Oriental Journal of Chemistry Vol. **24**(1), 213-222 (2008)

A study of Vat dyeing on cotton fabric assisted by zinc as reducing agent

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(Received: February 16, 2008; Accepted: April 07, 2008)

ABSTRACT

Vat dyes are one of the most popular dyes used on textiles particularly on cotton textile materials. This is because of its excellent fastness properties as well as other desired characters needed on cotton garments. 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 solubilising with sodium hydroxide. This process creates very high pollution problem. In this study, an attempt has been made to see the effect of zinc metal powder (2% owm) and the combination of zinc metal powder (1.5% owm) with hydrose (0.5% owm) as reducing agent. The results of these reducing agents were compared with those of the conventional vat dyeing with hydrose (2% owm), in terms of different parameters such as strength of the fabric, rubbing fastness, washing fastness, light fastness and effluent parameters.

Key words: Vat dyes, reducing agent, zinc metal powder, hydrose, fastness and effluent parameters, on weight of material (owm).

INTRODUCTION

Vat dye is the most popular among dye classes used for coloration of cotton, particularly, when high fastness standards are required to light, washing and chlorine bleaching[1].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 solubilising agent sodium hydroxide. The reduced dyestuff penetrates into the fiber and it is reoxidised on the fiber back to the insoluble form, which remains fixed in the fabric [2, 3]. The use of sodium hydrosulphite 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.

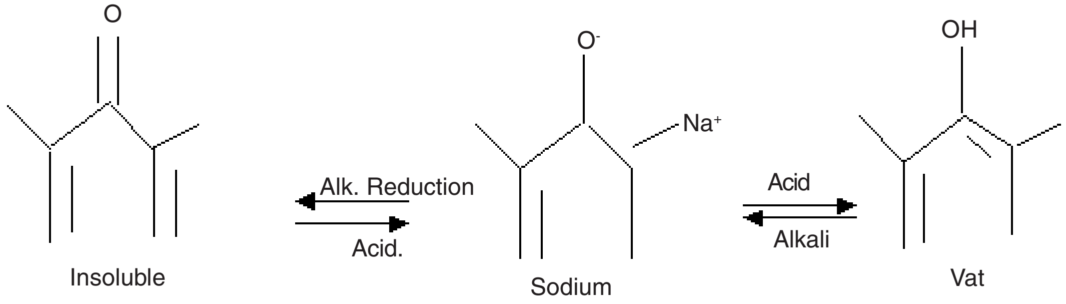
Hydrose as reducing agent

The most commonly employed reducing agent in vat dyeing is sodium hydrosulphite ($Na_2S_2O_4$), commonly known as hydrose. This compound is not stable in strong alkaline conditions in the absence of air. Alkaline solution of hydrose has a certain degree of reduction potential and thus, can reduce all commercial vat dyes to their water soluble forms, economically and quickly, without any chance of over reduction. As the leuco sodium salt of the vat dye results salt of strong alkali and weak acid, the sodium salt has the natural tendency to exist in enol form. To ensure complete conversion sodium hydroxide is added prior to hydrose addition. Since hydrose reacts with aqueous as well as atmospheric oxygen, it leads to the formation of a number of acidic compounds which have to be neutralized by sodium hydroxide[2].

$$2Na_2S_2O_4 + O_2 + 4NaOH \rightarrow 4Na_2SO_3 + 2H_2O$$

This is another reason why sodium hydroxide has to be added in excess to avoid the dye bath to become acidic due to the precipitation of leuco acid compound. The following chemical reaction depicts the general transformation, which take place at the time of dyeing.

To avoid oxidation of the leuco vat, a large excess of sodium hydrosulphite is used in conventional vat dyeing. The excess amount is at least five times the theoretical amount, which might lead to the problems like over reduction, hydrolysis and crystallization of vat dyes, especially at higher temperatures.



Vat process using reducing agents other than hydrose

Previous investigations were focused on the replacement of sodium hydrosulphite by an organic reducing agents like α-hydroxy ketones[5,6] which meets the requirements in terms of reductive efficiency and biodegradability. However, such compounds are expensive and their use is restricted to closed systems due to the formation of strong smelling of condensation products in an alkaline solution. Some other reducing compounds such as hydroxyalkyl sulphonate, thiourea, have also been recommended [7, 8]. The relatively low sulphur content and lower equivalent mass than that of hydrosulphite lead to lower amounts of sulphur based salt load in the waste water. However, in these cases too, it is not possible to dispense with sulphur based problems totally.

