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STUDIES ON THE RECOVERY AND RE-USE OF TRIAZINE REACTIVE DYES FROM TEXTILE EFFLUENT

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ABSTRACT

Textile effluent is the major source of pollution and threat to mankind. Most of the dyes used are synthetic with bulk carbon content. Reactive (Triazine) dyes are preferred for the dyeing of cellulosic fabrics because of their wide shade range, easy application and better colourfastness properties. But the drawback with these dyes is their great affinity for water. Due to this large amount (approx 30%) of the dye remains unreacted and discharged into effluent. This increases the cost of dyeing and pollution load. In the present work, recovery and re-use of untreated dyes from the textile effluent is studied by solvent extraction process using surfactants. Studies are carried out with Reactive Blue 171 from the triazine class of reactive dye having molecular weight of 1418.9. The solvent taken for the studies is iso-amyl alcohol as the lower alcohols are soluble in water. The process involves two steps: first step is the removal of unreacted dye from textile effluent i.e. aqueous phase into solvent phase using reverse micelles of cationic surfactant i.e. Hexadecyltrimethyl ammonium bromide. In the second step dye is backward extracted into the aqueous phase from the solvent phase using anionic surfactant i.e. Sodium dodecylbenzene sulfonate. Recovered dye is re-used to dye the fabric and the shade, colourfastness and strength properties of fabric are compared with the fabric dyed with native dyes. It is found that re-use of recovered dye is possible with almost similar properties by suitable makeup of the dye bath.

Keywords: triazine dyes; reverse micelle; surfactant; solvent extraction; colour fastness; tear strength; K/S; colour coordinates.

INTRODUCTION

We all are aware about the importance of colour fabrics in our day to day life. Without colour we can't even think about the fabric. This force the textile manufacturer's to colour the fabric using some dyes. Although many classes of dyes are available but triazine class of reactive dyes are preferred because of their shade range, easy application and colour fastness properties[1-2]. But drawback with these dyes is their great affinity for water and hence about 20%-30%[3-4]of dyes remain unreacted which is discharged into the effluent. This unreacted dye not only increases the pollution load but also has great impact on the cost of dyeing. Removal of the unreacted dye by the available methods such as Membrane-separation[5], Electrochemical[6], Flocculation-Coagulation[7-8] Reverses Osmosis, Ozone oxidation [9], Biological treatment [10-12] and Adsorption [13-16] is studied in detail. Although these methods are efficient in removing the dye from effluent but no method describes the recovery of dyes to make its re-use possible.

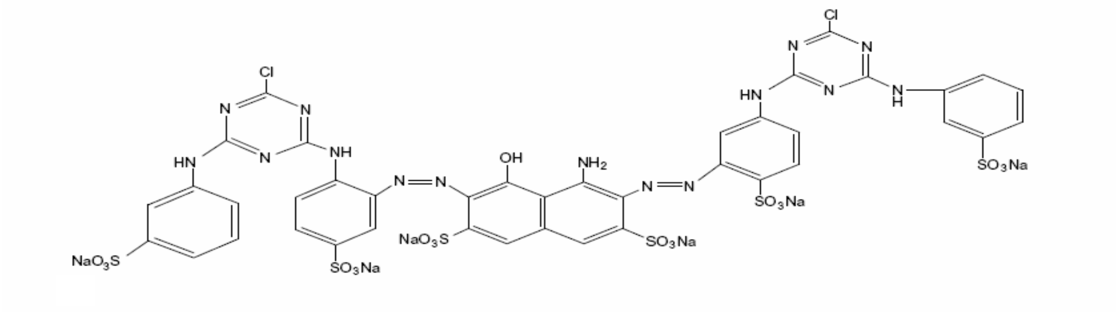
In the present work solvent extraction process using surfactants is studied in detail to recover and re-use the unreacted dye from the textile effluent. The purpose of the present study is to show that the recovered dyes can be re-used and almost same depth of shade can be obtained by suitable make-up of the dye bath. Also, by the removal of colour from the effluent, organic mass of the effluent is minimized to a great extent. For the present study, effluent is generated in lab using actual method of dyeing [17]

Unreacted dye is recovered from the effluent in two step extraction. First step is the forward extraction of dye from the effluent into organic solvent and second step is the recovery of dye from the organic solvent into fresh aqueous solution. Then recovered dye is re-used to dye the fabric by suitable make-up of the dye bath. The properties of fabric dyed with recovered dyes are compared with the fabric of the same depth of shade dyed with native dyes. As the dyeing has a significant impact on the shade, colourfastness and strength properties of fabric hence these properties of fabric are tested as per AATCC[18] and ASTM[19] test methods and compared.

