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# Performance Evaluation of Stripping Agents on Bi-Functional Reactive Dyes.

Nayon Chandra Ghosh[1], Dr. Ummul Khair Fatema[2], Afsana Munni[3]

[1](Department of Wet Process Engineering, Shahid Abdur Rab Serniabat Textile Engineering College, Barisal, Bangladesh)

[2](Department of Wet Process Engineering, Bangladesh University of Textiles, Bangladesh)

[3](Department of Wet Process Engineering, Primeasia University, Bangladesh)

Corresponding author: Nayon Chandra Ghosh

***ABSTRACT:*** *In dyeing textile fabric, it is often desirable to remove the color from the dyed fabric in order to correct faulty dyeing or to redye surplus fabric to a different color for reuse. Stripping is the process which is used to remove dye from dyed fabrics. However, reactive dyes cannot be stripped satisfactorily from cellulosic materials due to the formation of covalent bonds between dye and fibre. This research was undertaken using 1% and 3% hetero bifunctional (monochloro triazine/vinyl sulphone) reactive dyes on pretreated cotton fabric and dye stripping was carried out with hydrose and thiourea dioxide in alkali reductive stripping process. The aim of this study was to investigate the performance of stripping agents on bifunctional reactive dyed cotton fabric. Strength loss, weight loss and pilling resistance of stripped fabric were calculated to determine fabric quality. Though with the increase of concentration of both stripping chemicals, stripping percentages were improved; processing damage to the fabric such as losses in strength, weight and pilling resistance ratings was found. In case of stripping with thiourea dioxide degree of stripping and quality of stripped fabric were found better than stripping with hydrose.*

***KEYWORDS:*** *Thiourea dioxide, Hydrose, MCT/VS*

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## I. INTRODUCTION

Around 10,000,000 tons of synthetic dyes are annually used in the world by various industries for coloring numerous materials [1,2,3]. Textile industry accounts for two-thirds of the total dyestuff market [4,5]. Over 10,000 dyes with an annual production of over $7\times10^5$ metric tons are commercially available for use by this industry [6]. However, some common problems of textile dyeing industries include uneven or faulty dyeing and formation of color patches on the fabric surface during dyeing and downstream processing of textile materials [7,8]. Such problems in the finished quality of fabric are generally tackled through a chemical stripping process which is a common practice in dyeing industries for the deep shade batches. Stripping is one of the reproduction processes used in textile finishing to remove dyes from colored fabric. The process is either termed as 'back stripping' or 'destructive stripping'. In back stripping only the depth of shade is changed while in destructive stripping the dyes are chemically altered [7,9] such as dyes containing an azo group (-N=N-) can be chemically reduced to an almost colorless amine compound by using chemical reducing agents. Sometimes for the analysis of dyes or dyed fabrics, dyes may need to be stripped from the surface by either destructive or non-destructive methods. Non-destructive stripping is essential when the amount of dye on the fiber has to be estimated, or the dye has to be identified or analyzed by techniques such as chromatography. Laboratory methods for stripping dyes seldom mirror those used in bulk processing, since these are usually destructive methods based on strongly reductive or oxidative methods [10]. Depending on the individual dyes, complete chemical stripping may be carried out in one of the four ways: reduction only; reduction followed by oxidation;

oxidation only; and oxidation followed by reduction [11]. As sodium chlorite or peroxide solutions are used in oxidizing process, decreasing in strength of textile material is highly possible, so alkali reductive application is generally preferred for the stripping of reactive dyes. The mechanism of reductive stripping depends on the type of dyes, fibres and reducing agents. Dyes are commonly stripped from fabric using a reducing agent, and a stripping assistant which is used to enhance the stripping efficiency of a reducing agent. Various chemical combinations of reducing agents and stripping assistants are being used in stripping liquids to strip the dye from fabric [12]. The reductive stripping occurs from chemical reactions in case of cellulose dyed with reactive dyes. The chemical bonds on the chromophore group of reactive dyes are tried to break in order to dissolve of colorfulness. Reactive dyes cannot be stripped satisfactorily from cellulosic materials due to the formation of covalent bond between dye and fibre [13]. The stripping performance depends on several factors: raw materials, type of dyestuff, method of dyeing and stripping, type of stripping agents and auxiliaries, and working parameters such as time, temperature etc. Achieving the expected efficiency in the application of stripping process is a very important aspect for the success of reproduction [8]. However, alkaline reductive stripping also affects the quality of fabric as harsh chemicals as well as high temperature is applied in the stripping process. In this study hydrose and thiourea dioxide was used as stripping agents to remove bi-funtional reactive dyes from cotton knit fabric. The aim of this study is to evaluate the performance of these stripping agents on cotton knit fabric dyed with bi-functional reactive dyes.

