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Synthesis of Vinylsulfone Based Poly Anchor Reactive Dyes and their Applications on Cotton Fabric

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Three vinylsulfone based poly anchor reactive dyes have been synthesized by following condensation, diazotization and coupling reactions respectively, with a view to achieve bright shades and good fastness properties. Cotton fabric was desized, bleached and mercerized before dyeing and application studies. Pad-thermosol dyeing method was employed since it is more environment friendly due to high dye fixation. Effect of different dyeing parameters *i.e.* salt concentration, dyeing time, dyeing temperature and pH of dye solution were optimized. The dyed fabrics were subjected to CIE LAB and LCH system in order to evaluate the dyeing quality parameters by using Spectraflash SF-600 at Noor Fatima Textile Pvt. Ltd., Faisalabad. Fastness properties such as perspiration, light, washing, chlorinated water, dry cleaning and crocking were evaluated for the dyed fabrics by following ISO standard test methods.

Key Words: Poly anchor, Pad-thermosol dyeing, Fastness properties, Chroma co-ordinate, Hue angle.

INTRODUCTION

Reactive dyes are extensively used worldwide in textile industry not only to colour cotton but also wool and polyamide fibers because of their variety of colour shades, brilliant colours, high wet fastness properties and ease of application. A steady increase in reactive dye usage has been observed as a result of higher demand of cotton wear globally. For reactive dye the reaction between the reactive group, dichlorotriazinyl and the fiber involve a nucleophilic addition and substitution mechanism. Burkinshaw and Kabambe[1] accounted that for the dyeing of cotton fabric, pH of the dye solution and equilibrium concentration of cellulosate ions are increased as a result of formation of a covalent bond between the dye and the cellulosic fabric/cotton. However, due to the competition between the Cell O^- as well as OH^- ions in the dye bath at high pH, a portion of the dye reacts with OH^- ions instead of the cellulosate ions on the fiber which results in hydrolysis, reported by Epolito *et al.*[2].

Dyes can be classified by different means *e.g.* based upon their applications or on the basis of functional group present. According to application techniques by Kirk *et al.*[3], dyes may be classified as acid dyes, basic dyes, azoic dyes, direct dyes, mordant dyes, lake or pigment dyes, sulfur dyes, vat dyes, disperse dyes and reactive dyes. Among the varieties of dyes, reactive dyes were commercially most admired due to their acceptable price, good colour, bright shades, reasonable fastness properties and their applications to different materials as described by Konstantinova and Petrova[4]. The combination of different functional/ reactive groups in the dye molecule improves their dyeing ability and possibility of applications to a variety of fabric materials were scrutinized by Lewis *et al.*[5].

The distinguishing characteristic of reactive dyes is that they form covalent bonds with the substrate which is to be coloured. During the application process, the specific functional group in the dye molecule can endure addition or substitution reactions with the -OH, -SH and $-NH_2$ groups present in the fabric observed by Milena *et al.*[6]. The negative aspect of reactive dyes due to some environmental perspectives is their susceptibility to undergo hydrolysis during applications on fabric, which gives removes and incorporate colour in the effluent from dye industries. Alkaline conditions are generally employed in order to generate sufficient nucleophilic cellulosate anions during application procedure of reactive dyes, in such conditions some dye hydrolysis is unavoidable studied by Mousa[7]. The application of reactive dyes to cotton fabric has recently gained much attention, the publications that described by Renfrew and Taylor[8] showed the use of reactive dyes on cellulose show their use for other fibers too.

EXPERIMENTAL

All commercial reagents and solvents involved in the synthesis were of analytical grade and were used as received. Solid raw materials used for the synthesis of dyes were obtained from Harris Dyes and Chemicals, Faisalabad.

Applications and fastness tests were carried out by laboratory thermosol padder machine and spectrophotometer Spectraflash (SF- 600) respectively at Noor Fatima Textile Pvt. Ltd., Faisalabad. Crockmeter (SDL/CM-5 Atlas) for testing rubbing fastness, Lander-o-meter for testing washing and dry cleaning fastness and Fadometer for light fastness. UV/Vis spectrophotometer (CE- 7200) was used to determine λ_{max} for new synthesized dyes.

Synthesis scheme: Three reactive dyes with vinyl sulfone-type- fiber reactive groups were synthesized. Dyes B-1, B-2 and B-3 were synthesized following the route shown in scheme respectively.

