# Effect of Hardness of Water on Fixation and Total Wash off Percentage of Reactive Dyes When Applied to Cellulosic Fiber

## Elias Khalil\*, Joy Sarkar\*\*

<sup>\*</sup>Department of Textile Engineering, World University of Bangladesh <sup>\*\*</sup>Department of Textile Engineering, Khulna University of Engineering & Technology

*Abstract*- Dye-house water quality is the most important parameter to be confirmed before dyeing; precisely the presence of metal content i.e. Hardness. This research will investigate & analyses the impact of separate hardness (i.e. Calcium, Magnesium & Iron) on particular 'Turquoise' (C.I. Reactive Blue 21) & a 'High Exhaustion' class (C.I. HE Red 120, C.I. HE Yellow 84) of Reactive dye on cotton knitted-fabric. From evaluation of dyed fabric the range of metal content is sorted out where the quality starts to fluctuate as distinctive visible & spectral change of shade & fixation rate of the dye molecules has been found. The result of the work will help for further projection about water quality degradation in upcoming years & its effect on dyeing behavior, also the sustainability of present dyeing process to cope with the ever degrading quality of water.

Index Terms- Water hardness, Reactive dyes, Cellulosic fiber, Fixation & Wash off percentage

### I. INTRODUCTION

In textile wet process, the most substantial & influential role is played by water. Although several alternatives are getting into consideration, water is undoubtedly the most suitable as dyeing medium. So the quality of coloration is vastly dependent on quality of water. Throughout the time there have been lots of studies & works to evaluate & standardize dye house quality, however chronologically the water quality is degrading so alarmingly that dye houses are required to be more conscious about this. 'Right first time' dyeing hugely depended on the quality of water; quality of water is vast idea, the most important are the presence of metal ions (i.e. Hardness), alkalinity, turbidity etc. So before dyeing these parameters should be in control. This experimental work is to investigate the effect of Hardness in reactive dyeing, precisely the dyeing properties, build-up, strength & fastness etc. Hardness is generally referred to presence of calcium & magnesium in water. In this research dyeing with reactive dyes in different amount of hardness, artificially created in water, is done to investigate the dyeing behavior & other qualities which might be affected by Hardness. Dye-house water-hardness is defined as the presence of soluble calcium and magnesium salts in the water and is expressed as the CaCO<sub>3</sub> equivalent [1]. The presence of hardness in the water can cause dye precipitation, and the precipitates can further promote dye aggregations, which results in color specks and loss of depth [2].

The objectives of this study is as to investigate different aspects of increased hardness as change in wash off and fixation percentage Usually the dyeing with reactive dye is commenced in neutral solution in presence of electrolyte. Here electrolyte acts to promote the exhaustion of the dye. Electrolyte neutralizes the negative charge formed in the fiber surface & puts extra energy to increase absorption. During this period dye just only migrate into the fiber surface but do not react with the fiber. Usually the higher shade percentage is ensured by higher electrolyte percentage and higher temperature. In dye Fixation stage, by the reaction of the reactive group of the dye and the fiber, dye-fiber covalent bond is formed. And running the exhaustion stage for few minutes an appropriate alkali is added to increase its  $P^{H}$  (>10). The hydroxyl group of the cellulose is slightly acidic and due to the hydroxyl ion of the alkali, there causes some disassociation, forming cellulose ion.

Cell-OH + OH ----> Cell-O +  $H_2O$ 

And this cellulosate ion performs fixation by two distinct ways- (a) Nucleophilic Substitution & (b) Nucleophilic Addition [3].



Fig: 1 Nucleophilic substitution (a) and addition reactions (b) of reactive dyes with cellulosate ion

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Unfortunately under the alkaline condition, necessary for dyeing cellulose, some reactive dye hydrolyzed by the act of OH- of water as nucleophile. After dyeing unreacted and hydrolyzed dyes present in the cellulose must be removed by washing [4].

## II. MATERIALS AND METHODS

## A. Materials

By creating hardness artificially in water, investigations are done on dyeing. Following soluble salts has been used for this purpose-Calcium Chloride ( $CaCl_2$ ), Magnesium Chloride (MgCl<sub>2</sub>), Ferric chloride (FeCl<sub>3</sub>). Following reactive dyes are chosen for this experiment

C.I. Reactive Blue-21. (Turquoise)

C.I. Reactive Red-120. (High-exhaust)

C.I. Reactive Yellow-84. (High-exhaust)

## B. Water Hardness determination

The presence of calcium, magnesium and ferric salt in water is determined by the titration of sample water against a standardized solution (0.01M) of the di-sodium salt of Ethylene Di-amine Tetra Acetic acid (EDTA) solution [5].