## II. MATERIALS AND METHODS

### 2.1. Materials

#### 2.1.1. Fabric

100% Cotton Single Jersey Knit grey fabric of 160 GSM was used as substrate.

#### 2.1.2. Dyes

Reactive dyes containing hetero bifunctional reactive group were used for dyeing of cotton fabric and purchased from Clariant Ltd, Bangladesh and Huntsman Pte Ltd, Singapore as shown in Table-1.

**Table-1: List of reactive dyes and their properties.**

| Reactive group | Functionality | Name of dye | Manufacturer |
|---|---|---|---|
| Monochlorotriazine/ vinyl sulphone(MCT/VS) | Heterobifunctional | Drimarine Yellow CL-2R | Clariant |
| | | Drimarine Red CL-5B | |
| | | Drimarine Blue CL-BR | |

#### 2.1.3. Stripping Agents

Hydrose and thiourea dioxide were used as stripping agents for stripping reactive dyes from cotton knit fabric. Hydrose (Hydrosulfite) was purchased from BASF, Bangladesh, Ltd. and thiourea dioxide (KAPPATEX R 98) was purchased from KAPP-CHEMIE GmbH, Bangladesh, Ltd.

#### 2.1.4. Chemicals & Auxiliaries

The chemicals and auxiliaries used for scouring and bleaching of cotton knit fabric were Sodium Hydroxide (NaOH) of 98% purity, Hydrogen Peroxide ($H_2O_2$ 50%) of 98% purity, Wetting anent (Hostapal XTRA), Detergent (Imerol PCLF), Stabilizer (Stabilizer SOF) and Acetic acid ($CH_3COOH$) of 98% purity. Gluber's salt ($Na_2SO_4.10H_2O$) of 95% purity and Soda ash ($Na_2CO_3$) of 98% purity were used as dyeing chemicals. All chemicals and auxiliaries were purchased from Clariant Ltd, Bangladesh and were reagent grade.

### 2.2. Experimental Methods

#### 2.2.1. Fabric Preparation

For scouring and bleaching purposes, grey fabric was prewashed with the bath liquor containing 4 ml/l hydrogen peroxide (35%), 3 g/l caustic soda, 1.25 g/l sodium silicate as stabilizer, 1 g/l wetting agent and 1 g/l sequestering agent at pH 11.5, material to liquor ratio 1:20, temperature 100°C for 60 minutes, then washed thoroughly with 2g/l detergent followed by neutralization with 1 g/l acetic acid.

#### 2.2.2. Dyeing

Batch dyeing method was used for dyeing cotton fabric. Dyeing was carried out in AHIBA IR™ lab dyeing machine with reactive dyes containing hetero bifunctional reactive group (MCT/VS) with shade depth 1% owf (Light) and 3% owf (Dark) at temperature $60^0$C and their recipes of dyeing are mentioned in Table no-2.

**Table-2: Dyeing recipe.**

| Recipe for Light Shade (1%) | Recipe for Dark Shade (3%) |
|---|---|
| Drimarine Blue CL-BR= 0.33% owf,<br>Drimarine Red CL-5B= 0.33% owf<br>Drimarine Yellow CL-2R= 0.34% owf<br>Gluber's Salt= 40 g/l, Soda ash= 5 g/l | Drimarine Blue CL-BR= 0.99% owf,<br>Drimarine Red CL-5B= 0.99% owf<br>Drimarine Yellow CL-2R= 1.02% owf<br>Gluber's Salt= 70 g/l, Soda ash= 9 g/l |
| Material to Liquor ratio= 1:10, Temperature= 60$^0$C, Time= 30 min | |

### 2.2.3. Stripping

Exhaust method was used for stripping of reactive dyes from cotton fabric. Stripping was carried out using two different stripping agents (hydrose and thiourea dioxide) at 100$^0$C temperature in presence of strong alkali. The recipe of stripping is given in Table-3.