Ferrous hydroxide being a strong reducing agent in alkaline medium has also been explored for reducing organic dye stuffs. The reducing effect of ferrous hydroxide increases with increase in pH. However, ferrous hydroxide is poorly soluble in an alkaline solution and gets precipitated .It has to be complexed in order to hold it in solution[9]. A stable complex with good reducing power is obtained with weaker ligand, such as gluconic acid. Regarding eco-friendliness, gluconic acid can be eliminated in the sewage tank through neutralization with alkali. Free ferrous hydroxide can be aerated and converted to ferric hydroxide which acts as a flocculent and brings down waste water load. Tartaric acid has also been tried as a ligand by Chakraborty [10] for complexing ferrous hydroxide in the presence of sodium hydroxide for reduction and dyeing of cotton with indigo and other vat dyes at room temperature.

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. Unfortunately, it is impossible to use catalytic hydrogenation technique directly in the dye house due to high explosion and fire risk [11]. Therefore the dye suppliers offer concentrated pre reduced leuco indigo solutions for shipping to the dye house. However, the eco efficiency is negatively affected by high water content of the product. Therefore, still the method of choice would be an electrochemical reduction stock vatting technique. In recent times, various electrochemical reducing methods have been investigated, such as indirect electrochemical reduction employing a redox mediator, the direct electrochemical reduction of indigo via the indigo radical, the electro catalytic hydrogenation route and the direct electrochemical reduction on graphite. All these methods offer tremendous environmental and economic benefits, since they minimise the consumption of chemicals as well as effluent load. 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[12].

The present study is carried out to see the effect of zinc metal powder as reducing agent on textile material. The results of dyeing using zinc metal powder (2% owm) and zinc metal powder (1.5% owm) combined with hydrose (0.5% owm) as reducing agent have been compared with those of the conventional dyeing with hydrose, in terms of tensile strength, rubbing fastness, washing fastness, light fastness and effluent parameters.

EXPERIMENTAL

Materials

Substrate

100% cotton poplin fabric was used with following particulars:

Ends/Inch	:	132
Picks/Inch	:	70
Warp Count	:	37s
Weft Count	:	41s

Chemicals, auxiliaries and dye

Sodium hydrosulphite (AR) and zinc metal powder (AR) were used as reducing agents. Sodium hydroxide (AR), turkey red oil (LR), sodium carbonate (AR), and Soap powder (LR) were used as other main chemicals and auxiliaries. The dye selected was commercial Navinon Jade green FFBU/C (Jade green XBN).

Methods

Pretreatment given to the fabric

The grey cotton fabric was initially scoured and bleached using the following recipe;

Scouring (Recipe)			Bleaching (Recipe)		
Sodium hydroxide	-	3% (owm)	Sodium hypochlorite	-	2 g/L av. Cl_2
Sodium carbonate	-	2% (owm)	Sodium carbonate	-	0.5% (owm)
Turkey red oil	-	1% (owm)	Material Liquor Ratio	-	1:25
Material Liquor Ratio	-	1:25	Temperature	-	30°C
Temperature	-	95°C	Time	-	90 minutes
Time	-	4hours			

Dyeing procedure for vat dyes

1. Conventional Dyeing was carried out using sodium hydrosulphite as reducing agent[13].
2. Dyeing was carried out similar to the conventional one but with zinc metal powder as reducing agent and zinc combined with hydrose by the following recipe;

Vat Dye (Navinon JadegreenXBN) – 2% (owm)

T.R.O	-	2% (owm)
Zinc	-	2% (owm)
NaOH	-	2% (owm)
M.L.R	-	1: 30
Temp	-	50°C-60°C
Time	-	45 minutes

Vat Dye (Navinon JadegreenXBN) – 2% (owm)

T.R.O	-	2% (owm)
Zinc	-	1.5% (owm) + hydrose 0.5% (owm)
NaOH	-	2% (owm)
M.L.R	-	1: 30
Temp	-	50°C-60°C
Time	-	45 minutes

Fabric strength

The dyed fabrics were tested for its strength in warp and weft way using MAG Electronic Tensile Strength Tester with the specimen size of 25mm ×150mm by random sampling method.