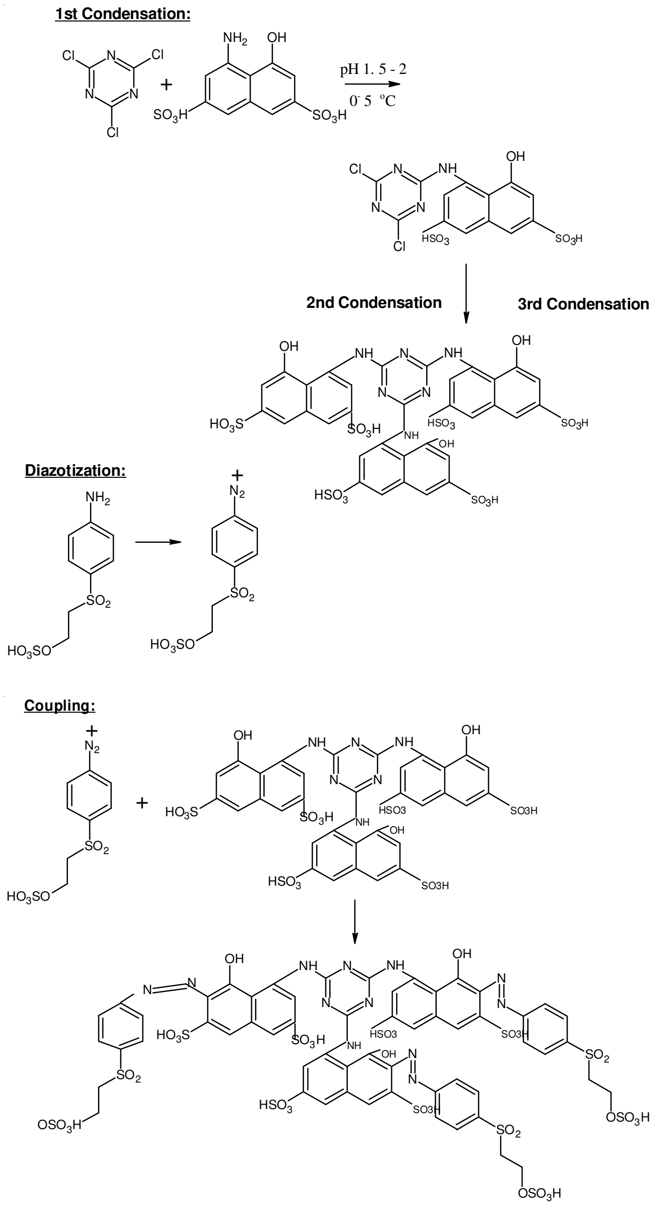
Synthesis route for Dye B-1: Suspension of 2,4,6-trichloro-1,3,5- triazine (Cyanuric chloride; 4 g/25 mL) was added drop wise to 50 mL solution of 1-amino-8- hydroxy-napthalene-3,6-disulphonic acid (H- acid) (0.03 moles; 80 % pure) by maintaining the at pH 7. The reaction mixture was condensed at stirrer for 1.5 h at reaction conditions of pH 1.5-2; Temperature 0- 5 ºC. 1st condensation was monitored chromatographically on Whattman filter paper using 2 % sodium chloride (NaCl) solution as eluent. The precipitated condensed product was filtered and to this 100 mL of H- acid (0.04 mol; pH 7) was added at once, heated slowly up to 45 ºC and stirred for 1 h for the completion of 2nd condensation. The reaction mixture was again heated up to 95-100 ºC with adjusting pH at 11-12 and stirred for 1 h. The resulting condensed product was again scrutinized chromatographically and adjust at pH 7 by adding small quantity of hydrochloric acid (HCl; 33 % pure).

Diazotization was followed by dissolving 200 mL of vinyl sulfone para ester (VSPE; 95% pure; 0.06 moles) into 150 mL oh hydrochloric acid (33 % pure). The reaction mixture was further stirred for one hour at 0 ºC. 50 mL of Sodium nitrite ($NaNO_2$; 0.1 M) was poured drop wise into vinyl sulfone para ester reaction mixture and stirred intensively for 1.5 h. The diazotized product formed was monitored with iodine-starch indicator paper. Small amount of sulfamic acid (H_3NSO_3) was also added to the diazotized product.

