

Eco-friendly Vat Dyeing on Cotton Fabrics at Bahir Dar Textile Share Company

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Abstract

For dyeing the cotton fabric with vat dyes, first it is required to reduce the dye using reducing agents. The reduction potential of reducing agent has to be matched with the dye for proper dyeing. Otherwise the problem of over reduction and under reduction may arise and leads to the change in shade. In conventional vat dyeing process, the vat dye is dissolved using hydroses, which is a powerful reducing agent followed by solubilizing with sodium hydroxide. This process creates very high pollution problem. In this study, an attempt has been made to replace hydroses by ferrous sulphate and hydroses combination as reducing agent on cotton fabric dyeing with vat dye and the results are compared with those of the treatment with conventional hydroses in terms of depth of shade, color fastness, color difference, tensile strength and effluent parameters. Among the ferrous sulphate + Hydroses combinations, 0.5g/L (10%) ferrous sulphate + 4.5g/L (90%) hydroses and 2g/L (40%) ferrous sulphate + 3g/L (60%) hydroses combinations as reducing agents give very good dyeing effect on the dyed cotton fabric with Bezathren Blue RS and Red LGG vat dyes respectively. These ferrous sulphate + hydroses combinations as reducing agents results higher color strength, lower BOD and COD values and higher fabric strength than hydroses. Therefore, hydroses can be replaced by ferrous sulphate + hydroses combinations depending on the reduction potential of a dye and by controlling the NaOH amount during dyeing.

Keywords: Eco-friendly; Reducing agent; Vat dyeing; Effluent; Reduction potential; COD; BOD

Introduction

Bahir Dar textile Share Company produces 100% cotton fabrics, which are dyed with reactive and vat dyes and are printed with pigment dyes, and other textile products. The Vat dyes are practically insoluble in water, but are converted into water soluble form (leuco dye) by reduction with strong reducing agent hydroses and solubilizing agent sodium hydroxide. Wet processing in textile dyeing and finishing can lead to effluents which have been subject to criticism for many decades. At Bahir Dar textile Share Company 10 years ago, the dominant problems were large amounts of foam in Blue Nile River and effluent hazards sometimes leading to the extinction of fish populations and of other aquatic organisms. Due to the enforcement of environmental legislation the situation has changed considerably.

Although man-made fibers have made inroads into applications previously reserved for cotton, cotton continues to be the major textile fiber due to its great versatility, availability, and cost [1,2]. Cotton can be dyed successfully with many natural colors extracted from natural sources and synthetic dyes, such as direct, reactive, sulphur, vat, azoic dyes etc. The choice of a dye depends on the required shade, its fastness and cost [3].

In the coloration of cellulose fibers /cotton, vat dyes still represent a relatively large part of the dyestuff market; among them about 120,000 tons of vat dyes are being used annually in worldwide [3,4]. They have excellent all round color fastness, which includes washing, light, perspiration, chlorine bleaching and rubbing fastness as well as other desired characters needed on cotton garments. They also are the only class of dyes which does not suffer severe shade changes during the application of topical, cellulose reactive, flame retardant finishes [4]. The vat dyestuffs show slight advantage than reactive dyestuffs in ecological costs, generating less molecules of CO₂, lower consumption of water and energy, greater possibility of reuse of treated effluent, which presented decolorisation efficiency above 99% [5,6].

However, the vat dyestuffs are insoluble in water. Before or during

the dying process, Vat dyes must be converted into a water soluble form (leuco form) by reducing agents in alkaline medium to give solutions containing individual molecules or molecular ions. The most common employed reducing agent in vat dyeing is hydroses. Unfortunately, the use of hydroses is being criticized for the formation of non- environment friendly decomposition products such as sulphite, sulphate, thiosulphate and toxic sulphur [7,8].

Previous investigations were focused on the replacement of hydroses by other ecologically more attractive alternatives. After several decades of research and development, there is still no commercial reducing technology, including electrochemical processes available today that can replace hydroses in all areas of vat dye application [3]. In addition to this, Md. Vaseem et al. stated that the reducing agent ferrous sulphate is not suitable either alone or in combination with hydroses and hydroxyl acetone [9].

Hence, the present study has been aimed at studying the effect of ferrous sulphate and hydroses combination as reducing agents on dyeing properties of cotton fabrics dyed with vat dyes. On the other hands, the effect of NaOH and Reduction potential of a dye on the ferrous sulphate and hydroses combination as reducing agents have been studied separately. The results are compared with those of the conventional reducing agent hydroses in terms of depth of shade, tensile strength,

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rubbing fastness, washing fastness, light fastness, shade uniformity, color difference and effluent parameters.

Materials and Methods

Materials

The materials required for this study are: 100% bleached cotton fabric, Rota beaker dyeing machine, Tensile strength tester, Crock meter, MBTL light fastness tester, Color eye 3100, COD (Chemical oxygen demand) Digester, BOD (Biological oxygen demand) Incubator, Digital pH meter, Whatman No. 42 filter paper and grey scale.

