Synthesis And Dyeing Properties Of Novel Bifunctional Reactive Dyes Via 4-(4-Methoxyphenyl)-Thiazol-2-Amine And 4-(4-Bromophenyl) -1, 3- Thiazol- 2- Amine On Nylon Fabric.

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Abstract: - Bifunctional reactive dyes are coloured compounds that posses more than one reactive moiety per molecule or groups, capable of forming covalent bonds between dye ions or molecules and the substrate. Two bifunctional reactive dyes 10c and 10d with a single monochlorotriazinyl and vinyl sulphone reactive groups were synthesised via (4-methoxyphenyl)-1,3-thiazol-2-amine and 4-(4-bromophenyl)-1,3- thiazol-2-amine. These intermediates were diazotized and coupled with J-acid and other coupling components to derive the dyes. Wavelength of maximum absorption (λ max ) of dyes were obtained. Dyes were applied on nylon fibres at various pH and temperature conditions. Optimum % exhaustion, % fixation and fixation efficiency were determined in glubber salt as the fixing agent. Washing and light fastness properties of dye samples were determined. The results revealed a λ max of 500nm(10c) and 480nm(10d) respectively, % exhaustion values of 69 and 67 at pH 11, 73% and 69% at 80°C in 70 minutes respectively, % fixation gave values of 69 and 65 at pH 11 respectively. The fixation efficiency values of 61% and 68% at pH of 11 respectively. The fairly good shades observed may be due to better, substantivity as well as good covalent fixation of the dyes with nylon fabrics. The colour strength and fastness properties of dyed fabrics were fairly comparable to that of cotton fabrics. The overall results suggest that bromo and methoxy groups introduced on the para position of benzene ring of dye molecules induced a hypsochromic shift of 10nm on 10c and 30nm on 10d with respect to 10a.

Key word: - Bifunctional Reactive dyes, %Exhaustion %Fixation, Fixation Efficiency and Fastness properties

I. INTRODUCTION

In general, acid dyes have attracted much attention to nylon substrates due to their interaction mechanism and easy method for application (Yoon, 2002). However, to achieve satisfactory levels of wash fastness, recourse is required to an after treatment with a commercial syntan and other fixing systems. While an after treatment of the dyed nylon substrates can improve wash fastness, this treatment can impart a change in shade of ground colour but also it is temporary in nature (Burkinshaw, 2001). Consequently upon this, application of reactive dyes to nylon substrates has attracted interests to solve those problems (Preston,1986). Reactive dyes react chemically with amino groups within nylon fibres to form a covalent bond. Theoretically, by virtue of the covalent nature of the dye-fibre bond, reactive dyeing on nylon fibres can display excellent wash fastness without any recourse to an after treatment. Especially, reactive dyes containing heterobifunctional groups can provide great opportunity for efficient dye-fibre reaction due to sulphatoethylsulphone and monochlorotriazinyl reactive systems(Broadbent, 2001). Thus, this paper concerns the build-up characteristics and wash fastness properties of the mixed anchor reactive dyes, of heterobifunctional reactive dyes (Hunger,2008). Exhaustion (%E), fixation (%F) and fixation efficiency (FE) were examined at various pH conditions and dyeing temperatures. These attach to nylon via ion-ion linkages between the cationic, protonated, amino end groups of the nylon (NH₃⁺) and the anionic sulphonate residue of the dye (Dye-SO₃⁻). Although this mode of attachment renders the dyeing of nylon straightforward, at least in principle, the wet fastness is usually less than ideal, and there is often a delicate balance to be struck between level dyeing performance and wet fastness. Loss of colour and staining of adjacent fabrics arises from the facile partial dissociation of ion-ion
links between dye and nylon. In order to render reactive dyes for nylon attractive to potential customers it is necessary that any such products exhibit an attractive balance of technical and commercial properties. Desirable technical features include high fixation, good build-up and fastness properties. The thrust of most published work on reactive dyes for nylon has been a comparison of the relative efficacies, of nylon, compared to existing cellulose reactive dyes. However, much less has been reported on the effect of other dye parameters, such as molecular size and fixed sulphonation, on the application properties of reactive dyes on nylon. Molecular size and shape are important in determining final dye fixation (Soleiman, 2005). In the case of dyeing nylon, at various pH, at fixed degree of sulphonation, hence low net negative charge, might be expected to lead to greater attraction with the positively charged fibre (Nylon-NH\textsubscript{3}\textsuperscript{+} under various conditions). Additionally, the net charge of nylon is negative, due to presence of anionic carboxylic acid groups and hence, at various pH values and fixed level sulphonation of dye, may lead to increased attraction between dye and nylon. Applying the dye at pH 11 generate two important advantages, firstly would increase the elimination of the temporarily anionic sulphatoethylsulphone groups, secondly maximize the concentration of the nucleophilic amino end groups on the fiber. This may suggest that the non-ionic bifunctional vinylsulphone derivative of the dye, generated from the elimination reaction of the two temporarily anionic sulphatoethylsulphone groups, in addition to the presence of the monochlorotriazine reactive group, can maximize the nucleophilic reaction with the amino groups on both fabrics.
II. EXPERIMENTALS

