Study of Cotton Fabric Dyeing by Reactive Dyes in Various Water Hardness Systems

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Summary: In the present work, effect of hardness on dyeing of cotton fabric using bi-functional reactive dyes has been investigated. Water hardness due to Ca, Mg & Fe with different anions has been considered. For hardness parameters anions types and concentration are varied during this work. For bi-functional reactive dye parameters, dye shades with variable concentration values have been considered. Effects of these parameters i.e. dye type, concentration, hardness type & its concentration are evaluated by variation in color value, rubbing and washing tests.

Keywords: Bi-functional reactive dyes, Water hardness, Ca, Mg, Fe

Introduction

The role of water in dyeing as a vital raw material is of fundamental importance. Water is used as a system for the distribution of dye and energy in dyeing machines as well as it participates in the formation of dye-fiber bonds. Hard water was coined to define its soap consuming power, indicating quality with respect to its washing characteristics [1]. Soap consuming capacity of water sample is mainly due to the presence of calcium and magnesium metal ions. Other metal ions like Fe and Al also react with soap in the same fashion, thus contributing to hardness. Generally these are present in natural waters only in traces. Further carbonic acids can also cause free fatty acid to separate fabric from soap solution and thus contribute to hardness. However in practice the hardness of water sample is usually taken as a measure of its Ca and Mg contents [2].

Reactive dyes are colorants used mainly on cotton to achieve high wash fastness on leisurewear. The basis for their good wash fastness is the formation of a covalent bond to cellulose chains during the fixation step. Unfortunately, fiber fixation is always accompanied by alkali-induced dye hydrolysis, leading to dye molecules that cannot undergo fixation with cellulose. Bi functional reactive dyes containing monochlorotriazine and sulphatoethylsulphonic groups give excellent color values, solubility, substainity & diffusion having physical and chemical properties of dye fabric, were controlled by the chemical structure of dye and dyeing conditions. Bi functional dyes were found more stable when compared with mono functional reactive dyes [3].

Hardness creates many undesirable effects in the wet processing. The textile dyes for cellulosic fibres are designed to have low solubility in water and these become very difficult to dissolve in very hard water because calcium and magnesium ions reduce the solubility of anionic dyes causing them to aggregate or even precipitate onto the fibre [4]. Aggregates and certainly precipitated dyes cannot migrate or diffuse [5, 6]. They usually remain on fibre surface as particulate deposits. Mg and Ca are undesirable because of precipitation of fatty acids derived from soaps. The impurities of Fe and Mg should be reduces to avoid yellow and brown staining of processed batch cloth in dyeing [7].

Iron also causes excessive shade change (i.e. red shades move dull and blue) [8-11]. It is investigated that in the primary exhaustion, the dyes are absorbed on the fibre by mechanism of intra molecular attraction and in the secondary phase having chemical bond with the fibre. High heat capacity of water makes it a good heat medium for heat transfer and provides greater security from uneven dyeing rates resulting from non-uniform heating in the system [12, 13].

Peter *et al.,* [4] studied that heating or coming in contact with alkalis during dyeing and soaping, calcium and Mg ions present in hard water are precipitated on fabric as whitish carbonates [4, 14]. Although concentration of these salts is small, yet it lowers the depth of dyed shades and mars purity and brightness of the hue [15]. If hardness of water is very high it may even cause non uniform dyeing. In package yarn dyeing precipitated particles hinder free flow of liquor through the package and tend to cause uneven dyeing [16-21]. The precipitated particles also impart harshness to the

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fibre. Under the normal working conditions the hardness producing salts in the water precipitate out and form scale inside dyeing machines.

Results and Discussion

Expected Chemical Reactions between Reactive Dyes and Cotton Fibers

Nucleophilic substitution characterizes dye-fiber fixation that occurs when a leaving group in the reactive system is displaced as a result of an interaction with a nucleophilic group on the polymer chain. The same process accounts for the competitive hydrolysis reaction between dyes and water during dye application [22].

Nucleophilic addition characterizes the dye-fiber reaction in which a nucleophilic group in the fiber adds across an activated carbon-carbon double bond in the reactive group. Systems based on activated double bonds also undergo a competitive hydrolysis reaction [22]. Fixation via nucleophilic addition of vinylsulphone dye is expressed as

$$Dye - SO_2CH_2 - CH_2 - OSO_3Na + NaOH \rightarrow Dye - SO_2CH = CH_2 + Na_2SO_4 + H_2O$$

$$Dye - SO_2CH = CH_2 + Cell - OH \rightarrow Dye - SO_2CH = CH_2 - O - Cell$$

Reaction of water with a vinylsulphone dye given as

$$Dye - SO_2CHCH_2 \xrightarrow{OH^-} Dye - SO_2CH_2CH_2OH$$

Measurement of Color Value: Samples dyed in distilled water is designated as H_0 and considered as a standard for comparison with all other samples. Following four parameters were studied for the dyeing of cotton fabric.