EXPERIMENTAL

Material & Method:
Dye: HE Brand Triazine dye (Atul India Ltd.)

C.I. Reactive Blue 171
λ_{max} =607 nm
Mol. Wt- = 1418.9



Chemicals: Iso-amyl alcohol, glacial acetic acid, sodium carbonate, sodium chloride.
Surfactants: The surfactants used are:
(1) Hexadecyltrimethyl ammonium bromide (HTAB, Chempure) – it is a cationic surfactant having cmc value of 350 mg/l and molecular weight of 364.6. The structure of HTAB is:
CH_3-$(CH_2)_{15}$-$N^+(CH_3)_3Br^-$ (Hexadecyltrimethyl ammonium bromide)
(2) Sodium dodecylbenzene sulfonate (SDBS, chempure) – It is an anionic surfactant having critical micelle concentration (cmc) value of 500 mg/l and molecular weight of 348.5. The structure of SDBS is: CH_3-$(CH_2)_{10}$-CH_2-$C_6H_4SO_3Na^+$ (Sodium dodecylbenzene sulfonate)
Cotton Cloth : For dyeing purpose 100% ready for dyeing cotton cloth is used which is procured from the local market. The specifications of the fabric used are:
Warp Yarn count:1/30 cc Weft Yarn count:1/40 cc EPI/PPI:70/42
Fabric weight: 90 GSM
Effluent: Effluent was generatd in the lab by dyeing cotton cloth by the actual dyeing method.
Dyeing Method: Dye bath was prepared by dissolving 0.8 gram w/w (for 0.1% depth of shade for 80 g fabric) of dye in 2 litre of water. To this added 80 gram of cotton cloth to maintain a M:L ratio of 1:25. Started heating on the hot plate and increased the temperature to 45°C at a rate of 2°C per minute. Then added 3 gram of sodium chloride to the dye bath and further increased the temperature to 85°C.Then added 3 gram more of Sodium chloride and run the bath for 15 minutes. Then added 4 gram of sodium carbonate and run the bath for 20 minutes. Cooled the bath and removed the fabric for washing and neutralization. Fabric was labeled as A and kept for further testing. Drain was collected in a bottle for further use as an effluent.
Procedure:
The procedure involves two steps. The first step is the dye removal step, where dye was removed from the effluent by solvent extraction process using reverse micelle. The second step is the dye and solvent recovery step, where dye is backward extracted to water by using anionic surfactant.
(a) Dye Removal: - 50 ml of the effluent was added to 25 ml of amyl alcohol having 120 mg of cationic (HTAB) surfactant. The aqueous and solvent phases were mixed using a mechanical stirrer (Universal Motor) at a fixed rpm of 4000 for two minutes. The two-phase dispersion was transferred to a separating funnel to separate the aqueous and solvent phases by gravity. This resulted in the formation of two clear liquid phases in one hour: the solvent phase containing the dye encapsulated in the reverse micelle and the clear aqueous phase. The samples were collected from the aqueous phase and analysed in UV spectrophotometer (Analytik Jena Specord 200) to determine the amount of dye separated, suspended solids and total dissolved solids.

(b) Recovery of Dye and Solvent: - The experiments on backward transfer were conducted using process similar to forward extraction. To the 25 ml of the solvent phase containing the extracted dye was added 50 ml of fresh aqueous phase containing 550 mg of anionic surfactant (SDBS). The aqueous and solvent phases were mixed using a mechanical stirrer (Universal Motor) at a fixed rpm of 4000 for two minutes. The two-phase dispersion was transferred to a separating funnel to separate the aqueous and solvent phases by gravity. This resulted in the formation of two clear liquid phases in one hour: an aqueous phase containing dye and a clear solvent phase. The aqueous phase was analysed using UV spectrophotometer (Analytik Jena Specord 200) to quantify the dye recovered.