Colour fastness to rubbing, washing and light

AATCC standardized crock meter was used to determine the rubbing fastness under wet and dry condition to asses the colour change and staining property. The dyed samples were washed under condition IIIA of the AATCC Test Method 124-

2001 to determine the colour change effect of fabrics. Light fastness tests were carried out according to AATCC Test Method 16 E-1998. The samples were exposed to 5, 10 AFUs (AATCC Fading Unit) to determine the colour change[14].

Effluent load from dye effluent

The effluent parameters such as TDS, total alkalinity, sulphate ion, sodium ion, COD, BOD and pH are tested from the effluent load of the vat dyed baths.

FTIR analysis

Fourier Transfer Infra-Red Spectrophotometer (FTIR 8400's SHIMADZU, Japan) was used to analyze the functional group of the dye samples which inturn 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.

SEM study

Scanning Electron microscope studies were taken using JEOL6360 microscope made by Japan. It has operated in the range of different wavelength and magnitude dimensions. (2000, 1250,500 %).

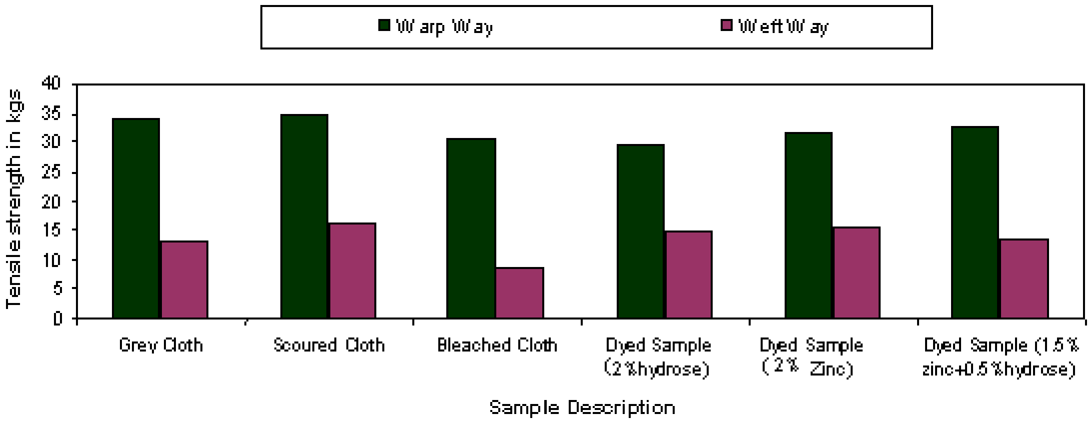
RESULTS AND DISCUSSIONS

Tensile strength of cotton fabric

The tensile strength both in warp direction and in weft direction of cotton fabric in grey form, and after different treatments (scouring, bleaching, and dyeing) is given in Table 1 and shown in Graph 1. There is a substantial reduction in the tensile strength of cotton fabric both in warp

Table 1: Effect of Reducing Agents on Fabric Strength

S. No.	Sample Description	Tensile Strength in Kgs	
		Warp way	Weft way
1.	Grey Cloth	33.99	13.25
2.	Scoured Cloth	34.84	16.21
3.	Bleached Cloth	30.59	8.41
4.	Dyed Sample (2% hydrose)	29.43	14.80
5.	Dyed Sample (2% Zinc)	31.86	15.54
6.	Dyed sample (1.5% Zinc + 0.5% hydrose)	32.52	13.67



Graph 1: Effect of reducing agents on fabric strength

direction and weft direction after bleaching. Due to vat dyeing, the tensile strength of cotton fabric in warp direction is reduced while in weft direction it is increased. The cotton fabric dyed with vat dye using zinc (2% owm) as reducing agent shows good average fabric strength both in warp and weft directions (31.86 Kg and 15.54 Kg respectively) compared with vat dyeing using other form of reducing agents (hydrose 2% owm and zinc 1.5% owm + hydrose 0.5% owm). The tensile strength in warp direction is reduced after dyeing using different form of reducing agents (hydrose 2% owm, zinc 2% owm and zinc 1.5% owm + hydrose 0.5% owm) compared with that of grey cotton fabric (33.99 Kg), while it is increased in weft direction after vat dyeing using different form of reducing agents (hydrose 2% owm, zinc 2% owm and zinc 1.5% owm + hydrose 0.5% owm) compared with that of grey cotton fabric (13.25 Kg).

