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Reduction Process of Vat Dye on Cotton Fabric Assisted by Ferrous Sulphate

P. SANTHI[1,*] and J. JEYAKODI MOSES[2]

[1]Department of Chemistry, Muthayammal Engineering College, Rasipuram, Namakkal-637 408, India
[2]Department of Chemistry, PSG College of Technology, Coimbatore-641 004, India

*Corresponding author: E-mail: santhiperiasamy@gmail.com; jj_moses2k2@yahoo.co.in

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Among all the dyestuff, vat dyes are one of the most popular dyes used on textiles particularly on cotton textile materials. However, vat dye is originally insoluble in water. In conventional vat dyeing process, the vat dye is dissolved using sodium hydrosulphite (hydrose) which is a powerful reducing agent followed by solubilizing with sodium hydroxide. This process creates high pollution problem. Hence, an attempt has been made to see the effect of other reducing agents like ferrous sulphate (2 % owm) and combination of ferrous sulphate with hydrose in various proportions as reducing agent. The results of these reducing agents were compared with those of the vat dyeing with hydrose (2 % owm), in terms of reduction potential of vat dye bath, depth of shade of the fabric and FTIR analysis of vat dye and vat dyed cotton fabric.

Key Words: Vat dyes, Reducing agent, Ferrous sulphate, Reduction potential, Depth of shade, FTIR.

INTRODUCTION

Among the cellulose polymeric variety, cotton is considered as one of the important textile fibers. It is used worldwide and its consumption is increasing day by day, due to the comfort values. Cotton can be dyed with many natural colours extracted from natural sources and synthetic dyes such as direct dye, reactive dye, sulphur dye, vat dye, *etc*[1]. In the colouration of cellulose fibers, vat dyes (including indigo) still represent a relatively large part of the dyestuff market; among them about 120000 tons of vat dyes are being used annually[2]. Vat dyes are practically insoluble in water, but can be converted into water soluble form called leuco dye by reduction with a strong reducing agent like hydrose and solubilizing agent sodium hydroxide. The reduced dyestuff penetrates into the fiber and it is reoxidized on the fiber back to the insoluble form, which remains fixed in the fabric[3]. The use of sodium hydrosulphite (hydrose) is being criticized for the formation of non-environment friendly decomposition products such as sulphite, sulphate, thiosulphate and toxic sulphur[4]. Therefore many attempts are being made to create alternate for the sodium hydrosulphite that cause less pollution.

Vat process using reducing agents other than hydrose: Many previous investigations were carried out to focus on the replacement of sodium hydrosulphite by other reducing agents like organic reducing agent α-hydroxy ketone[5], sodium borohydride[6], hydroxy alkyl sulphonate, thiourea[7], complex ferrous hydroxide with tartaric acid, gluconic acid, citric acid[8], glucose and dextranil[9], natural ingredients namely fenugreek, jaggery, lime and soda ash[10] and glucose[11].

Other alternate reduction technolologies like, reduction using ultrasonic reactor[12], catalytic hydrogenation using raney nickel[13], catalytic hydrogenation using Pd catalyst[14], electrolytic method[15], electrochemical techniques[16] like direct electrochemical reduction[17,18] and indirect electrochemical reduction[19,20] were also studied.

After several decades of research and development there is still no commercial reducing technology, including electrochemical processes available today that can replace sodium hydrosulphite in all areas of vat dye application. Until now, however, the electrochemical reactor performance is too low for the complete reduction of a stock solution in case of continuous dyeing. As a consequence, the operating costs, return on investment and dyeing efficiency are not attractive for an application in the dyestuff industry[21].

The present study is carried out to see the effect of ferrous sulphate and its combination with hydrose as reducing agent on textile material. The results of dyeing using ferrous sulphate (2 % owm) and combination of ferrous sulphate with hydrose such as ferrous sulphate (1.5 % owm) + hydrose (0.5 % owm), ferrous sulphate (1.0 % owm) + hydrose (1.0 % owm), ferrous sulphate (0.5 % owm) + hydrose (1.5 % owm), as reducing agent have been compared with those of the conventional dyeing with hydrose (2.0 % owm), in terms reduction potential of vat dye bath, depth of shade of the fabric and FTIR analysis for functional groups present in vat dye and vat dyed fabric.