Colour Measurement: All colour measurements of solutions were carried out with UV spectrophotometer (Analytik Jena Specord 200) operating in the visible range in absorbance mode. Absorbance values were recorded at the wave length for maximum absorbance (λ_{max}) corresponding to each dye.

% Dye Recovery: It is calculated by the following formula:

$$\% \text{ Dye Recovery} = \frac{Ab_2}{Ab_1} \times 100$$

Ab_1 = Absorbance of effluent originally, Ab_2 = Absorbance after recovery of dye. The conc. of the dye bath was determined from the linear graph of dye conc. vs. absorbance.

Re-use of recovered dye- Recovered dye bath was make up into two different concentrations by adding fresh dye.

1. Make-up of concentration upto the initial concentration of native dye bath. Fabric was dyed in the bath and labeled as Fabric B.
2. Make up of concentration 10% more than the initial concentration of native dye bath. Fabric was dyed in the bath and labeled as fabric C.

Physical Testing of Fabric : Following properties of the fabrics are tested using standard test methods of AATCC and ASTM.

Shade : Shade values refers to the colour coordinates, K/S value and dE value. Colour coordinates are l values (lighter or darker), a values (redder or greener) and b values (yellower or bluer). A positive value of l,a and b means lighter , redder and yellower and a negative value means darker , greener and bluer respectively. K/S is the absorbance/scattering value and dE is the value of total colour difference between two fabrics which is calculated by the formula:

$$dE = \sqrt{dl^2+da^2+db^2}$$

$$K/S = (1-R)^2 / 2R$$

All the values of shade of fabric are analysed by Data Colour Instrument (datacolour 600)

Colourfastness to washing: The test is done on textile fabrics which are expected to withstand frequent launderings. It is done by test method no. AATCC 61 2A.

Colourfastness to Water: This test method is designed to measure the resistance to water of dyed textiles. It is done by test method no. AATCC 107.

Colourfastness to Perspiration: The test method is used to determine the fastness of coloured textiles to the effects of acid perspiration. It is done by test method no. AATCC 15.

Colourfastness to Rubbing: The test method is designed to determine the amount of colour transferred from the surface of coloured textile materials to other surfaces by rubbing. It is done by test method no.AATCC 8. Fastness results are reported on the basis of AATCC grey scales of 1to5 grade. Grade refers to the stain visible on white piece of fabric as:

Grade 5	Excellent	No Change
Grade 4	Good	Slight change
Grade 3	Fair	Noticeable change
Grade 2	Poor	Considerable change
Grade 1	Very poor	Much Change

Tear Strength: This test covers the determination of the force required to propagate a single-rip tear starting from a cut in a fabric and using a falling pendulum type apparatus. It is done by test method no. ASTM D 1423. Results reported are average of five readings in each case.

RESULTS AND DISCUSSION

The recovery of dye from the effluent is found to be 85% of the unreacted dye discharged into effluent. This removal of dye from the effluent to solvent layer is due to the formation of reverse micelle of surfactant (HTAB) in organic layer with entrapment of dye anion and the backward recovery of dye from the solvent layer to the fresh aqueous layer in the presence of anionic surfactant (SDBS) is due to the breaking of reverse micelles of HTAB in solvent layer by counterionic SDBS. Subsequently, encapsulated dye gets released and passes into aqueous layer due to its ionic nature.

Suspended Solids and Total Dissolved Solids – It is clear from the table that suspended solids
Physical & Chemical Properties of the Fabric: To confirm the nature and usability of recovered Reactive Blue 171 dye, following properties of the fabrics are compared:

(a) **Shade:** From the Table-1, we can see that the fabric B is 9.5% lighter than the fabric A and strength of fabric C is almost equal to fabric A. It is seen from the values of colour coordinates that the fabric B is lighter, redder and yellower and has a total colour difference of 3.6 but fabric C has almost similar colour coordinates as that of fabric A and total colour difference of 1.36 which is well below the universal norms of textile industries. From the Fig-1 & Fig-2 it is observed that the tanctorial properties of all the three fabrics are same, which is confirmed by the similar curves of K/S values but the strength of fabric B is lesser as confirmed by the K/S value of fabric A, B & C which is 2.0, 1.5 & 1.9. Similar tanctorial properties confirm that the chromophore of the recovered dye has not undergone any change and still it has almost similar colour value as in the native form.
(b) **Colourfastness to washing**: It is clear from the Table-2, Fig-3, Fig-4 and Fig-5 that changes in shade and staining on all the six fibres is grade 4 or better on a scale of grade 1 to 5 in all the three fabrics.
(c) **Coloufastness to water:** We can see from the Table-2, Fig-6, Fig-7 and Fig-8 that staining on the cotton fibre is more i.e 3 in all the fabrics but it is in acceptable range on all other five fibres.
(d) **Coloufastness to perspiration:** The results obtained are similar in all the fabrics which can be seen from the Table-2 & Fig-9, Fig-10 & Fig-11.
(e) **Colourfastness to rubbing:** From the Table-2 it can be seen that the results of rubbing on dry & wet are comparable in all the three fabrics. From the colourfastness properties, we can conclude that recovered dye have equally good affinity for the fabric as the native dyes. This indicates that the auxochrome of the recovered dye has similar structure as that in the native dye.
(f) **Tear Strength:** Values of tear strength in the table-2 confirms that the recovered dyes have no negative impact on the strength properties of substrate.

CONCLUSION

The great affinity of the reactive (Triazine) dyes for water results the large amount of dye remains unreacted and discharged into the effluent. This increase, the cost of dyeing and ultimately has a great impact on the pockets of consumers. The present work has given very encouraging results and we have seen that almost complete recovery and re-use of the unraected dye is possible by solvent extraction process. From the results we have seen that

1. Re-use of recovered dye is possible by the suitable make-up of dye bath which is confirmed by the similar colourfastness properties of the three fabrics.
2. By suitable make-up of the dye bath , we can obtained the similar shade in terms of colour coordinates and K/S value and this way we can save upto 20%(approx) of the dye.
3. Surfactant and solvent recovered at the end of process can be recycled which is very important for the economic aspect of process.
4. By the complete removal of dye from the effluent, resulted clean water can be re-used or released which maintains a green earth and pollution free environment.

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Table-1: Colour Cordinates of Fabric A, B & C

CI name of Dye	l	a	b	dE	Strength (%)
Fabric A	56.01	-6.68	-14.67	Std.	100
Fabric B	59.01	-5.21	-13.12	3.60	90.5
Fabric C	56.13	-5.88	-13.41	1.36	98.9

Table-2: Colourfastness Properties of Fabric Dyed with RB 171

Properties	Change in Shade	Staining on Fibre					
		Cellulose Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
Colourfastness to Washing , Fabric A	4	4	3	3-4	3-4	3-4	3
Colourfastness to Washing , Fabric B	4	4	3-4	4	4	4	3-4
Colourfastness to Washing , Fabric C	4	4	3	3-4	4	4	3-4
Colourfastness to Water, Fabric A	4	4	3	3-4	4	4	3
Colourfastness to Water, Fabric B	4	4	3-4	4	4	4	3-4
Colourfastness to Water, Fabric C	4	4	3-4	3-4	4	4	3-4
Colourfastness to Perspiration, Fabric A	4	4	3-4	4	4	4	3-4
Colourfastness to Perspiration, Fabric B	4	4	3-4	3-4	4	4	3-4
Colourfastness to Perspiration, Fabric C	4	4	4	4	4	4	3-4
Colourfastness to Rubbing, Fabric A	4	Dry/Wet 4/4					
Colourfastness to Rubbing, Fabric B	4	Dry/Wet 4/4					
Colourfastness to Rubbing, Fabric C	4	Dry/Wet 4/4					

