbonyl (C=O) functional group. Urea absorbs moisture from the atmosphere and therefore is typically stored either in closed or sealed bags on pallets. Urea can be irritating to skin, eyes, and the respiratory tract. Repeated or prolonged contact with urea on the skin may cause dermatitis. Urea can cause algal blooms to produce toxins.
- Textile and Apparel Industry due to the characteristics of quick response solve environmental problems. The quality reaches with Water & Energy-saving features in a more prominent way. The viability of using an alternative to urea in reactive dye print pastes for cotton materials can be explored. Eco-printing of cotton with reactive dyes, the prints obtained have good shade depth, print quality with considerable dyestuff savings and thus eliminates the print effluents. Leading to a reduction of the wastewater load. A step forward for cleaner production technology within the textile industry.

References

1. Khatri, A., M.H. Peerzada, M. Mohsin, M. White. (2015). *A review on developments in dyeing cotton fabrics with reactive dyes for reducing effluent pollution. Journal of Cleaner Production.* 87, 50-57.
2. Khatri, A., (2011). *Use of biodegradable organic salts for pad-steam dyeing of cotton textiles with reactive dyes to improve process sustainability. International Proceedings of Economics Development and Research* 18, 84-89.

3. Padhye, R., A. Khatri, M. White. (2010). *Use of tetra-sodium ehtylene diamine tetra-acetate in pad-steam dyeing of cotton with reactive dyes.* *Quaid-E-Awam University Research Journal of Engineering, Science* and Technology. 9 (1), 1-6.
4. Review of Study on "*Resin Dye-Fixatives on Cotton Fabrics".* (2009). Yikai Yu School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, China E-mail: yuyikai1980@163.com Yuejun Zhang School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China vol3 (10). 9-16. *Journal of Modern Applied Science.*

Contacts:

Dr Geeta Mahale

Prof. Dept Textile and Apparel Designing
College of Community Science
Univ. of Agricultural sciences, Dharwad 580005.
Karnataka, India
mahalegeeta@gmail.com