EXPERIMENTAL

Sodium hydrosulphite (AR), ferrous sulphate (AR) and their combinations were used as reducing agents. Sodium hydroxide (AR), turkey red oil (AR), sodium carbonate (AR), hydrogen peroxide (AR) and soap powder were used as other main chemicals and auxiliaries. The dye selected was commercial Navinon Jade green FFBU/C commonly called as Jade green XBN (Vat Green 1, C.I.59825).

Textile fabric: 100 % cotton poplin fabric was used with following particulars: Ends/inch: 132, picks/inch: 70, warp count: 37 s, weft count: 41 s.

Pretreatment given to the fabric: The grey cotton fabric was initially pretreated by standard scouring treatment using sodium hydroxide and bleaching treatment using hydrogen peroxide as per the standard method[22].

Dyeing of pretreated cotton fabric using vat dyes: Conventional vat dyeing was carried out on pretreated cotton fabric using hydrose as a reducing agent[12]. Vat dyeing was carried out on pretreated cotton fabric similar to conventional one but with ferrous sulphate and its combination with hydrose, in different compositions as alternate reducing agents by the following recipe.

Ferrous sulphate and its combination with hydrose as reducing agent

Vat dye (Jadegreen XBN)-2.0 % (owm)		Vat dye (Jadegreen XBN)-2.0 % (owm)	
T.R.O	2.0 % (owm)	T.R.O.	2.0 % (owm)
$FeSO_4$	2.0 % (owm)	$FeSO_4$	0.5 % (owm)
NaOH	2.0 % (owm)	Hydrose	1.5 % (owm)
M.L.R.	1:30	NaOH	2.0 % (owm)
Temp. (°C)	60	M.L.R	1:30
Time (min)	45	Temp. (°C)	60
		Time (min)	45

Vat dye (Jadegreen XBN)-2.0 % (owm)		Vat dye (Jadegreen XBN)-2.0 % (owm)	
T.R.O.	2.0 % (owm)	T.R.O.	2.0 % (owm)
$FeSO_4$	1.0 % (owm)	$FeSO_4$	1.5 % (owm)
Hydrose	1.0 % (owm)	Hydrose	0.5 % (owm)
NaOH	2.0 % (owm)	NaOH	2.0 % (o
M.L.R.	1:30	M.L.R.	1:30
Temp. (°C)	60	Temp. (°C)	60
Time (min)	45	Time (min)	45

Evaluation of reduction potential of vat dye bath: The reduction potential of vat dye bath with various reducing agents such as ferrous sulphate and its combination with hydrose and conventional reducing agent (hydrose) were determined by using digital potentiometer (DP001, Pico make) at different time intervals[9,23].

Depth of the shade (k/s value) on the vat dyed cotton fabric: The k/s value at 630 nm was determined by Jaypak spectrophotometer. The vat dyed samples using various reducing agents like ferrous sulphate and its combination with hydrose and conventional reducing agent (hydrose), were folded 4 times and after calibration of spectrophotometer, were exposed to two times (front and back) and the mean value was taken[24].

FTIR analysis of vat dye and vat dyed cotton fabric: Fourier transfer infra-red spectrophotometer (FTIR 8400's Shimadzu, Japan) was used to analyze the functional group of the dye and dyed samples using various reducing agents like ferrous sulphate and its combination with hydrose and conventional reducing agent which in turn reveal about the colour absorption properties of the organic dye molecules. Data with respect to the functional groups, aromatic and achromatic ring chains indicated the presence of structural groups in the dye molecules[25].

RESULTS AND DISCUSSION

Reduction potential of vat dye bath using ferrous sulphate and its combination with hydrose as reducing agent: The reduction potentials of vat dye bath using ferrous sulphate and its combination such as ferrous sulphate 2.0 % owm, ferrous sulphate 1.5 % owm + hydrose 0.5 % owm, ferrous sulphate 1.0 % owm + hydrose 1.0 % owm, ferrous sulphate 0.5 % owm + hydrose 1.5 % owm and hydrose 2.0 % owm are given in Table-1.

The reduction potential is very high in the vat dye bath using hydrose 2.0 % owm as reducing agent compared with its combination with ferrous sulphate. The reduction potential of vat dye bath using ferrous sulphate 2.0 % owm, ferrous sulphate 1.5 % owm + hydrose 0.5 % owm, ferrous sulphate 1.0 % owm + hydrose 1.0 % owm, ferrous sulphate 0.5 % owm + hydrose 1.5 % owm and hydrose 2.0 % owm decreases steadily as the dyeing time increases.