- H (Hardness)
- C (concentration)
- S (Dye)
- Salts of Ca, Mg, Fe

The samples are analyzed visually and by spectrophotometer for color shade and strength. The color values regarding color fastness of standard specimens were considered 100%. Fig. 1 shows the trend of color values with respect to hardness of different cations during dyeing process on cotton fabric in range of 0.5% to 3.0% of dye.

Results pertaining to colors, inferred that color S_2 (Yellow) recorded maximum color with mean value 98.92% followed by S_3 (Blue) and S_1 (Red) with their means values 91.81% and 89.51% respectively. From Fig.1 it is observed that decreasing order of color value is $S_3<S_2<S_1$. It reveals that minimum color value is obtained for low concentrations of dyes and hardness of dyeing water is important for light/pastel shades [18]. The color value for different hardness generated from salts of Ca, Mg and Fe ions are 93.40%, 94.95% and 91.89% respectively. These results infer that decrease in color value is maximum for Fe hardness and then for Ca salts. Fe may combine with reactive dyes and cause dullness of shades [4].

The color values for the interactions of H, S, C & Salts referred to experimental section are described in Fig.1. The maximum value is recorded for the combination of $H_1xS_3xC_1$ for Mg salt hardness that is 99.87%. It means that best color value is obtained at minimum hardness concentration H_1 and at low dye concentration C_1 for blue shade whereas minimum value is attained for the combination of $H_2xS_1xC_1$ for Fe salt hardness which is 60.30%. It means that S_1 (Red) is adversely affected by water hardness of Fe salt, whereas for yellow color values increased greater than standard values (100%) which are out of acceptable limits

Statistical Analysis of Color Value: The statistical analysis of variance for color value of the dyed cotton knitted fabric in five hardness levels is given in Table 1. Hardness produced by Calcium, Magnesium and Iron salts having three concentrations each. Table 1 presents colors, each with three concentrations and shows that all variables have significant effect on the color value and indicates that color value decreases with the increase of hardness. The color value falls in range of 94.36% to 92.10% for H_1 to H_5 hardness levels.

Fig.1 also reveals that the treatment for concentrations C_3 (3%) gave maximum color value of 94.68% followed by C_2 (1.5%) and C_1 (0.5%) with values of 94.11% and 91.45% respectively.

Rubbing fastness: For the evaluation of color fastness against rubbing, results of all reactive dyed cotton knitted fabric samples dyed in distilled water and with five different hardness produced by Ca, Mg and Fe salts. The obtained grey shade change for all specimens was examined. It is observed that hardness H_0 have values of dry rubbing fastness are 4-5 while 3-4 for all three colors. Samples dyed in H_1 media, dry rubbing fastness of each color and at each concentration falls near standard value i.e. 4-5 and was not so affected by hardness of Ca, Mg and Fe salts whereas wet rubbing was 2-3 at this hardness level. For H_2 and H_3 dry rubbing falls to 2-3 and wet rubbing further decreased as compared with standard and same results shown with H_5. It is described that because of the metallic impurities in reactive dye bath which influence wet rubbing [20]