**Table-3: Stripping recipe.**

| Chemicals | Concentration |
|---|---|
| Hydrose/Thiourea dioxide | 2 g/L, 4 g/L, 6 g/L, 8 g/L and 10 g/L |
| Sodium hydroxide | 5 g/L |
| **Stripping Parameters** | |
| M:L | 1:15 |
| Time | 30 min |
| Temperature | 100$^0$C |

## 2.3. Measurements and Testing

### 2.3.1. Colorimetric Values of Stripped Samples

Colorimetric values are very important parameters for evaluation of degree of stripping. The more the color removed from dyed sample the more the success of stripping. The degree of stripping was measured on the basis of lightness value (L*) of stripped samples and total color difference value (ΔE) between stripped sample and pretreated sample. The more the color removal during stripping the higher will be the lightness value and vice versa. The lesser the color difference value the higher will be the color removal during stripping. These values were determined using spectrophotometer (Datacolor 600®) and measurements was taken with the specular component of the light included and the UV component excluded, using illuminant D65 and 10° Standard Observer. The samples were folded to ensure opacity and an average of four readings was calculated.

### 2.3.2. Efficiency of Stripping

Efficiency of stripping depends on the color removal from dyed sample. The higher the color removal from dyed sample during stripping the higher will be the stripping efficiency. It was calculated to find out stripping performance of reactive dyed samples and stripping agents (hydrose and thiourea dioxide) by the following formula:

$$\text{Stripping efficiency} = \frac{\text{Lightness value of stripped sample}}{\text{Lightness value of pretreated sample}} \times 100\%$$

### 2.3.3. Stripped Fabric Quality

Stripped fabric quality was measured in terms of bursting strength, weight loss and pilling resistance. The bursting strength of stripped sample has been evaluated in Auto Burst 28 bursting tester according to standard of ASTM D 3786 [39]. Loss in weight of stripped fabric was measured by the ratio of difference in weight before and after stripping to the weight of fabric before stripping expressed as a percentage following the method of BS 4784 [40] and pilling resistance was assessed by Abra Smart pilling tester following the test method of ASTM D-4970 [41]. The observed resistance to pilling was reported on an arbitrary scale ranging from 5 to 1 (no pilling to very severe pilling).

# III. RESULTS AND DISCUSSIONS

### 3.1. Redox Potential of Stripping Agents

Higher the redox potential higher will be the stripping efficiency. That is why measurement of redox potential is very important to evaluate the stripping performance as hydrose and thiourea dioxide were used in this study as stripping agents for stripping of bi-functional reactive dyes from cotton fabric. Their redox potential was given in Table-4. From this Table, it was seen that the maximum redox potential of hydrose was found -844 mV at 8 g/L concentration whereas for thiourea dioxide it was found -947 mV at 4 g/L.

**Table-4: Redox potential of stripping agents.**

| Concentration of stripping agents | Redox potential of Hydrose | Redox potential of Thiourea dioxide |
|---|---|---|
| 2 g/L | -790 mV | -880 mV |
| 4 g/L | -810 mV | -969 mV |
| 6 g/L | -830 mV | -947 mV |
| 8 g/L | -844 mV | -938 mV |
| 10 g/L | -825 mV | -930 mV |

### 3.2. Degree of Stripping Processes of Differently Dyed Samples

Degree of stripping processes of differently dyed samples was evaluated on the basis of lightness values of stripped samples and color difference value between stripped samples and pretreated sample as discussed below:

**3.2.1. Lightness Values (L*) of Stripped Samples**

L* value is a crucial colorimetric parameter in order to decide the degree of stripping and also adequacy of the process. L* value ranges from 0 to 100 where L* = 0 means black and L* = 100 means white. The L* values of the stripped samples were shown in Figure 1 & 2 for light and dark shades respectively. When compared the L* values of the stripped samples to original L* values of dyed samples as shown in Table-5, it is a fact that the dye linked to OH group of the cellulose can be removed partly or completely. Figure-1 shows the lightness value of samples stripped with hydrose for light and dark shades respectively. From this figure it was seen that increasing concentration of hydrose up to 8 g/L, lightness value (L*) increased for both light and dark shades; after that lightness values decreased. From Figure-2 it was observed that increasing concentration of thiourea dioxide up to 4 g/L, lightness values increased. Further increasing concentration of thiourea dioxide greater than 4 g/L, lightness values decreased. So the lightness values of stripped samples were found maximum at 4 g/L concentration of thiourea dioxide.