Synthesis of Intermediate

4-(4-Methoxyphenyl)-1,3-thiazol-2-Amine(1c) and 4-(4-BromoPhenyl)-1,3-thiazol-2-Amine(1d). Resublimed iodine (7.6g, 0.03mol) was added to the slurry of acetophenone (0.03mol) and thio-urea (4.56g, 0.6mol) and the mixture was heated in an oil bath at 130-140°C over night. After cooling, the reaction mixture was diluted with distilled water (50ml) and heated to dissolve most of the solid, again cooled to ambient temperature and treated with 25% aqueous ammonium hydroxide (to pH 9-10). The precipitated thiazole was collected and purified by crystallization from hot ethanol. The yield was computed and recorded. The melting point experiment was performed and the result recorded.

Preparation of the Coupling Component using J-ACID.

Cyanuric Chloride (1.9504g, 0.0106 mole) was stirred with acetone (40ml) and water (10ml) for 1 hour to form a fine suspension at the temperature (-2°C). After 1 hour, a neutral solution of 5-naphthol-2-amino-7-sulphonic acid (3.4g, 0.01 mole) was added in water and concentrated sodium bicarbonate solution (10%W/V) in such a way that the temperature did not exceed a level above 5°C. The reaction mass was stirred maintaining the pH 6.9 to 7 up to 3 hours. To the above solution, a further addition of newly neutralize solution of 2-methoxy-5-methyl-4-(β-Sulphatoethyl) Sulphonyl aniline (3.18g, 0.098mole) in water (10ml). The mixture was stirred for half an hour at 0-5°C, with a gradually rising of the temperature to 35°C adjusting the pH to 7.5. The mixture was stirred for 3 to 4 hours. Filtered, was held with cold water and the resultant product was used for subsequent coupling reactions. (Dalal and Desai 1996).

General Method of Diazotization

Diazotization was carried out by method prescribed by Dalai and Desai(1996)

General Method of Coupling

The coupling compound prepared (7.56g,0.01mole) was stirred thoroughly in water at 0°C, the diazonium chloride solution of 1c and 1d (0.01 mole) were added slowly over 1 hour maintaining the pH at 7.0. The pH was adjusted to 7 or below such that sulphatoethyl sulphone remain as a functional group. The stirring was continued for 4 hours at 0-5°C. A solution of sodium hydrogen phosphate (0.42g) and potassium dihydrogen phosphate (0.83g) in water followed by sufficient sodium chloride (15.20g) was added to precipitate the product. Organic impurities were extracted by washing with a small portion of diethyl ether. (Dalal and Desai, 1996).

Purification of Fabric

Cotton fabrics were purified by scouring, bleaching and mercerization by methods prescribed Sadov et al.,(1973;Anon,1998 and Trotman,1975)

Dyeing

Dyeing was carried out as described by Giles. Weighting were carried out using Sauter RC 8021 digital weighing balance and optical density measurements were conducted using Jenway 6305 Spectrophotometer. Two dye baths were prepared and a blank containing all the regents except the dye. The dye baths were adjusted to pH of 3,5,7,9,11, and 13 respectively with acetic acid and sodium hydroxide. The dye % exhaustion of the solution in the dye bath and blank was taken using syringes. The samples drawn were diluted to 25ml and were evaluated for absorbance at λmax of 510 and 480nm with UV spectrophotometer. The initial and final absorbance values obtained were used to calculate % exhaustion for the dyeing at various pH. The values were tabulated and the graph of % exhaustion was plotted against pH. The experiment was repeated varying temperature 40 – 90°C and Time 0-90-min and their % exhaustion were plotted against each variable respectively. (Ajayi, 2005).

III. MEASUREMENT AND ANALYSES

Determination of dye % Exhaustion

The dye % exhaustion of nylon fabrics (E%) was calculated according to the following equation(Ajayi,2005)

\[ \% \text{ Exhaustion} = \frac{\text{Initial OD} - \text{Final OD}}{\text{Initial OD}} \times 100 \]

Where OD = Optical density
OD0 = values taken before the start of dyeing
OD1 = values taken at the end of dyeing.
Determination of $\lambda_{\text{max}}$

The concentration (M/l) of dye solution was measured on Jenway 6305 UV visible Spectrophotometer at 0.001% of solution at $\lambda_{\text{max}}$ (510 and 450nm) respectively for 10c and 10d.

IV. FASTNESS TESTING

The dyed samples are tested according to the American Association of Textile Chemists and Colourists (AATCC) standard methods(AATCC,1999).