The reduction potential of ferrous sulphate combination with hydrose gives uniform trend throughout the completion of vat dyeing. Among the ferrous sulphate combination with hydrose, ferrous sulphate 1.0 % owm + hydrose 1.0 % owm combination shows good reduction potential. The good and uniform reduction potentials for ferrous sulphate combinations with hydrose as reducing agents are due to the effective reduction capacity of both ferrous sulphate and hydrose in the vat dye bath.

Depth of shade of cotton fabric dyed with vat dye using ferrous sulphate and its combination with hydrose as reducing agent: Depth of shade of cotton fabric dyed with

TABLE-1
REDUCTION POTENTIAL OF VAT DYE BATH USING FERROUS SULPHATE AND ITS COMBINATION WITH HYDROSE AS REDUCING AGENT

Reducing agents used during vat dyeing on cotton fabric	Reduction potential of the vat dye bath (volts)↓						
Time (min)→	0	5	10	15	20	25	30
$FeSO_4$ 2.0 % owm	-0.370	-0.328	-0.279	-0.253	-0.253	-0.248	-0.245
$FeSO_4$1.5 % owm + hydrose 0.5 % owm	-0.439	-0.409	-0.403	-0.381	-0.342	-0.340	-0.329
$FeSO_4$ 1.0 % owm + hydrose 1.0 % owm	-0.643	-0.387	-0.377	-0.360	-0.346	-0.344	-0.315
$FeSO_4$ 0.5 % owm + hydrose 1.5 % owm	-0.537	-0.455	-0.444	-0.412	-0.405	-0.393	-0.360
Hydrose 2.0 % owm	-0.835	-0.824	-0.805	-0.778	-0.723	-0.542	-0.357

vat dye using ferrous sulphate and its combination such as ferrous sulphate 2.0 % owm, ferrous sulphate 1.5 % owm + hydrose 0.5 % owm, ferrous sulphate 1.0 % owm + hydrose 1.0 % owm, ferrous sulphate 0.5 % owm + hydrose 1.5 % owm and hydrose 2.0 % owm is given in Table-2.

TABLE-2
DEPTH OF SHADE ON COTTON FABRIC DYED WITH VAT DYE USING FERROUS SULPHATE AND ITS COMBINATION WITH HYDROSE AS REDUCING AGENT

Reducing agents used during vat dyeing on cotton fabric	k/s at 630 nm (λ_{max})	Strength (%)	ΔE
$FeSO_4$ 2.0 % owm	1.421	55.67	22.251
$FeSO_4$ 1.5 % owm + hydrose 0.5 % owm	2.409	94.44	2.333
$FeSO_4$ 1.0 % owm + hydrose 1.0 % owm	2.530	99.17	1.728
$FeSO_4$ 0.5 % owm + hydrose 1.5 % owm	2.309	90.52	1.919
Hydrose 2.0 % owm	2.551	100.00	0.000

From the Table-2, the k/s value at λ_{max} 630 nm for dyed fabric using ferrous sulphate 1.0 % owm + hydrose 1.0 % owm is 2.530 (strength 99.17 %), for dyed fabric using ferrous sulphate 1.5 % owm + hydrose 0.5 % owm the k/s value is 2.409 (strength 94.44 %) and for dyed fabric using ferrous sulphate 0.5 % owm + hydrose 1.5 % owm the k/s value is 2.309 (strength 90.52 %) compared with the vat dyed fabric using ferrous sulphate 2.0 % owm. Since the reduction potential of ferrous sulphate combination with hydrose gives uniform trend throughout the completion of vat dyeing, the effect of dyeing is also uniform accordingly. Among the various ferrous sulphate combinations with hydrose, the depth of the shade of the cotton fabric dyed with vat dye using ferrous sulphate 1.0 % owm + hydrose 1.0 % owm (strength 99.17 %) shows similar effect on the depth of shade as that of the dyed fabric using hydrose 2.0 % owm (strength 100 %)[26].

FTIR study of vat dye and vat dyed cotton fabric: The IR spectral analysis showed that the main functional groups present in the vat dye (Jade green XBN) are non-bonded hydroxyl group (OH) (3700-3600), hydrogen bonded -OH- stretch (3300-3200), terminal aldehyde -CH- stretch (2800-2700), thiols -SH- stretch (2600-2500), -OH- stretch of carboxylic acid (2400-2300), transition metal carbonyl group (2000-1800), carbonyl group (1800-1700), aromatic primary amine -CN- stretch (1300-1200) and secondary amine -CN- stretch (1200-1100)[25].