**Table -5: Lightness values of pretreated & dyed samples.**

| Shade | Reactive dye | Lightness value (L*) |
|---|---|---|
| 1 % | MCT/VS type | 49.28 |
| 3 % | MCT/VS type | 34.82 |
| Pretreated sample | - | 94.06 |

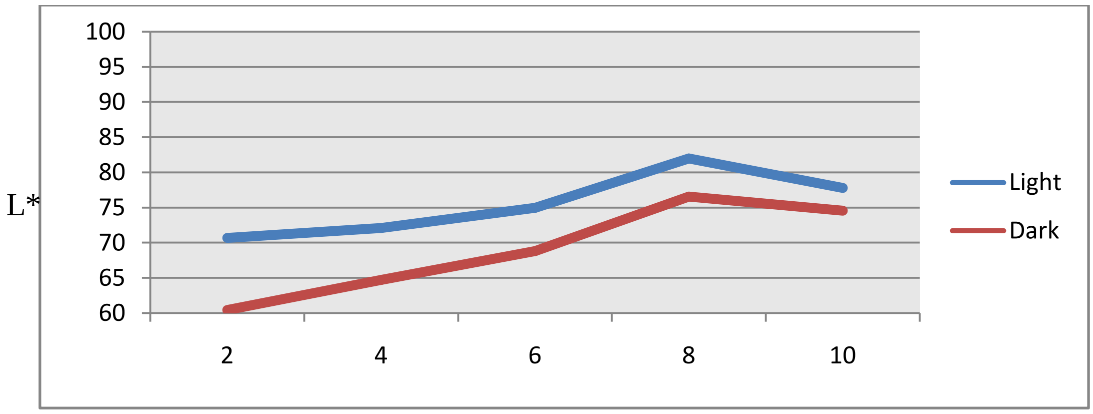


**Figure-1: L* values of the stripped samples for stripping light and dark shade with hydrose. Concentration of hydrose (g/L)**