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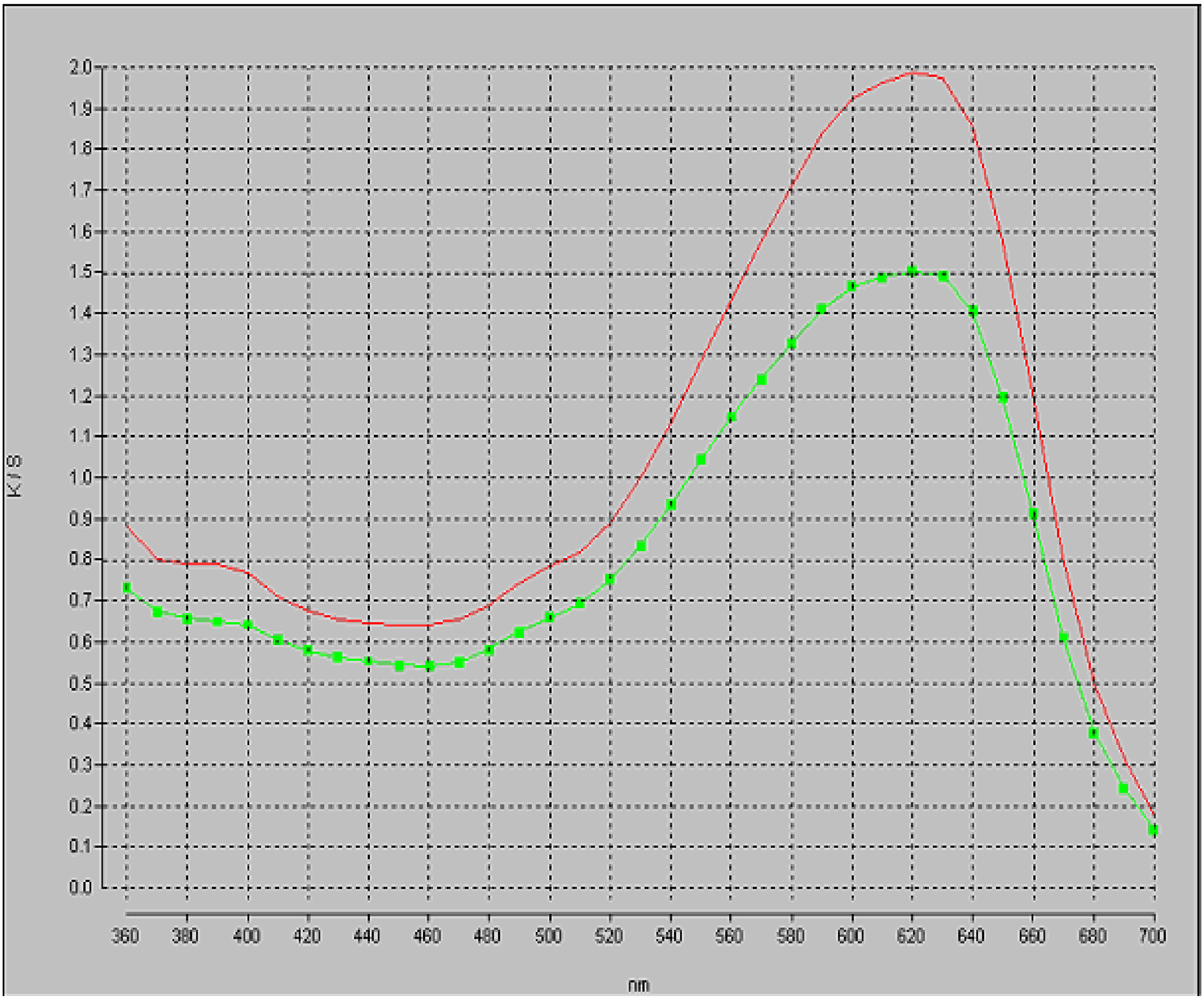

Fig.-1: Comparative K/S curves of Fabric A (Solid Red Line) & Fabric B (Dotted Green Line)

Fig.-2: Original Multifibre

Fig.-3: Colourfastness to washing(Fabric A)

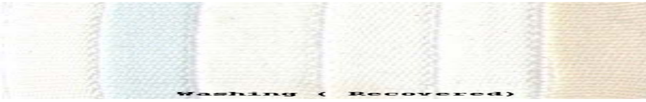

Fig.-4: Coloufastness to washing(Fabric B)

Fig.-5:Coloufastness to washing(Fabric C)

Fig.-6: Colourfastness to water(Fabric A)

Fig.-7: Coloufastness to water(Fabric B)

Fig.-8: Coloufastness to water(Fabric C)

Original Multifibre Strip

Fig.-9: Colourfastness to perspiration(Fabric A)