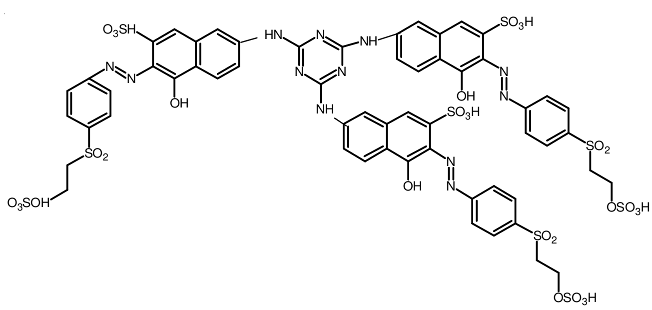
The final condensed product was coupled with diazotized product by intensive stirring at reaction conditions pH 7; temperature 10-15 ºC. The synthesized dye was then oven dried at 80-90 ºC (**Scheme-I**).

Synthesis route for Dye B-2 and B-3: By following the same synthesis scheme, dyes B-2 and B-3 were also synthesized by using J- acid (6-amino-1-naphthol-3-sulfonic acid) and γ-acid (6-amino-1 naphthol- 4- sulfonic acid) respectively. New dyes were prepared with slight modification in above mentioned synthesis steps. The final proposed structures of synthesized dyes *i.e.* B-2 and B-3 are given as under (**Scheme-II**).

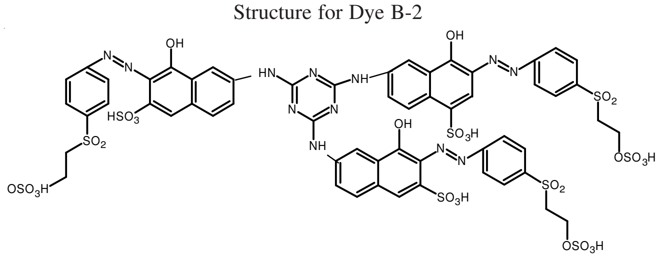
Spectrophotometric measurements: The ultraviolet-visible maximum absorption wavelength (λ_{max}) of all synthesized dyes in aqueous solution was recorded using a UV/VIS spectrophotometer (CE-7200).



Scheme-I: Structure for Dye B-1



Structure for Dye B-2



Scheme-II: Structure for Dye B-3

Pretreatment of cotton fabric: Pure cotton fabric was desized by applying 1 % HCl solution for 15 min near boiling temperature of 70 ºC. Desizing was done in order to eliminate waxes, proteins *etc.* from the surface of the fabric. Desized cotton fabric (5 g) was bleached by treating the fabric with 4 % hydrogen peroxide (H_2O_2) and 2 % sodium hydroxide (NaOH) solution. Cotton fabric was further treated for mercerization using 16 % solution of NaOH. The pretreatment procedure caused swelling of cotton cellulose which helps in dye uptake.

Optimization of dyeing quality parameters: In order to evaluate the dye ability of synthesized poly anchor reactive dyes, the dyeing quality parameters were optimized such as concentration of Glauber's salt (sodium sulfate), dyeing time, temperature and pH of the dye solution to acquire maximum colour strength values. Series of subsequent dyeing experiments were carried out using each dye on laboratory thermosol padder machine at Noor Fatima Textile Pvt. Ltd., Faisalabad. Twelve sets dyeing experiments with a group of three for each variable were categorized for three synthesized reactive dyes. To optimize dyeing time 1, 1.5 and 2 min were carried out at standard condition chosen *i.e.* (160 ºC, no salt, pH 8 and 1 min of dyeing time). Similarly three dyeing experiments were done with varying dyeing temperature to 140, 150 and 170 ºC respectively. Another set of three experiments was set up at pH; 7, 9 and 10 and salt concentration; 5, 10 and 15 g/L keeping all other conditions at constant. For each dyeing experiment, 3 % dye in stock solution was used according to the weight of the fabric. Mill scoured, bleached and mercerized cotton fabric was used throughout this work.

The dyes cotton fabrics using B-1, B-2 and B-3 dyes were washed with hot water (60 ºC) twice rinsed under tap water for 3-4 min and dried in dry cleaner (SDL- ATLAS).

Colour assessment of dyed fabric: The system of coordinates designated as L*, a* and b* were recommended by CIE. One colour can be completely determined by three coordinates: L*, a* and b* or L*, C* and H*. Dyed fabrics were subjected to CIE LAB and LCH system in order to evaluate the dyeing quality parameters such as dL* (difference in lightness co-ordinate), da* (difference in red/ green co-ordinate), db* (difference in yellow/ blue co-ordinate), dC* (difference in chroma co-ordinate), dH* (difference in hue angle) and dE* (total colour difference) values reported by Miljkovic *et al.*[9] with the help of spectrophotometer Spectraflash (SF- 600) at Noor- Fatima textile Pvt. Ltd., Faisalabad.