Chemicals and reagents: The chemicals or reagents used for these work are: Bezathren Blue RS and Red LGG Dyes (IN special), hydrose, ferrous sulphate, sodium hydroxide, calcium chloride solution, magnesium sulphate solution, ferric chloride solution, ferrous ammonium sulphate, potassium carbonate, distilled water, mercuric sulphate crystals, potassium dichromate, vat paper and phenolphthalein paper.

Methods

Pre-treatment of cotton fabric: The half bleached 100% cotton fabric sample, having the specification ends/inch 24, picks/inch 18, warps count 20 and weft count 20 are used. The water absorbency of textiles is measured by using drop test. A measured drop of water is placed on the fabric 1cm from the surface. Thus, time recorded for the first sample was below 5 seconds and for the second and third samples was above 60 seconds according to the AATCC/ASTM Test Method TS-018.

Vat dyeing on cotton fabric: The rota beaker dyeing machine was used for sample dyeing. The method of dyeing of cotton fabric was exhausted dyeing because Jigger is the main dyeing method in Bahir Dar Textile Share Company. In this thesis work, three types of experiments were done in order to replace hydrose by the combination of ferrous sulphate and hydrose. The ferrous sulphate and hydrose combination ratio, the amount of NaOH and the type of dyes are the main factors for vat dyeing on cellulosic fabrics.

- **Experiment 1: Vat dyeing with Bezathren Blue RS using ferrous sulphate and hydrose combinations at constant and Different amount of NaOH**

The dyeing recipe includes Bezathren Blue RS vat dye 2.0% o.w.f, Wetting agent 2g/L, NaOH 15g/L, MLR 1:10, temperature 70°C, treatment time 45 minutes and reducing agents were prepared in different combination of ferrous sulphate and hydrose.

The different combination of ferrous sulphate and hydrose was designed for reducing agent of vat dyes. There are 11 possible choices of ferrous sulphate and hydrose combination having 11 experimental treatments. The complete design of ferrous sulphate (FeSO_4 (g/L)) and hydrose ($\text{Na}_2\text{S}_2\text{O}_4$ (g/L)) combination for Bezathren Blue RS vat dyeing are 0+5; 0.5+4.5; 1+4; 1.5+3.5; 2+3; 2.5+2.5; 3+2; 3.5+1.5; 4+1; 4.5+0.5 and 5+0 in g/L. After dyeing, the dyestuff needs an oxidation in order to returns into the original insoluble form.

After using different combination of reducing agent, the reducing agent combination were constant at (0.5 + 4.5g/L) and varying amount of NaOH from 1g/L to 11g/L to know the effect of NaOH on vat dyeing. After dyeing samples, the dyestuff needs an oxidation in order to returns into original insoluble ones.

- **Experiment 2: Vat dyeing with Bezathren red lgg using Ferrous Sulphate and Hydrose combinations**

The Bezathren red LGG vat dye was dyed by using the same dyeing conditions to know the effect of the reduction potential of dyes on the amount of the ferrous sulphate and hydrose combinations. The dyeing recipe includes Bezathren Red LGG vat dye 2.0% o.w.f, Wetting agent 2g/L, NaOH 6g/L, MLR 1:10, temperature 70°C treatment time 45 min and 11 combinations of reducing agents of ferrous sulphate and hydrose as explained in experiment 1.

After completion of dyeing, oxidation process are carried out to returns the dyed samples into original insoluble samples. Upon exposure to an oxidizing agent, 2g/L hydrogen peroxide at 45°C for 30 minutes. Finally, the dyed fabric was washed off with 2g/L anionic detergent at 45°C for 30 minutes. After soaping, the specimen is removed, rinse twice in cold water and then in cold running tap water. Squeezed and dried at 60°C.

Measurement of reduction potential of vat dye bath: The reduction potential of vat dye bath with various reducing agents such as hydrose and its combination with ferrous sulphate. Conventional of reducing agent (hydrose) were determined by using digital potentiometer (MT-091, PICO Make) before dyeing and after dyeing. This potentiometer measured oxidation-reduction potential (ORP) platinum electrode and the Ag/AgCl reference electrode with KCl electrolyte, connected to a pH meter (Mettler Toledo, Inlab) and recorded in (mV) [10].

Dyed fabric quality analysis

Shade properties (K/S Value, color difference and shade uniformity): The colour/shade strength K/S Value, color difference and shade uniformity at 600 nm for Bezathren Blue RS and at 480 nm Bezathren Red LGG vat dye were determined by Color eye-3100 Spectrophotometer. The vat dyed samples using reducing agents such as ferrous sulphate and hydrose combination and conventional reducing agent (hydrose), were folded four times and after calibration of Color eye-3100 Spectrophotometer, were exposed to two times (front and back) and the mean value was taken.