The FTIR spectral analysis of cotton fabric dyed with vat dye using different reducing agents such as $FeSO_4$ 2.0 % owm, $FeSO_4$ 1.5 % owm + hydrose 0.5 % owm, $FeSO_4$ 1.0 % owm + hydrose 1.0 % owm, $FeSO_4$ 0.5 % owm + hydrose 1.5 % owm and hydrose 2.0% owm, were also performed. The functional groups present[25] in the cotton fabric dyed with vat dye using ferrous sulphate 2.0 % owm and representative combination ferrous sulphate 1.0 % owm + hydrose 1.0 % owm and hydrose 2.0 % owm, are compared with the functional groups of original vat dye (Jadegreen XBN) and the following findings were obtained.

(A) Between original vat dye and cotton fabric dyed with vat dye using $FeSO_4$ 2.0 % owm: Non bonded hydroxyl group (-OH-) is available both in original vat dye and fabric dyed with vat dye using ferrous sulphate 2.0 % owm. Hydroxyl group (hydrogen bonded -OH- stretch) is present in both the cases. Thiols (-SH-) stretch is present in original vat dye but absent in vat dyed fabric. -OH- stretch of carboxylic acid is available in original vat dye but absent in vat dyed fabric. Transition metal carbonyl group and carbonyl group are present in original dye, but both are absent in vat dyed fabric. The primary amine -CN- stretch is present in both the cases, however secondary amine -CN-stretch is absent in vat dyed fabric using ferrous sulphate 2.0 % owm.

(B) Between original vat dye and cotton fabric dyed with vat dye using hydrose 1.0 % owm + $FeSO_4$ 1.0 % owm: Non bonded hydroxyl group (-OH-) is present in both the cases. Hydroxyl group (hydrogen bonded -OH- stretch) is present in the vat dye but absent in the vat dyed fabric using hydrose 1.0 % owm + $FeSO_4$ 1.0 % owm. Thiols (-SH-) stretch is present in both the cases. -OH- stretch of carboxylic acid is available in original vat dye but absent in vat dyed fabric. Both transition metal carbonyl group and carbonyl group are present in original dye, however absent in vat dyed fabric. In the vat dyed cotton fabric the secondary amine -CN- stretch is present, however primary amine -CN- stretch is absent.

(C) Between original vat dye and cotton fabric dyed with vat dye using hydrose 2.0 % owm: Non-bonded hydroxyl group (-OH-) is available both in original vat dye and fabric dyed with vat dye using hydrose 2.0 % owm. However, hydrogen bonded -OH- stretch is not present in the vat dyed fabric using hydrose. Thiols (-SH-) stretch is present in both the cases. -OH- stretch of carboxylic acid is also present in both the cases. Transition metal carbonyl group and carbonyl group are present in original dye, but both are absent in vat dyed fabric using hydrose 2.0 % owm. The amine -CN- stretch is present in both original vat dye and vat dyed cotton fabric using hydrose 2.0 % owm.

Conclusion

The reduction potential of the reducing agents used for the dissolution of vat dye is good for ferrous sulphate with hydrose combinations. However, ferrous sulphate 1.0 % owm + hydrose 1.0 % owm combination as reducing agent gives uniform reduction potential and this is changed evenly throughout the dyeing period. Because of this, there is a good dyeing effect on the cotton fabric.

The depth of shade of vat dyed cotton fabric obtained using various reducing agents such as hydrose, ferrous sulphate and their combination is varied for each and every reducing agent. The ferrous sulphate + hydrose combination gives good average depth of shade. This is highly significant for ferrous sulphate 1.0 % owm + hydrose 1.0 % owm combined reducing agent, similar to that obtained for hydrose 2.0 % owm. The effective reducing power of ferrous sulphate 1.0 % owm + hydrose 1.0 % owm combination as reducing agent gives more depth of shade on vat dyed cotton fabric.

It is observed from the FTIR analysis of vat dye that, there are good number of hydroxyl groups, thiol group and carbonyl group. These groups are considered to be responsible for dyeing on cotton fabric through strong linkage. The application of reducing agents in presence of alkali reduces these groups so as to convert the dye into water soluble. After dyeing, these groups are once again oxidized to the original form and linked to the cotton fabric. The overall good dyeing effect given by $FeSO_4$ 1.0 % owm + hydrose 1.0 % owm combination is also supported by FTIR analysis, as the functional groups present in the vat dye is effectively involved in the dyeing on cotton fabric. The commercial cost of ferrous sulphate is similar to that of hydrose and hence the process cost could be affordable to the textile industries.

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