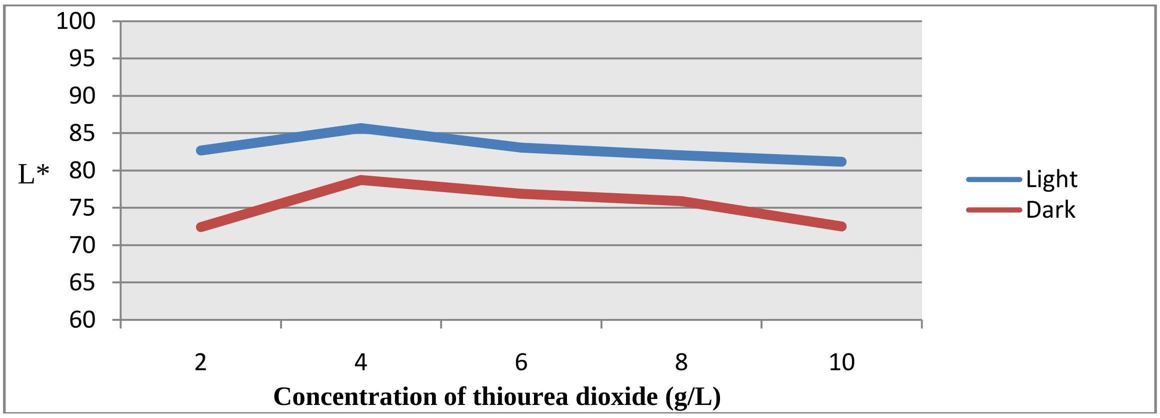


**Figure-2: L* values of the stripped samples for stripping light and dark shade with thiourea dioxide.**

**3.2.2. Color Difference Value (ΔE) between Stripped and Pretreated Sample**

The main aim of the stripping applications is to remove the dye from the fibre structure as completely as possible for successful redyeing without having any color matching problem. ΔE values are very important output for colorants because of this reason. The lower the ΔE value of stripped sample the better will be the success of stripping. While calculating these values, the pretreated sample and stripped samples were treated as reference and batch respectively. Figure-3 & 4 show the ΔE values of all the stripped samples for stripping light and dark shades with hydrose and thiourea dioxide at $100^0$C. From Figure-3 it was seen that increasing concentration of hydrose, ΔE values decreased up to 8 g/L and after that it increased. The minimum ΔE values were found when concentration of hydrose was 8 g/L for bi-functional reactive dyes. Again from Figure-4 it was seen that increasing concentration of thiourea dioxide up to 4 g/L, ΔE values decreased. Further increasing concentration of thiourea dioxide greater than 4 g/L, ΔE values increased. From these discussions it can be said that redox potential plays an important role to lower the ΔE value. As redox potential is maximum at 8 g/l concentration of hydrose and 4 g/l concentration of thiourea dioxide lowest ΔE values are realized at these concentrations.

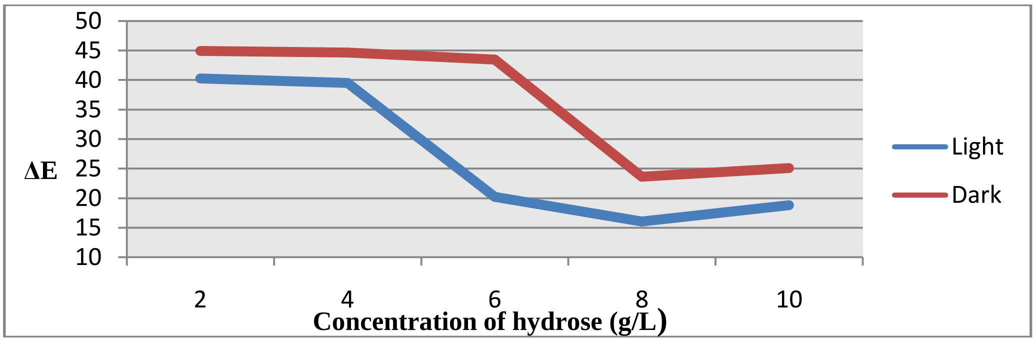


**Figure-3: ΔE values between pretreated sample and stripped samples for stripping light and dark shade with hydrose.**

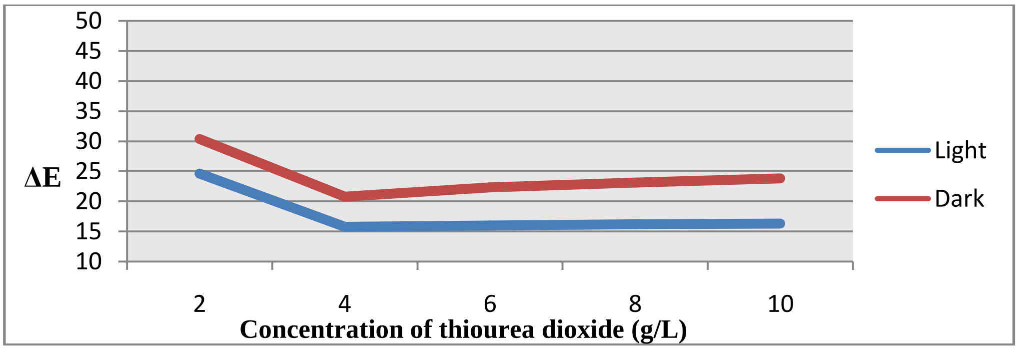


**Figure-4: ΔE values between pretreated sample and stripped samples for stripping light and dark shade with thiourea dioxide.**

### 3.3. Stripping Efficiency of Bi-functional Reactive Dyed Sample

The success of stripping depends on the types of reactive group present in reactive dye and types of stripping agent used. Figure-5 shows the stripping efficiency of MCT/VS reactive dyed samples stripped with hydrose and thiourea dioxide for both light and dark shades. From this figure it was observed that stripping efficiency increased for both light and dark shades with increasing concentration of hydrose up to 8 g/L. The maximum efficiency was found 81% for dark shade and 87% for light shade when concentration of hydrose was 8 g/L. In case of stripping with thiourea dioxide, stripping efficiency increased for both light and dark shades with increasing concentration up to 4 g/L and after that it decreased. The maximum stripping efficiency was found 86% for dark shade and 91% for light shade at 4 g/L concentration.