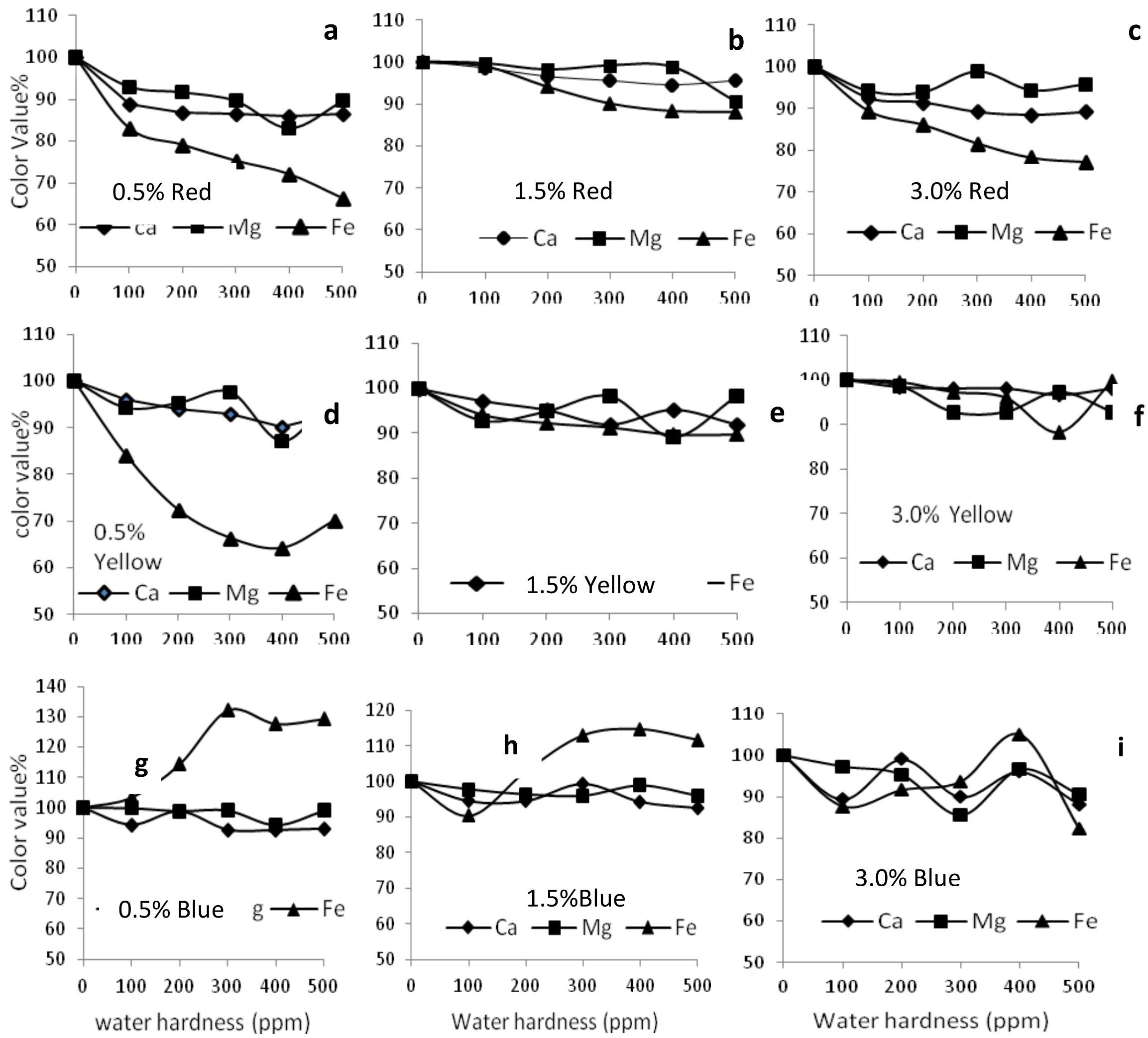

Fig. 1: Effect of various water hardness of Ca, Mg and Fe on dyeing at different concentrations of dyes.(S_1: Sumifix Red E-XF, S_2: Sumifix Yellow E-XF and S_3: Navy Blue BS).

Table-1: Analysis of variance for color value.

S.O.V	D.F.	S.S.	M.S.	F.Vaue	Sig.
H	4	310.100	77.525	122407.882	.000**
S	2	6489.010	3244.505	5122902.572	.000**
C	2	797.798	398.899	629840.614	.000**
Salts	2	629.415	314.708	496906.846	.000**
HxS	8	1784.249	223.031	352154.388	.000**
HxC	8	531.418	66.427	104885.035	.000**
SxC	4	7934.162	1983.541	3131906.067	.000**
HxSxC	16	682.432	42.652	67345.238	.000**
HxSalts	8	164.418	20.552	32451.004	.000**
SxSalts	4	8784.487	2196.122	3467560.756	.000**
HxSxSalts	16	2832.682	177.043	279540.947	.000**
CxSalts	4	247.824	61.956	97825.240	.000**
HxCxSalts	16	405.027	25.314	39969.740	.000**
SxCxsalts	8	7090.755	886.344	1399491.140	.000**
HxSxCxSalts	32	1312.189	41.006	64746.180	.000**
Error	270	0.171	0.001		
Total	405	3574338.184			
Corrected Total	404	3999.137			

Adjusted R^2 = 1.000 **highly significant

Washing fastness: In distilled water hardness level H_0 rated excellent level 5 and 4-5 on the grey scale for all colors at each concentration. Results of H_1 shows that washing fastness of all colors is 4 for Ca and Mg salts excluding Fe hardness which affect more on at the same level of hardness and Fe hardness for all colors are 3 at H_2 and 2-3 at H_3. For Ca and Mg salts at H_4 and H_5, washing fastness decreases to 2-3 for red and blue and 3 for yellow. In case of Fe salt H_4 and H_5, poor washing fastness observed which decreases to 2. It clearly shows that Fe salts are deleterious inn dyeing process.