Fig.-10: Coloufastness to perspiration(Fabric B)

Fig.-11: Coloufastness to perspiration(Fabric C)

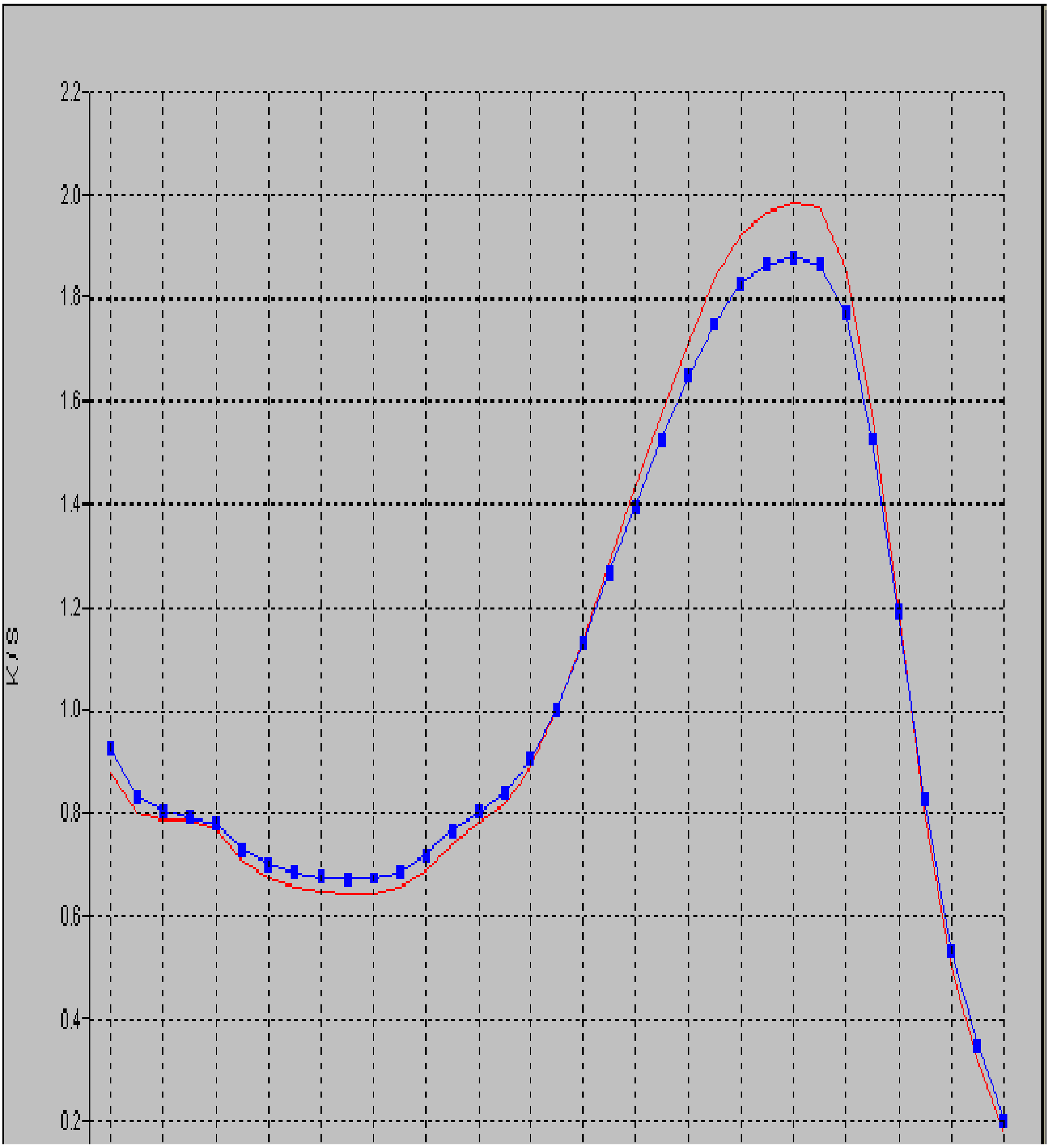

Fig.-12: Comparative K/S curves of Fabric A (Solid Red Line) & Fabric C (Dotted Blue Line)

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