Fastness testing: Fastness tests *i.e.*, colourfastness to crocking (ISO 105-X12), colourfastness to light (ISO 105-B02), colourfastness to washing (ISO 105-CO3), colourfastness to perspiration (ISO 105-E04), colourfastness to chlorinated water (ISO 105-E03), colourfastness to dry cleaning (ISO 105-D01) were also performed according to the standard methods specified by American Association of Textile Chemists and Colourists and International Organization for Standardization (AATCC and ISO) also observed by Soleimani-Gorgani and Taylor[10].

RESULTS AND DISCUSSION

The focal idea behind this research work was to synthesize novel poly anchor reactive dyes based upon vinyl sulfone groups and to study their applications and chemical characteristics. General proposed molecular formulae for the synthesized dyes are B-1; ($C_{56}H_{47}N_{12}O_{36}S_{12}$), B-2; ($C_{57}H_{48}N_{12}O_{30}S_9$) and B-3; ($C_{57}H_{48}N_{12}O_{30}S_9$) respectively.

The colour output of the dyed fabrics using synthesized dyes at optimum conditions was determined by Spectraflash (SF-600) at Noor-Fatima Textile Pvt. Ltd., Faisalabad. The values obtained with dyeing quality parameters such as dL* (difference in lightness co-ordinate), da* (difference in red/ green co-ordinate), db* (difference in yellow/ blue co-ordinate), dC* (difference in chroma co-ordinate), dH* (difference in hue angle) and dE* (total colour difference) values and colour indication illustrated that batch is lighter redder less yellow for dye B-1, lighter less red less yellow batch for dye B-2 and lighter redder yellow for dye B-3 respectively.

Effect of salt concentration on colour strength: Salt plays an important role in exhaust dyeing but in order to explore the effect of concentration in case of pad-thermosol dyeing, different concentrations of glauber's salt *i.e.* 5, 10 and 15 g were used. The results of colour strength using different concentrations of salt were compared for three vinyl sulfone reactive dyes B-1, B-2 and B-3 as shown in the Fig. 1. The effect of salt addition to the pad-thermosol dyeing on the fastness of these dyes is reported in the present research work. Similar results were also reported by Soleimani-Gorgani and Taylor[11] in which they used sodium sulfate/ electrolyte to the dye liquor of reactive dyes to increase the uptake of dye to pretreated fabric. Salt concentration of 10 g was found to be the optimum since the colour strength was significantly increased for all synthesized dyes; however 66.38 % colour strength was accomplished in case of dye B-3, which was highest among all. Concentration more than optimum might cause dye aggregation and lower migration, which leads to uneven dyeing. Insufficient than the optimum concentration of salt may cause inadequate colour yield to poor fixation. The salt effect can be rationalized by the fact that its presence in dye bath enhances dye substantivity towards the fabric thread and also neutralizes the negative charge that may exist on the surface of the fiber. It is demonstrated by Yingling *et al.*[12] previously that salt (sodium sulfate) concentration can be effectual to get the higher colour output/ strength for the reactive dyes on the fabric.

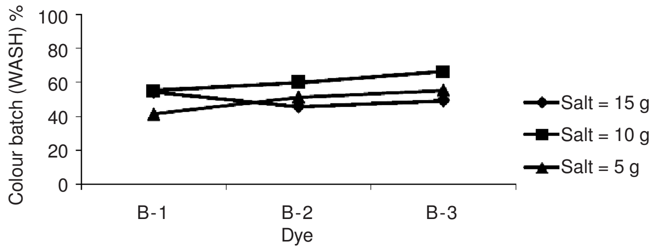


Fig. 1. Comparison of colour strength at different salt concentrations of dyes

Effect of dyeing time on colour strength: The data obtained from the padder dyeing for the reactive dyes B-1, B-2 and B-3 showed that there was an increasing trend of colour strength with different dyeing times of pad-thermosol dyeing. Maximum colour output achieved at 2 min dyeing in case of dye B-2 which was 80.56 %. It is revealed from results that 2 min was appropriate for the maximum uptake of dye particles by the cotton fabric through covalent bonding. Comparative results of different dyeing time with colour output for the synthesized dyes B-1, B-2 and B-3 were summarized in the Fig. 2.