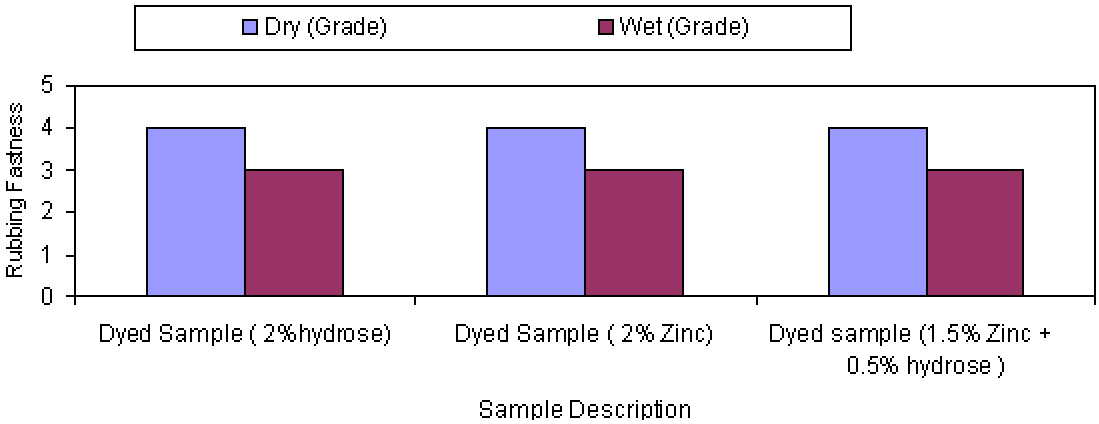
The percent loss in tensile strength of cotton fabric in warp direction after dyeing using the reducing agents hydrose 2% owm, zinc 2% owm and zinc 1.5% owm + hydrose 0.5% owm is 13.4%, 6.3% and 4.3% respectively, while in the weft direction it is in the increasing trend of 11.7%, 17.3% and 3.2% respectively. The average tensile strength both in warp direction and in weft direction in the cotton fabric vat dyeing using reducing agents using hydrose 2% owm, zinc 2% owm and zinc 1.5% owm + hydrose 0.5% owm is 1.7% loss, 11% gain and 1.1% loss respectively.

Rubbing fastness, washing fastness and light fastness of vat dyed cotton fabric

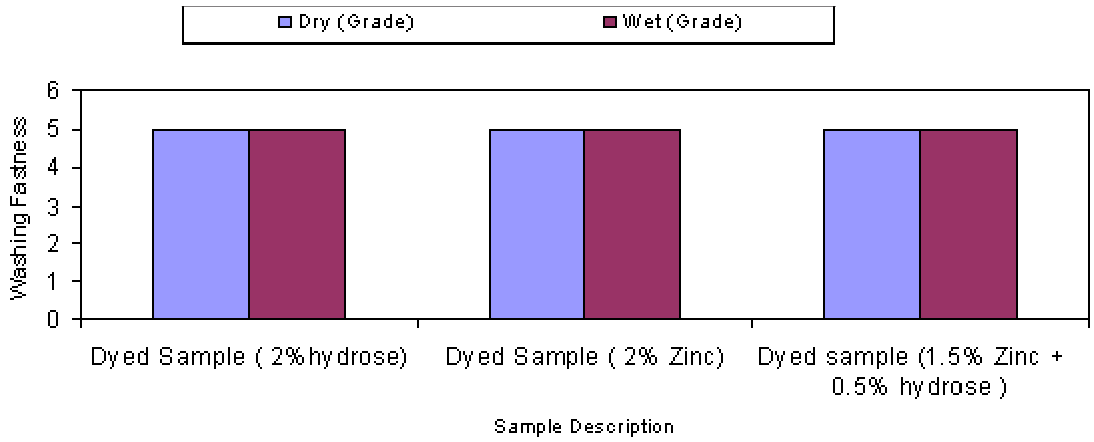
The fastness properties (rubbing fastness, washing fastness and light fastness) of vat dyed cotton fabric using different form of reducing agents (hydrose 2% owm, zinc 2% owm and zinc 1.5% owm