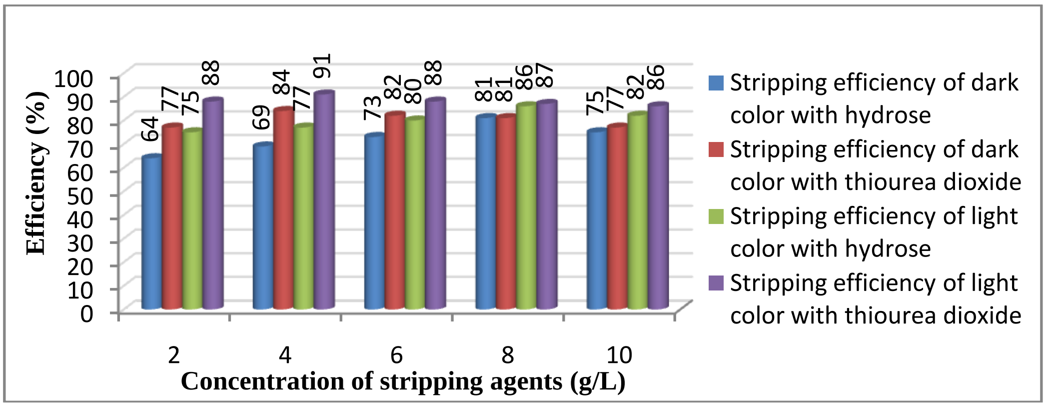


**Figure-5: Stripping efficiency of MCT/VS reactive dyed fabric with different stripping agents.**

### 3.4. Performance of Stripping Agents on Bi-functional Reactive Dyed Samples at Optimum Stripping Condition

Performance of stripping agents depends on removal of color from dyed sample and types of functional group present in reactive dyes. Higher the removal of color from dyed sample, higher the performance of stripping agents and lower the bond strength between reactive dye & fibre in stripping condition. Optimum stripping condition is such in which highest stripping efficiency was found. It was found 8 g/L for hydrose and 4 g/L for thiourea dioxide. Figure-6 shows the maximum stripping efficiency of hydrose and thiourea dioxide on bi-functional reactive dyed samples for both light and dark shades. From this figure it was found that stripping with thiourea dioxide performed better than hydrose for bi-functional reactive dyed samples. It was also observed that stripping efficiency was higher in stripping light shade than dark shade. So increasing depth of shade decreased the stripping efficiency.