## C. Dyeing of fabric adding different hardness

Fabric is dyed adding different hardness in the dye bath in LABTEC dyeing machine following mentioned recipe on Table 1.1 Name of the machine: LABTEC Dyeing m/c Bath: Glycerin bath Maximum Temp: 150°C Machine Type: Sample dyeing m/c

## D. Dye liquor transmittance measurement by Minolta CM-2500D Spectrophotometer

Designed for versatility in various applications, the CM-2500d is a portable integrating sphere spectrophotometer incorporating Numerical Gloss Control. The CM-2500D is a high performance, low cost, portable spectrophotometer ideal for measuring the transmittance of dye liquor [6].

The Beer-Lambert law relates light absorption in a transparent material to concentration of colorant in the material and thickness of the material. The law is actually a combination of two separates laws- Beer's law relates absorbency of light by a colored solution to the absorbance of light by a colored solution to the thickness of the absorbing substance. This law is usually valid only when monochromic light is used. On the other hands, dye solution having high concentration or where dye is an aggregated state in the solution, Beer-Lambert law cannot be applied. That's why before applying this law in spectrophotometer; the solution has to be diluted around hundred times for the specific dyes to lower the concentration of the dye liquor [7].

## E. Dyeing Procedure

The following sequence has been used in the dyeing of the fabric samples-

- 1. Bath set in room temperature.
- 2. Additional water, hard water, salt, sample fabric, dye solution added.
- 3. Temperature raised to 80°C at 2°C/sec.
- 4. Run the bath for 30 min.
- 5. Soda added at  $80^{\circ}$ C & then run for 1 hour.
- 6. Bath drop

Recipefor dyeing with MgCl <sub>2</sub>	Recipefor dyeing with FeCl <sub>3</sub>
SolaHE Red 3B –2%	SolaYellow 4RN –2%
Salt –65 g/l	Salt –65 g/l
Soda–25 g/l	Soda–25 g/l
M:L-1:8	M:L-1:8
Hard water-as per following amount	Hard water-as per following amount
Temp.& Time –Soda at 85°C (30	Temp.& Time –Soda at 85°C (30
min) & Run for 1 hr. at	min) & Run for 1 hr. at
80°C	80°C
	Recipefor dyeing with MgCl <sub>2</sub> SolaHE Red 3B –2% Salt –65 g/l Soda–25 g/l M:L –1:8 Hard water-as per following amount Temp.& Time –Soda at 85°C (30 min) & Run for 1 hr. at 80°C

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#### F. After treatment

At first cold wash 1 and 2 were done in open bath without any reagent at room temperature on neutral condition for five minutes on a liquor ratio 1:5. Acid wash was done in open bath with green acid of 2g/l at room temperature for five minutes on same liquor ratio. Then hot wash in closed bath without any reagent at  $70^{\circ}$ C for 5 minutes. Soap wash with standard soap of 2g/l at  $90^{\circ}$ C for 5 minutes in closed bath. Then hot and soap wash again with previous condition.

#### III. RESULTS OF FINDING

In all cases it has been observed that with the increase of hardness, total wash off % is increased. During dyeing, aggregated dye molecules deposited on fabric surface. As these dyes are not fixed with the fiber, in washing stage they are very easily washed off. That is why, higher water hardness shows higher wash off %.

With the increase of hardness, fixation % is gradually decreased. As the pick-up % were not very significantly with hardness, but wash off % increased, so total fixation is decreased with increase of hardness.

## A. Effect of CaCl<sub>2</sub>

Table 1.2: Fixation % and Total wash off % of Turquoise Blue G with hard water containing Calcium Chloride (CaCl<sub>2</sub>)

Beaker	Before	After	$1^{st}$	2 <sup>nd</sup>	Acid	Hot	Soap	Final	Final	Total	Pick	Fixation
No	Dyeing	Dyeing	Cold	Cold	Wash-	(70°C)	(90°C)	Hot	Cold	wash	up%	%
	(Std.)	%	Wash-	Wash-	off %	wash-	wash-	(70°C)	wash-	off %		
	%		off %	off %		off %	off %	wash-	off %			
1	100	15.098	12.356	8.729	1.349	10.223	9.585	4.553	1.517	48.312	84.902	38.455
2	100	16.523	10.785	10.666	1.312	12.422	11.394	3.676	1.811	49.012	83.477	36.052
3	100	14.836	10.665	9.715	1.09	5.887	14.471	4.313	1.77	51.097	84.164	33.067
4	100	15.042	13.107	9.536	5.455	14.246	8.166	5.303	1.742	52.964	84.958	30.034
5	100	16.154	12.142	11.766	1.057	4.119	18.186	3.071	1.679	53.459	83.846	30.387
6	100	15.071	10.433	8.161	1.56	11.379	12.334	5.41	2.12	54.612	84.929	30.317
7	100	15.329	11.608	9.053	1.282	11.163	11.186	5.365	2.078	54.958	84.671	29.713
8	100	13.378	8.941	7.986	1.757	10.865	11.148	5.413	2.057	55.012	83.622	28.61