Table 2: Effect of reducing agents on fastness properties

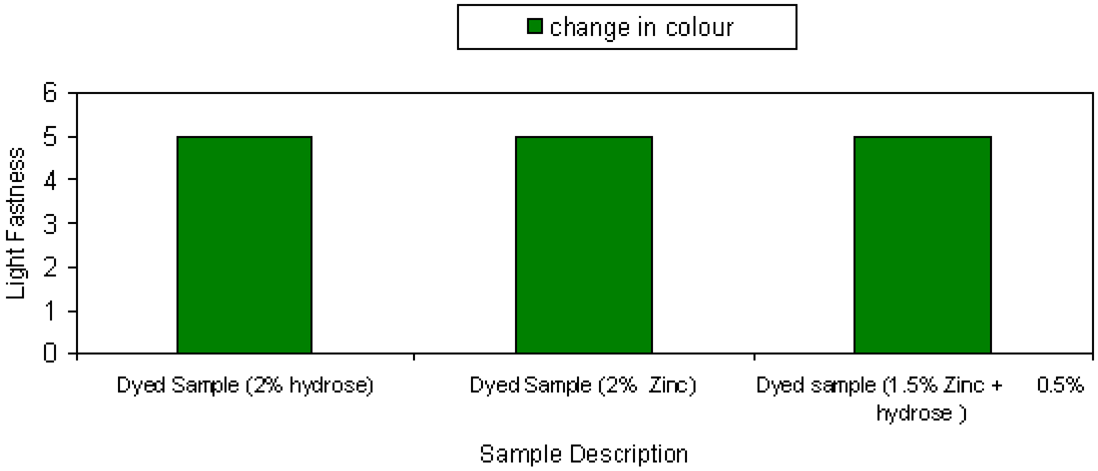
S. No	Sample Description	Fastness Properties				
		Rubbing Fastness		Washing Fastness		Light Fastness
		Dry (grade)	Wet (grade)	Staining	Change in colour	-
1.	Dyed Sample (2% hydrose)	4	3-2	5-4	5	5
2.	Dyed Sample (2% Zinc)	4	3-2	5-4	5	5
3.	Dyed sample (1.5% Zinc + 0.5% hydrose)	4	3	5	5	5



Graph 2: Effect of reducing agents on rubbing fastness



Graph 2a: Effect of reducing agents on washing fastness



Graph 2b: Effect of reducing agents on light fastness

Table 3: Analysis of effluent load

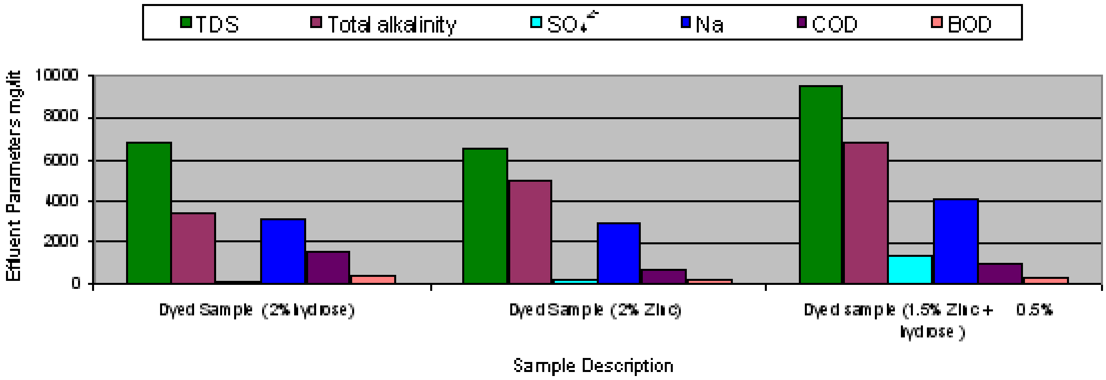
Effluent parameters	Effluent from dyed sample (2% Hydrose)	Effluent from dyed sample(2% Zinc)	Effluent from dyed sample (1.5% Zinc+0.5%hydrose)
pH	11.87	11.97	12.07
TDS (mg/lit)	6811	6500	9512
Total alkalinity (mg/lit)	3445	4946	6781
So_4^{2-} (mg/lit)	159	234	1373
Na (mg/lit)	3125	2921	4118
COD (mg/lit)	1560	760	998
BOD (mg/lit)	462	188	268

+ hydrose 0.5% owm) are given in Table 2 and shown in Graphs 2, 2a and 2b. There is an overall good fastness properties on the cotton fabric dyed with vat dye using different form of reducing agents such as hydrose 2% owm, zinc 2% owm and zinc 1.5% owm + hydrose 0.5% owm. As understood, the rubbing fastness of vat dyed cotton fabric obviously gives good rating in the dry state (range 4) compared to the wet state (range 3-2) for all the reducing types involved in vat dyeing.The washing fastness is excellent (rating 5) on the cotton fabric dyed with vat dye using all these reducing agents (hydrose 2% owm, zinc 2% owm and zinc 1.5% owm + hydrose 0.5% owm). The light fastness is also good (rating 5) on the cotton fabric dyed using vat dye with the help of different form of reducing agents (hydrose 2% owm, zinc 2% owm and zinc 1.5% owm + hydrose 0.5%owm).