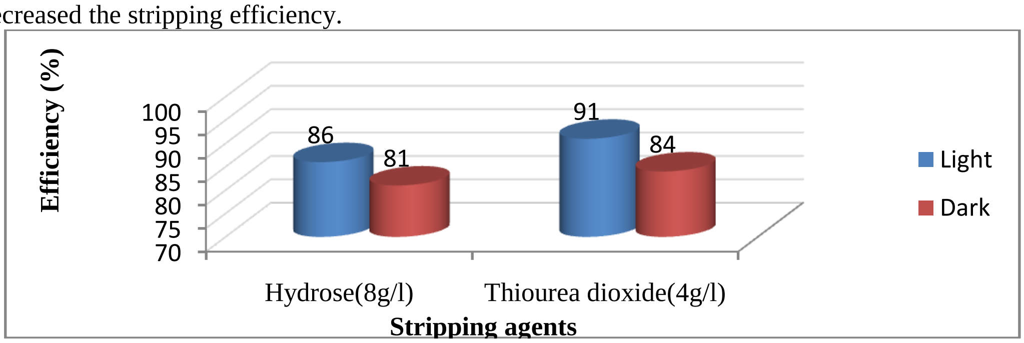


**Figure-6: Stripping efficiency of hydrose and thiourea dioxide at optimum condition.**

### 3.5. Bursting Strength of Stripped Samples

Figure-7 shows the bursting strength of stripped samples treated with hydrose and thiourea dioxide for stripping light and dark shades respectively. From this figure it was found that increasing concentration of both stripping agents, bursting strength decreases. This decrease was more in stripping with hydrose than thiourea dioxide. At optimum condition, bursting strength of sample stripped with hydrose was found around 86 lb/in$^2$ and bursting strength of sample stripped with thiourea dioxide was found around 102 lb/in$^2$ for both light and dark shades. These results demonstrated the stripping process using thiourea dioxide as a superior one as compared to stripping with hydrose regarding the durability. Because less cellulose chain breakage was occurred during stripping with thiourea dioxide than stripping with hydrose.

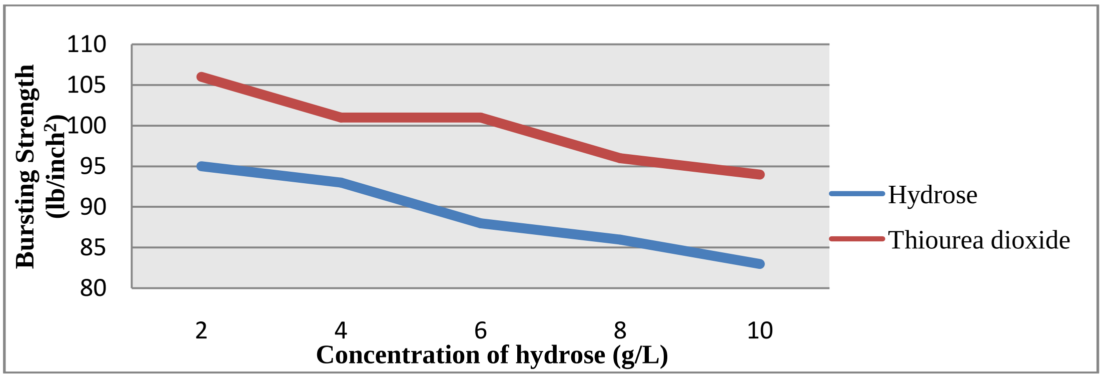


**Figure-7: Bursting strength of stripped samples treated with hydrose and thiourea dioxide for stripping both light and dark shade.**

### 3.6. Weight Loss of Stripped Samples

Performance of stripping agents was evaluated by measuring the weight loss of stripped samples. Higher the weight loss of stripped sample, lower the performance of stripping agent. It is natural to lose weight during stripping as certain amount of dyes was removed. But if high polymer degradation of cotton fibre occurs, more weight loss results that will deteriorate fabric quality and lower the performance of stripping agent. Figure-8 shows the weight loss of samples stripped with hydrose and thiourea dioxide. From this figure it was found that increasing concentration of stripping agents, weight loss of stripped samples increased for both light and dark shades. At optimum stripping condition weight loss of samples stripped with hydrose was found around 5% and weight loss of samples stripped with thiourea dioxide was found around 2%. These results showed the significantly higher weight loss in stripped samples treated with hydrose than thiourea dioxide. This test demonstrated the stripping using thiourea dioxide as a superior one as compared to stripping with hydrose to maintain the quality of fabric in terms of weight loss.