Experimental

Materials and Methods

Chemicals and reagents: 100% cotton knitted fabric was taken from Interloop Pvt. Ltd. Faisalabad, Pakistan. Commercial dyes Sumifix Supra Red E-XF, Sumifix supra Yellow E-XF and Navy Blue BS from Sumitomo, Japan. Calcium Chloride ($CaCl_2$), Calcium sulphate ($CaSO_4$), Magnesium chloride ($MgCl_2$), Magnesium sulphate ($MgSO_4$), Iron chloride ($FeCl_2$), Iron sulphate ($FeSO_4$), Calcium bicarbonate $Ca(HCO_3)_2$, Magnesium bicarbonate $Mg(HCO_3)_2$ and Iron bicarbonate $Fe(HCO_3)_2$ are of analytical grade and all from Merck. All chemicals were used as such without further purification.

Hard water: Three stock solutions of hard waters for Ca, Mg and Fe were prepared by adding required amounts of salts. Three different salts with Cl^-, SO_4^{2-} and HCO_3^- ions for each Ca, Mg and Fe were taken in equal ratio. Three set of stock solutions of 1000 ppm hardness for ca, Mg and Fe were prepared. Five Sub solutions from stocks were prepared for different hardness as H_1: 100 ppm, H_2: 200 ppm, H_3: 300 ppm, H_4: 400 ppm, H_5: 500 ppm H_0: distilled water used as zero hardness level.

Dye solutions: Three concentrations (w/v) of each dye shade were prepared by dissolving 0.5g, 1.5g and 3.0 g in 100 mL of water to obtain C_1 = 0.5%, C_2 = 1.5% and C_3 = 3.0% respectively.

Recipes:

Color recipe	Conc.(%age)	Common salt (g)	NaOH (g)	Liquor Ratio (mL)	Time (min)	Temp. (°C)
S1=Red /	C_1 = 0.5	20	5.0	1:12	60	60
S2=Blue/	C_2 = 1.5	40	10.0	1:12	60	60
S3=Yellow	C_3 = 3.0	50	12.0	1:12	60	60
Scouring	100% cotton knitted fabric, Sandopan DTC : 0.5g/l, NaOH: 2g/l, Time: 15 min, Temp: 60°C-90°C. Neutralised alkali with Citric acid for 10min.					
Bleaching	Sandopan DTC:0.25 g/l, Stabilizer Sifa: 0.5g/l, H_2O_2: 1.5 g/l, Time: 25 min, Temp: 70°C-90°C					
Finishing	Citric acid: 0.5 g/l, Alka soft: 1.5 g/l, Fixer kevin FK 400 : 1.0 g/l					

Instrumentation: Measurement of color values was performed by Spectrophotometer model Data color SF600, Crock meter was used for rubbing fastness whereas washing fastness was measured by Rota wash.

Procedures:

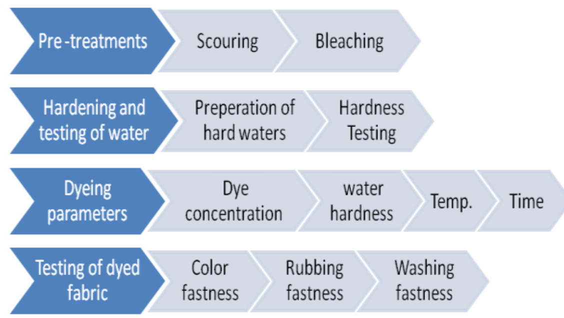

Fig. 2: Sequence of processes involved in dyeing of cotton knitted fabrics.

Testing procedure

Waterhardness: Prepared various hard waters were first cheked using EDTA and $K_2Cr_2O_7$ titrations [23] for Ca/Mg and Fe concentration respectively, then applied for further work.

Color fastness: ISO-105-J03 (AATCC 2002) [24] was used to measure color values of standard and dyed samples.

Rubbing fastness: ISO-105-X12 (AATCC 2002) [24] was used for rubbing fastness for each sample in dry and wet conditions.

Washing fastness: ISO-105-C01, AATCC 2002 [24] was taken up for washing test.

Dyeing procedure:

Seven specimens of 100% cotton knitted fabrics were selected for dying. Exaust (All in one) method has been adopted for dyeing using bi funtional dyes. Six jars for dyeing of light and medium shades of one colour were utilised. Each dye solution recipe was pipetted out in every pot and water was added to compelte the liqour ratio. A properly wet 20 gm piece of fabric was dipped into each pot and added salt and soda ash according to the recipe of each shade. Each pot was fitted in dyeing machine. Samples were then squeezed, cold rinsed for five minutes and hot rinsed at 70°C for five minutes. Then the alkali was neutralised with 1.5 g/l citric acid followed by cold rinsing. Finally finishing treatment was applied to each sample according to the mentioned recipe.

Conclusion

1. Distilled water is the best fit for reactive dyeing process.
2. Color fastness are equally good under H_1 (100 ppm) hard water but only for Ca and Mg salts.
3. Poor color fastness properties were achieved using Fe salt hard water and presence of Fe is deleterious for level dyeing of any color and shade.

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