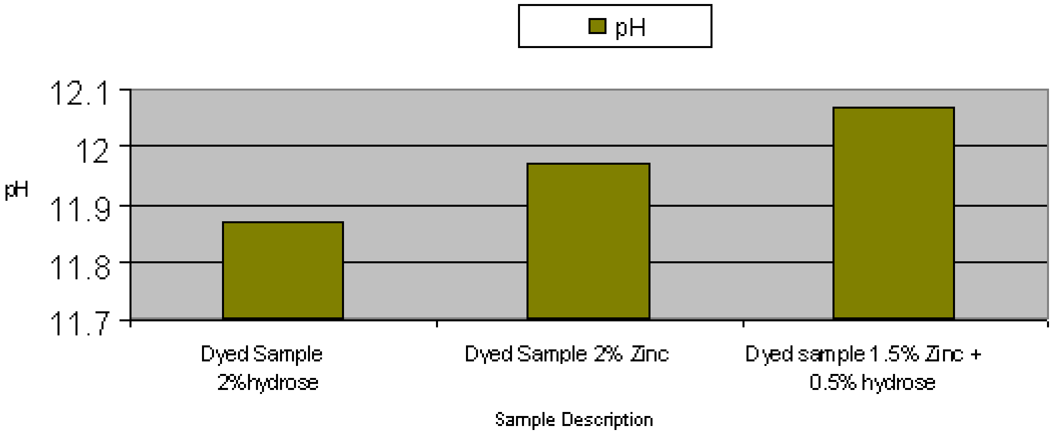
The reducing agent zinc (2% owm) and its combination (1.5% owm zinc) with hydrose (0.5% owm) also helps to give good fastness properties (Rubbing fastness, washing fastness and light fastness) on cotton fabric dyed with vat dye, similar to the conventional reducing agent, hydrose (2% owm).

Effluent from dye solution

The data of effluent loads obtained from different dye baths involved for vat dyeing on cotton using the reducing agents such as hydrose 2% owm, zinc 2% owm and zinc 1.5% owm + hydrose 0.5% owm are given in Table 3 and shown in Graphs 3 and 3a. The parameters such as TDS, total alkalinity, sulphate ion, sodium ion, COD, BOD and pH are considered in the effluent load. The parameters TDS, total alkalinity and sodium ion are very high in the effluent of dye baths using



Graph 3: Analysis of effluent load



Graph 3a: Analysis of pH in effluent load

different reducing agents (hydrose 2% owm, zinc 2% owm and zinc 1.5% owm + hydrose 0.5% owm). These parameters are very high in the dye bath of zinc 1.5% owm + hydrose 0.5% owm reducing agent (6781 mg/L) compared with other two (hydrose 2% owm → 3445 mg/L and zinc 2% owm → 4946 mg/L). The effluent parameters such as TDS, sodium ion, COD and BOD are least in the dye bath using zinc 2% owm as the reducing agent. There is no least factor from the effluents of dye bath from zinc 1.5% owm + hydrose 0.5% owm.

FTIR study on vat dyed cotton fabric

The results of FTIR spectra of vat dye and vat dyed cotton fabric using hydrose 2% owm, zinc 2% owm, and zinc 1.5% owm + hydrose 0.5% owm are shown in Figures 1, 2, 3, and 4 respectively. From the figure 1 it is seen that there is a stretching frequency of alkane(-CH_3) group at 3000cm^{-1}, carbonyl group (C=O) at 1700 cm^{-1}, bending vibration of CH group at 1300 cm^{-1}, two substitutes due to CH or NH stretching at 1000 cm^{-1}, and ether group (C-O-C) at 750 cm^{-1}.