Colour fastness to washing:

(i) The composite specimens are sewed between two pieces of bleached cotton and wool fabrics.
(ii) The composite specimen is immersed into an aqueous solution containing 5g/l soap non-ionic detergent, at 60°C with L.R. 1:50, the samples were then removed, rinsed in hot and cold distilled water.
(iii) Evaluation of the wash fastness is established using the Grey-Scale for the change in colour for dyed samples and staining for bleached cotton fabrics (BS 1006, 1999).

Colour fastness to light:

(i) A specimen from the dyed fabrics to be tested and standards were exposed simultaneously under specified amounts of colour change.
(ii) The specimens were exposed to the light for about 20 hours.
(iii) Evaluation of results were carried out by using the Grey-
(iv) Scale (BS1006,1999). If the final assessment is greater, the preliminary assessment becomes significant with very high light fastness, standard fades to a contrast equal to Grade 5 in grey scale (Fan et al.,2004). If the final assessment is lower, the rating to a contrast equals to grade 3 indicates that the sample has change very slightly.

V. STRIPPING PROCESS

The dye fixation ratio (%F) is the percentage of the exhausted dye chemically bound to the fabrics (nylon). This was measured by refluxing the dyed fabric samples in 25% pyridine for 10min at liquor ratio (LR) 1:20 to extract the unfixed dye (Abofarha, 2010). The procedure was sustained until the extract was clear. The concentration of extract was measured spectrophotometrically at $\lambda$ max of the dye. The % fixation ratio (%F) and fixation efficiently (FE), which is the percentage of dye chemically bound relative to the total amount of dyes used, were calculated using equation (2) and (3) respectively.

\[
\%F = \frac{D_0 - D_T - D_e}{D_0 - D_T} \times 100 \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cd -

Result.

Table 1: The dye numbers, $\lambda_{\text{max}}$, molecular weight and melting point.

<table>
<thead>
<tr>
<th>Dyes</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>molecular weight</th>
<th>Mpt°C</th>
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<tbody>
<tr>
<td>10c</td>
<td>500</td>
<td>1031.95</td>
<td>303</td>
</tr>
<tr>
<td>10d</td>
<td>480</td>
<td>1088.2</td>
<td>309</td>
</tr>
<tr>
<td>10a</td>
<td>510</td>
<td>1009.33</td>
<td>300.5</td>
</tr>
</tbody>
</table>

Table 2: Colour fastness according to AATCC Standards for dyes 10c and 10d at 2% Shade in glauber salt at pH 11.0.

<table>
<thead>
<tr>
<th>Period in weeks</th>
<th>10c</th>
<th>10d</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wash fastness</td>
<td>Light fastness</td>
</tr>
<tr>
<td>1</td>
<td>4-5</td>
<td>4-5</td>
</tr>
<tr>
<td>2</td>
<td>4-5</td>
<td>4-5</td>
</tr>
<tr>
<td>3</td>
<td>4-5</td>
<td>4-5</td>
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<tr>
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<td>4-5</td>
<td>4-5</td>
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<td>5</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>
Fig. 1: EFFECT OF TEMPERATURE ON % EXHAUSTION OF DYE 10a - 10f ON NYLON FABRICS

Fig. 2: EFFECT OF PH ON % EXHAUSTION OF DYE 10a - 10f ON NYLON FABRICS
Fig. 3: EFFECT OF TEMPERATURE ON % FIXATION OF DYE 10a - 10f ON NYLON FABRICS

Fig. 4: EFFECT OF PH ON % FIXATION OF DYE 10a - 10f NYLON FABRICS
EFFECT OF TEMPERATURE ON % EXHAUSTION OF DYE 10c and 10d ON NYLON FABRICS

The effect of temperature on the absorption of dyes 10c and 10d on nylon 6,6 is investigated in temperature range of 40-90°C at 2% shade and pH 11.0 in presence of 50g/l SS and 20g/l sodium carbonate. Figure 1 shows the effect of temperature on percentage exhaustion of dyes 10c and 10d on nylon fabrics. In figure 1, the % exhaustion (10c) increases with temperature from 40% at 40°C to 73% at 80°C and, the % exhaustion of dye10d on nylon fabric increased from 48% at 40°C to 69% at 80°C and decreased as the temperature is extended above 80°C. The decrease in % exhaustion at the temperature above 80°C for nylon may be due to instability of dye molecules at high temperature. Figure 1 shows that adsorption of dyes 10c and 10d on nylon enhanced with raise in temperature up to 80°C for both dyes indicate that high temperature favoured dye adsorption onto nylon fibre. However, temperature higher than 80°C for 10c and 10d dyes, respectively resulted to decrease in adsorption, which may be attributed to dye molecule instability at higher temperatures (Ali, 2009).