## B. Effect of MgCl<sub>2</sub>

Table 1.3: Fixation % and Total wash off % of Sola Yellow 4RN with hard water containing Magnesium Chloride (MgCl<sub>2</sub>)

Beaker	Before	After	1 <sup>st</sup>	2 <sup>nd</sup>	Acid	Hot	Soap	Final	Final	Total	Pick	Fixation
No.	Dyeing	Dyeing	Cold	Cold	Wash-	(70°C)	(90°C)	Hot	Cold	wash	up%	%
	(Std.)	%	Wash-	Wash-	off %	wash-	wash-	(70°C)	wash-	off %		
	%		off %	off %		off %	off %	wash-	off %			
1	100	8.645	4.231	2.015	1.025	3.079	6.953	3.025	1.009	21.34	91.36	70.018
2	100	8.64	4.958	2.125	1.195	3.856	6.852	3.715	1.252	23.95	92.07	68.117
3	100	8.39	5.025	2.659	2.032	3.965	7.025	3.698	2.095	26.5	91.61	65.111
4	100	7.769	5.869	2.891	2.791	4.015	7.893	3.967	2.125	29.55	92.23	62.68
5	100	7.684	5.024	3.265	1.925	7.065	11.015	3.852	0.125	32.27	92.32	60.045
6	100	7.195	5.534	3.958	1.015	7.025	11.625	3.265	1.025	33.45	92.81	59.358

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### B. Effect of FeCl<sub>3</sub>

Table 1.4: Fixation % and Total wash off % of Sola Yellow 4RN with hard water containing Ferric Chloride (FeCl<sub>3</sub>)

Bea-	Before	After	1 <sup>st</sup>	2 <sup>nd</sup>	Acid	Hot	Soap	Final	Final	Total	Pick-	Fixation
ker	Dyeing	Dyeing	Cold	Cold	Wash-	(70°C)	(90°C)	Hot	Cold	wash	up	%
No.	(Std.)	%	Wash-	Wash-	off %	wash-	wash-	(70°C)	wash-	off %	%	
	%		off %	off %		off %	off %	wash-	off %			
1	100	10.23	4.231	2.015	1.025	3.079	6.953	3.025	1.009	21.34	89.8	68.433
2	100	10.97	4.958	2.125	1.195	3.856	6.852	3.715	1.252	23.95	89	65.077
3	100	9.64	5.025	2.659	2.032	3.965	7.025	3.698	2.095	26.5	90.4	63.861
4	100	10.15	5.869	2.891	2.791	4.015	7.893	3.967	2.125	29.55	89.9	60.299
5	100	9.25	5.024	3.265	1.925	7.065	11.015	3.852	0.125	32.27	90.8	58.479
6	100	9.61	5.534	3.958	1.015	7.025	11.625	3.265	1.025	33.45	90.4	56.943

## IV. CONCLUSION

The change of fixation and total wash off percentage of high exhaust and turquoise reactive dyes on cellulosic fiber under changing of presence of metal ion is presented in this paper. Fixation is gradually decreases while wash off gradually increases for any kinds of metallic salt present in water. It is important to use a sequestering agent or water softening agent that is compatible to chemicals and auxiliaries used in this dyeing also cost effective and available. It is the best way to utilize natural soft water which eliminates water softening processing costs as well as achieving the desired result.

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#### AUTHORS

**First Author** – Elias Khalil, M.Sc. (Textile), B.Sc.(Textile), Lecturer, Department of Textile Engineering, World University of Bangladesh. Email: *eliaskhalil52@gmail.com* 

Second Author – Joy Sarkar, M.Sc. (Textile), B.Sc. (Textile), Department of Textile Engineering, Khulna University of Engineering & Technology, Khulna-9203, Bangladesh, Email: joy.ctet@gmail.com

**Correspondence Author** – Elias Khalil, M.Sc. (Textile), B.Sc.(Textile), Lecturer, Department of Textile Engineering, World University of Bangladesh. Email: eliaskhalil52@gmail.com