In Fig 2, 3, and 4 the alkyl group remains the same as that of Figure 1, however, the wavelength has slightly deviated with the range of 3500cm^{-1} – 3000 cm^{-1} instead of at 3000 cm^{-1} in Fig. 1. In Figure 2 and 4 the NH group is present at the range of 2000 cm^{-1} which has separated and gained individual presence compared with that of the original dye shown (Figure 1) for NH group at the range of 1000 cm^{-1}, but in Figure 3 the identity of NH group is oscillating from the range of 2500 cm^{-1} to 2000 cm^{-1}. In Figures 2, 3 and 4, the CH bending vibration, stretching, stretching vibrations

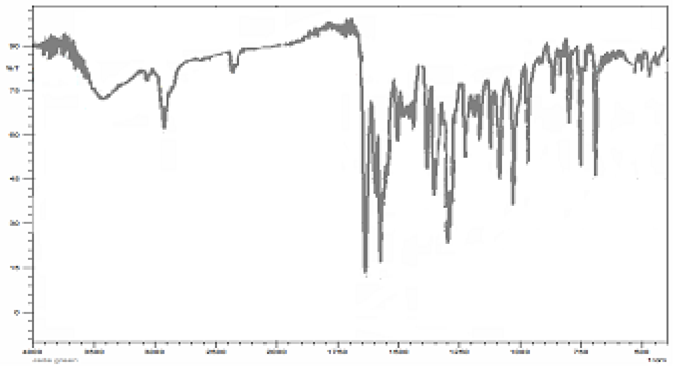


Fig. 1: The FTIR spectra of vat dye (jade green powder)

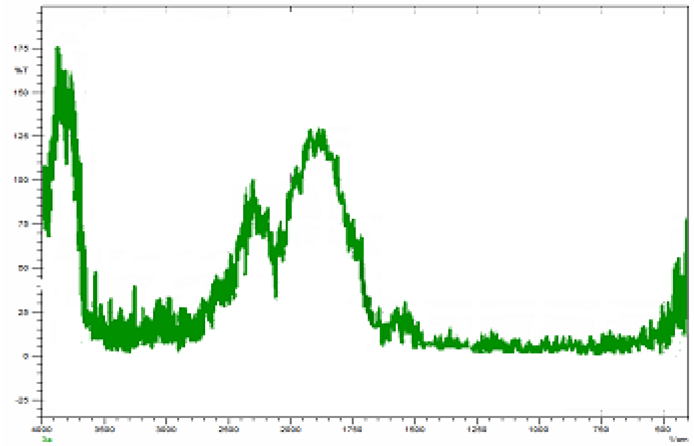


Fig. 2: The FTIR spectra of vat dyed fabric with hydrose 2% owm

and ether group have missed their presence, however, there is a ring stretch of CH group at the range of 1600 cm^{-1}.

SEM analysis for dyeing effect

The SEM images of vat dyed fabric using hydrose 2% owm, zinc 2% owm and zinc 1.5% owm + hydrose 0.5% owm are shown in Figures 5, 6 and 7 respectively. The Figures 5 and 6 show deep shade of dyeing on the yarns of cotton fabric that of fig. 7. The influence of the effect of reducing agents is visible in the SEM figures. The effluent load from the dye bath using zinc 1.5% owm + hydrose 0.5% owm is very high which reveals that this reducing agent is not effectively performed for good dyeing and hence the contents are more in the residual bath. The effect of zinc 2% owm as reducing agent is good on dyeing on cotton fabric as evidenced in the SEM image and in the effluent load data that are near to the effect achieved by hydrose 2% owm.