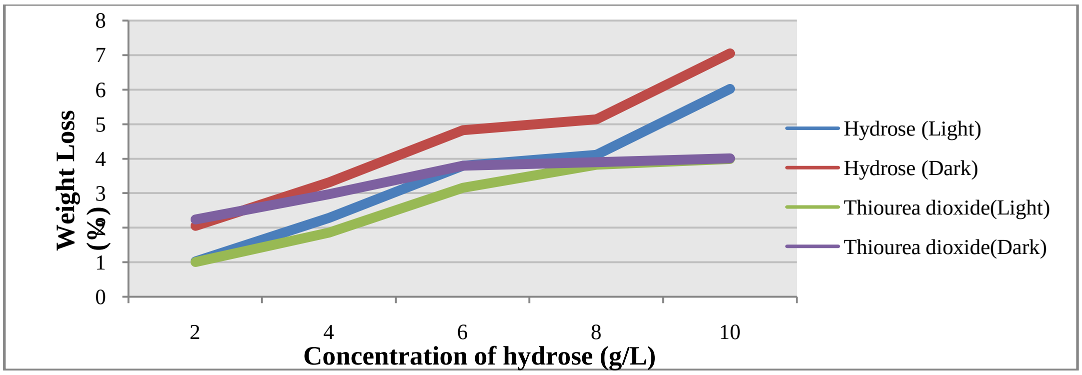


**Figure-8: Weight loss of samples stripped with hydrose and thiourea dioxide.**

### 3.7. Pilling Resistance of Stripped Samples

Pilling is a condition that arises in wear due to the formation of little pills of entangled fibre clinging to the fabric surface giving it an unsightly appearance. Pills are formed by a rubbing action on loose fibres which are present on the fabric surface. Figure-9 shows the pilling resistance of stripped samples for stripping light and dark shades with hydrose and thiourea dioxide. From this figure it was seen that pilling resistance of stripped samples decreased with increasing concentration of both stripping agents. Pilling resistance rating of stripped sample was found 4 for hydrose and 5 for thiourea dioxide at optimum stripping condition. This result demonstrated that the stripping process using thiourea dioxide performed better than hydrose regarding the surface property of cotton fabric.

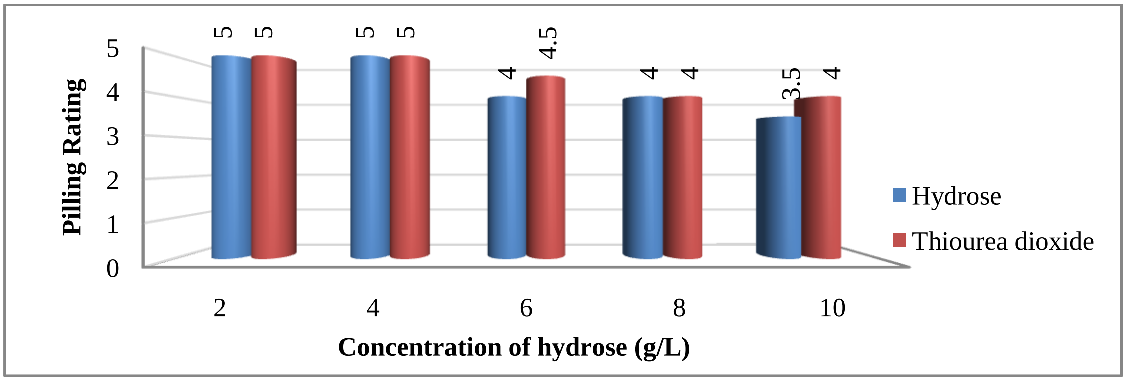


**Figure-9: Pilling resistance of samples stripped with hydrose and thiourea dioxide.**

## IV. CONCLUSIONS

In this study, an investigation of performance evaluation of hydrose and thiourea dioxide as stripping agents on MCT/VS bi-functional groups of reactive dyed cotton fabric was carried out. Based on this experimental study, the following conclusions were drawn:

1. Redox potential of thiourea dioxide was found higher than hydrose.
2. Stripping efficiency was found better using thiourea dioxide than hydrose for reactive dyed cotton fabric.
3. The highest degree of stripping was found at 4 g/L concentration of thiourea dioxide and 8 g/L concentration of hydrose.
4. Degree of stripping was found better for stripping light shade than dark shade.
5. At optimum stripping condition bursting strength of stripped fabric treated with hydrose was found around 86 lb/in$^2$ and treated with thiourea dioxide it was found around 102 lb/in$^2$ for both light and dark shades.
6. More weight loss was observed in stripped sample treated with hydrose than thiourea dioxide at optimum stripping condition.
7. Pilling resistance rating stripped sample was found 4 treated with hydrose and treated with thiourea dioxide it was found 5 at optimum stripping condition.

As stripping is a bond breaking process using harsh chemicals, there is no way to stop completely their adverse effects on fabric quality, but this can be controlled within a certain range by selecting appropriate stripping agent that causes less processing damage. The results of the study was expected to form the basis for development alternative process for color stripping of cotton fabric dyed with reactive dyes that could furnish an idea to replace the hydrose with thiourea dioxide.

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