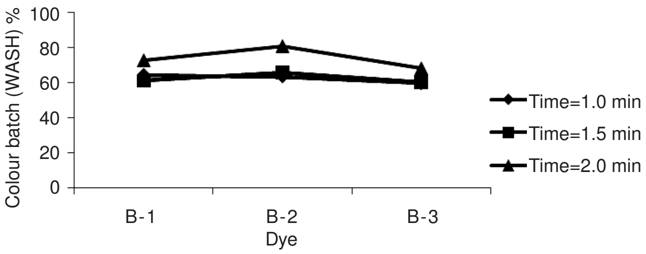


Fig. 2. Comparison of colour strength at different dyeing times of dyes

Effect of dyeing temperatures on colour strength: Temperature is considered as an important constraint for dyeing process because dyeing at low temperature may remain incomplete and high temperature may leads to the degradation and desorption of the dyes. To optimize the effect of moderate temperature on the bad- batch dyeing, cotton fabric was dyed at different temperatures *i.e.* 140, 150 and 170 ºC. The data obtained was plotted in Fig. 3 using all the synthesized dues B-1, B-2 and B-3 respectively. Highest colour strength was observed at 150 ºC comparatively B-3 dye showed better colour strength. Temperature more than 150 ºC lowers the colour strength value which might be due to the desorption of the dye from the fabric to the dye bath by shifting its equilibrium at higher temperature.

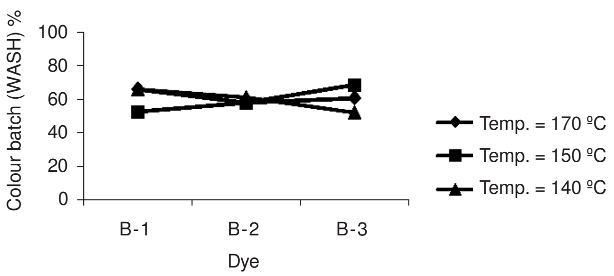


Fig. 3. Comparison of colour strength at different dyeing temperatures of dyes

Effect of pH on colour strength: Colour strength values for the synthesized dyes was achieved at different values of pH i.e. 7, 9 and 10 respectively. The end results which are revealed in the Fig. 4 indicated maximum colour strength value *i.e.* 79.35 % at pH = 10 intended for dye B-3. There is an increasing trend in the colour output with increasing pH values which is due to the fact that vinyl sulfone (VS) based reactive dyes works better on alkaline pH, which was in accordance to the colour output results of the reactive dyes. Results obtained by Youssef *et al.*[13] demonstrated high substantivity rate to the cotton fabric at high pH values due to covalent binding linkages between the dye and fiber. Consequences of colour strength values for dyes at optimum pH = 9 were higher, due to the rate of hydrolysis of the reactive group became lower at higher pH.

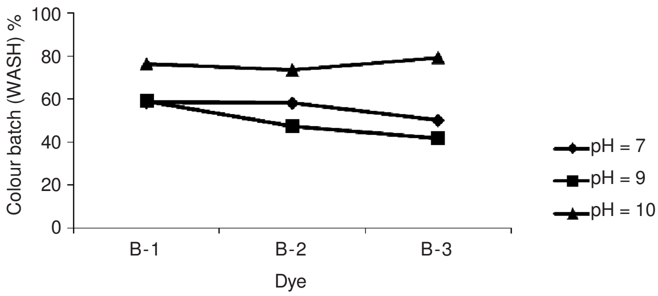


Fig. 4 Comparison of colour strength at different pH of dyes

TABLE-1
SPECTRAL DATA OF SYNTHESIZED DYES

Sr. #	Dye	λ_{max}[a](nm)
1.	B-1	511
2.	B-2	486
3.	B-3	492

[a]Measured in distilled water

Fastness properties: Fastness properties such as fastness to washing, crocking, light, perspiration, chlorinated water and dry cleaning were assessed using ISO standard fastness test protocol. The change in the shade was evaluated visually using grey scales. The fastness properties for all three reactive dyes *i.e.* B-1, B-2 and B-3 on cotton fabric dyed in 3 % dye solution at optimized dyeing parameters were examined and shown significant results in Tables 2-4 respectively.