The increase in temperature increase mobility of large dye ions as well as produce a swelling effect with internal structure of the fibre, thus enabling large dye molecules to penetrate further (Yoshida et al., 1993; Venkat et al., 2007). This may also be due an increase in mobility of dye molecules with an increase in their kinetic energy, and enhanced rate of intra particle diffusion of sorbate with rise in temperature. It is clear that the sorption of dyes 10c and 10d onto nylon fibre is an endothermic process.

EFFECT OF pH ON % EXHAUSTION OF DYE 10c and 10d ON NYLON FABRICS

Figure 2, shows the effect of pH on % exhaustion on both nylon fabrics. In figure 2, the % exhaustion of dye 10c on nylon fabrics increased with pH from 24% at pH 3 and attains a maximum value of 69% at pH 11 while 10d increased from 16% at pH 3 and attains a maximum of 67% at pH 11 and decreased as the pH is extended further. The low % exhaustion at the acidic medium may be due to the non ionization of the amino group of nylon fabric which facilitate the covalent bonding between the more electrophilic reactive groups of dyes base on monoclorotriazine and vinyl sulphone and the NH₂ groups of nylon fabric. This reflects the advantages of the combined reactive groups having different reactive levels, that complement each other for variations in dyeing conditions. Applying the dye at pH 11 generate two important advantages, firstly would increase the elimination of the temporarily anionic sulphatoethylsulphone groups, secondly maximize the concentration of the nucleophilic amino end groups on the fibre (Mohammed et al., 2013). This may suggest that the non-ionic bifunctional vinylsulphone derivative of the dye, generated from elimination reaction of two
temporarily anionic sulphatoethylsulphone groups, in addition to the presence of monochlorotriazine reactive group, can maximize the nucleophilic reaction with amino groups on both fabrics.

EFFECT OF TEMPERATURE ON % FIXATION OF DYE 10c and 10d ON NYLON FABRICS

The results given in Figure 3 clearly show that dye displays good build up and exhibits good rate of exhaustion on nylon fabrics then equilibrate in sample(d) but decreased in sample (c) at further dyeing temperature, probably due to its good substantivity. It is also clear that total fixation yield of dye increases as dyeing proceeds. This may be due to hydrophobic character of non-ionic (vinylsulphone)/ MCT reactive systems in the dyes, generated from elimination reaction of temporarily anionic (SES) groups, not only imparts high substantivity under alkaline dyeing but also effectively exhibits high fixation efficiency. Figure 3 shows the effect of temperature on % fixation of dyes 10c and 10d on nylon fabrics. In figure 3, the % fixation of dye 10c on nylon fabrics increased with temperature from 36% at 40°C and attains a maximum value of 69% at 80°C while 10d increased from 35% at 40°C and attains a maximum fixation of 65% at 80°C and decreased as the temperature is extended further. The observation is similar to the report of Rattanaphani (2007).

VI. FIXATION EFFICIENCY

The fixation efficiency shows the effectiveness and efficiency of the dye in the dyeing process. It gives a comparison between exhaustion and fixation of dye on fabrics (nylon) with respect to pH. (Rattanaphani, 2007). Figure 4 shows the fixation efficiency of dye 10c on nylon fabrics increased with pH from 35%, at pH 3 and attains a maximum value of 61% at pH 11, while 10d increased from 14% at pH 3 and attains a maximum of 68% at pH 11, but decreased as pH is extended further, probably due to its good substantivity, this gradually equilibrates at dyeing pH 13 on both fabrics. This may be due to hydrophobic character of non-ionic bis(vinylsulphone) reactive system in the dye, generated from elimination reaction of bis sulphatoethylsulphone) groups. This not only imparts high substantivity under the alkaline dyeing but also effectively exhibits high fixation rate.( Farouk et al, 2012)

Fastness properties
The fastness properties of dyes on nylon fabrics at 2% shade, liquor ratio 250:1, pH 11 and 80 °C, were investigated and are given in Table 2. The results show that the fastness to washing and light on nylon displayed a good fastness to washing and light.

VII. CONCLUSION

A new bifunctional reactive dye, derived from 2-amino thiazole containing two anionic SES and MCT reactive groups, has been synthesised and shown to have good dyeing performance on nylon 6,6 fabrics. Optimum exhaustion and fixation on fabrics was achieved by dyeing at pH 11 and 80°C. The β-elimination of the two anionic SES groups under alkaline conditions results in the formation of a non-ionic reactive vinylsulphone derivative in combination with monochlorotriazine as having different reactivity levels, achieving a supplementary behaviour to resist variations in dyeing conditions, which in turn increase the dye–fibre interaction and thus improve dye fixation on nylon 6,6 fabrics. Bromo and methoxy groups introduced on the para position of benzene ring of dye molecules induced a hypsochromic shift of 10nm and 30nm with respect to 10a.

VIII. REFERENCES


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