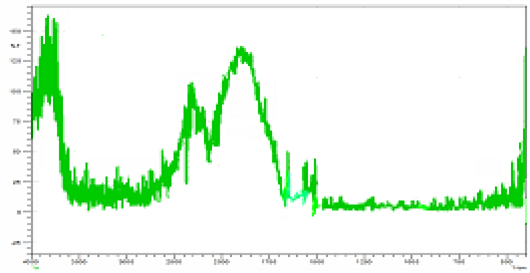


Fig. 3: The FTIR spectra of vat dyed fabric with Zinc 2% owm

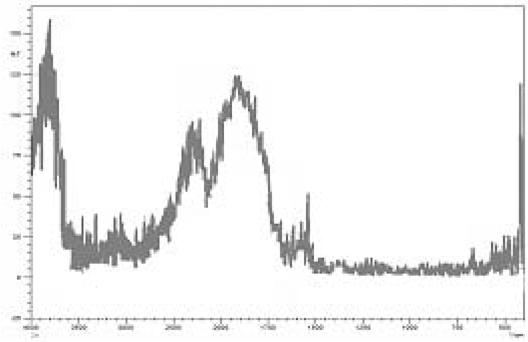
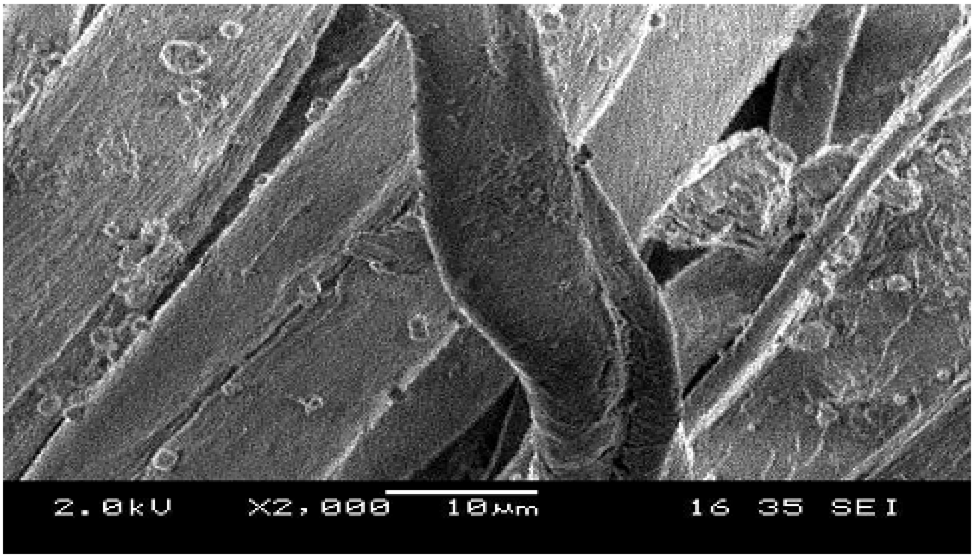


Fig. 4: The FTIR spectra of vat dyed fabric with Zinc 1.5% owm and hydrose 0.5% owm



Fig, 5: SEM image for conventional vat dyed fabric with hydrose 2% owm

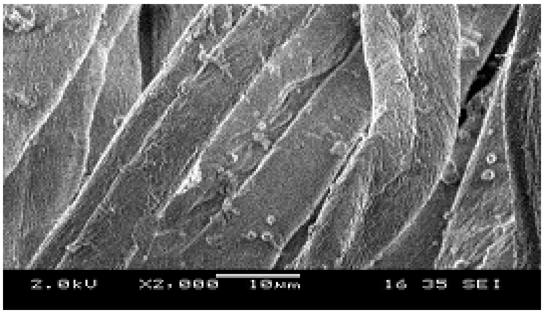


Fig. 6: SEM image for vat dyed fabric with Zinc 2% owm

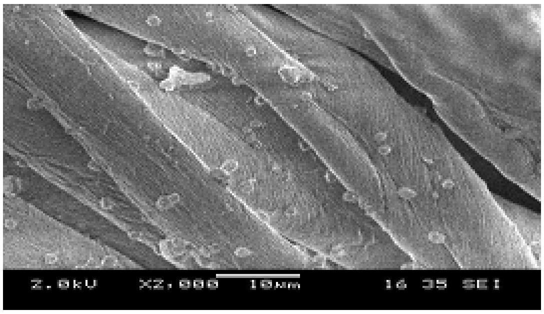


Fig. 7: SEM image for vat dyed fabric with Zinc 1.5% owm and hydrose 0.5% owm

CONCLUSION

The application of zinc as a reducing agent in vat dyeing is appreciable based on its results concluded as follows;

The average fabric strength of cotton fabric dyed with vat dyes using zinc as reducing agent is good similar to that of undyed fabric, and higher than those obtained using other reducing agents, that is, hydrose 2% owm and zinc 1.5% owm + hydrose 0.5% owm.

The fastness properties such as rubbing, washing and light are very good in the all the cases of vat dyeing and zinc assisted dyeing are not inferior to hydrose assisted vat dyeing.

The average effluent load from the vat dye bath using zinc 2% owm is less compared with those of hydrose assisted vat dye baths.

The effect of dyeing on the cotton fabric dyed with vat dye assisted by zinc 2% owm is very good similar to that of hydrose 2% owm as per the SEM evidence.

From the FTIR data it is concluded that the vat dye reduced by zinc 2% owm is utilized to the maximum extent for dyeing.

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