The values for colour fastness to washing and crocking (dry and wet) were in the range of 4-5 which are of good quality. Wash fastness results of reactive dyes were evaluated using ISO 105CO6/C2S which were also found satisfactory when employed at every depth of shade according to illustrated methods. Zolriasatein *et al.*[14] observed the fastness test results for light, perspiration and chlorinated water satisfactory (4-5). The better fastness results are probably due to the reactive nature of three synthesized dyes and have a ability to

TABLE-2
FASTNESS PROPERTIES OF THE SYNTHESIZED DYE B-1 ON PRETREATED COTTON FABRIC

Dyeing characteristics	Salt concentration (g)			Dyeing temperature (ºC)			Dyeing time (min)			Dyeing p^H		
	5	10	15	140	150	170	1	1.5	2	8	9	10
Light fastness	4	4-5	3-4	4	4-5	4	3-4	4-5	4	4	5	4-5
Washing fastness	3	3-4	4	4	4-5	4	3-4	4-5	5	4	4-5	4-5
Dry cleaning fastness	4-5	3-4	4	4	3-4	5	3-4	4-5	4-5	4	4-5	4-5
Perspiration fastness	4	3-4	3-4	3	4-5	4	4	4	4-5	4	4-5	4-5
Chlorinated fastness	3-4	4	5	4	3-4	4	3-4	4	4- 5	4	4	4-5
Crocking fastness	4-5	4	3-4	4	5	4	4	5	4	3-4	4	4-5

TABLE-3
FASTNESS PROPERTIES OF THE SYNTHESIZED DYE B-2 ON PRETREATED COTTON FABRIC

Dyeing characteristics	Salt concentration (g)			Dyeing temperature (ºC)			Dyeing time (min)			Dyeing pH		
	5	10	15	140	150	170	1	1.5	2	8	9	10
Light fastness	4	4-5	3-4	4	4-5	4	3-4	4-5	4	5	4	4
Washing fastness	3	3-4	4	4	3	3-4	3-4	4-5	5	3-4	4-5	4-5
Dry cleaning fastness	4-5	3-4	4	4	3-4	5	3-4	5	4-5	4	4-5	4-5
Perspiration fastness	4	3-4	3-4	3	4-5	4	4	4-5	4-5	4	4-5	4-5
Chlorinated fastness	3-4	4	5	4	3-4	4	3-4	4	4- 5	4	4	4-5
Crocking fastness	4-5	4	3-4	4	3-4	3-4	4	5	4	3-4	4	4-5

TABLE-4
FASTNESS PROPERTIES OF THE SYNTHESIZED DYE B-3 ON PRETREATED COTTON FABRIC

Dyeing characteristics	Salt concentration (g)			Dyeing temperature (ºC)			Dyeing time (min)			Dyeing pH		
	5	10	15	140	150	170	1	1.5	2	8	9	10
Light fastness	3-4	4	4	4	4	3-4	3-4	4	4	4	4-5	4-5
Washing fastness	4	3-4	5	3-4	3-4	4	3-4	5	4-5	3-4	4-5	4-5
Dry cleaning fastness	3-4	4	4-5	4-5	3-4	4-5	3-4	4-5	4-5	4	4-5	4-5
Perspiration fastness	4	4	4	3-4	4	4	4	4-5	4-5	4-5	4-5	3-4
Chlorinated fastness	3-4	3	4-5	4-5	4	4-5	4	4	4-5	4	5	4-5
Crocking fastness	4	3	4	4-5	4	4-5	4-5	4-5	4	4	4	4-5

fix well onto cotton fabric even after washing and drying. Previous study regarding colour fastness to washing, wet and dry rubbing and perspiration using reactive dyes on the pretreated cotton fabric seemed accordingly.

Conclusion

Three new vinyl sulfone-type fiber reactive dyes B-1, B-2 and B-3 were synthesized by condensation and diazonium-coupling reactions with three different acids *i.e.* H- acid, J- acid and γ-acid. Synthesized dyes were then applied in 3 % dye (stock) solutions on the mill scoured, bleached and desized cotton fabric and their application properties were studied. Pad-thermosol dyeing method was used for dyeing cellulosics which forces the dyestuff inside the fabric for greater penetration while removing excess dye solution. Even and deep shades were obtained using pad- thermosol dyeing method at optimized dyeing conditions. The highest colour strength yield on cotton was obtained at pH 9 with dye B-3 and 2 min of dyeing time for dye B-2 at standard conditions selected for optimization. In case of colour fastness test and other physico-chemical tests, all three synthesized dyes give adequate results from good to excellent visualized by grey scale.

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