Colour fastness: The colour fastness to washing can be tested using ISO-2 test employing following conditions in launder-o-meter. A 10 × 4 cm swatch of the dyed fabric is taken and is sandwiched between two adjacent fabrics and stitched. The sample and the adjacent fabric were washed with 5g/l of soap in a solution with liquor ratio 50:1, at a temperature of 50°C, for 45 minutes. After soaping treatment, the specimen is removed, rinse twice in cold water and then in cold running tap water. Squeezed and dried at 60°C [11]. The colour fastness to crocking can be tested employing AATCC Test Method-8-2005, using Crock meter. The staining on cotton rubbed fabric can be evaluated using AATCC grey scale for staining.

The colour fastness to light can be tested using AATCC Test Method 16-2004. The Carbon Arc or Xenon Arc Lamp source is used for determining the color fastness towards light. The light fastness rating system is based on the rate of fading of eight AATCC blue-dyed wool standard samples. The samples were exposed to 10 hours to determine the colour change.

Tensile strength: The dyed fabrics were tested for its strength in warp and weft way direction by universal Strength Tester with the specimen size of 100 mm × 150 mm by random sampling method according to ASTM D5034.

Analysis of dye effluent

The important parameters considered in this study included pH, total dissolved solids, BOD and COD. The effluent parameters were tested from the effluent of the vat dyed baths. The dye effluents were assessed or analysed after dyeing. The effluents from every stage were collected and equalized to create model effluent composition. Polyethylene bottles were used for the sample collection.

Results and Discussions

Reduction potential of vat dyes

The reduction potential of vat dyes gives an idea about the level of difficulty involved in their reduction. Higher the reduction potential of the dye, higher is the reducing power required in the dye-bath for its reduction process. The mean Reduction Potentials of vat dye bath using hydroses (5g/L) and its combination with different amounts of FeSO_4 and hydroses have been shown in Table 1 and Figure 1.

The reduction potential is very high in the vat dye bath using hydroses (5g/L) as reducing agent compared with its other combination with ferrous sulphate. As the amount of hydroses (2.5g/L) and ferrous sulphate (2.5g/L) is equal (reach 1:1) the reduction potential is high in both before dyeing (-700mV) and after dyeing (-570mV) which shows the optimum reduction process and a dye bath with a lower (more negative) reduction potential have a tendency to lose electrons to the new species (i.e. to be oxidized by reducing the new species). The reduction potential is invariably non-uniform from the initial period (before dyeing) till the completion of dyeing (after dyeing) as described in the Table 1 and Figure 1.

Effect of ferrous sulphate and hydroses combinations on bezathren blue RS vat dye

Effect of ferrous sulphate and hydroses combinations on dyed fabric quality: Following are the combined effects of ferrous sulphate and hydroses into the quality of dyed fabric.

Shade properties: The depth of shade (K/S) on cotton fabric dyed with Bezathren Blue RS vat dye using different ferrous sulphate and hydroses combinations as reducing agents is shown in Figure 2. Among the ferrous sulphate and hydroses combinations, 0.5g/L (10%) ferrous sulphate + 4.5g/L (90%) hydroses combination as reducing agent gives very good dyeing effect with anticipated uniformity on the vat dyed cotton fabric than hydroses (5g/L). The K/S value at 600 nm for dyed fabric with Bezathren Blue RS using 5g/L hydroses and 0.5g/L (10%) ferrous sulphate + 4.5g/L (90%) hydroses combination as reducing agent are 6.61 and 5.82 respectively. Hence, the depth shade of cotton fabric

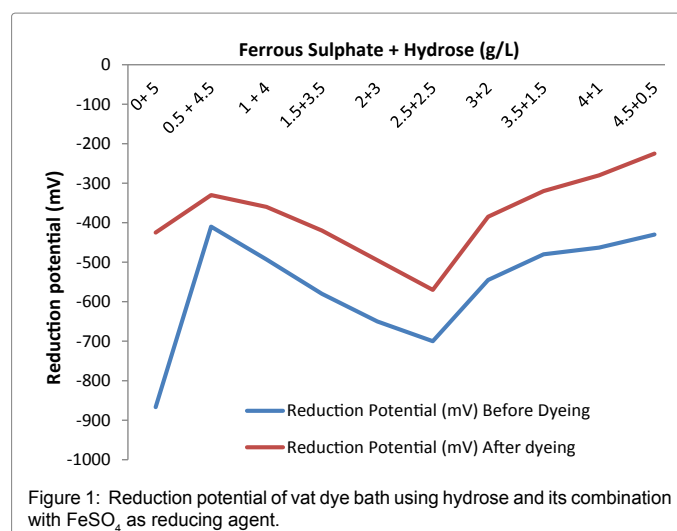


Figure 1: Reduction potential of vat dye bath using hydroses and its combination with FeSO_4 as reducing agent.

dyed with vat dye using FeSO_4 + hydroses combination shows similar effect as that of dyed fabric with hydroses (strength 100%). This indicates that the reduction potential of the Bezathren Blue RS (-860mV) could be matched with 0.5g/L (10%) ferrous sulphate + 4.5g/L (90%) hydroses combination as reducing agent more than hydroses (5g/L). The depth of shade decrease when the concentration of ferrous sulphate increases and hydroses decreases in the ferrous sulphate and hydroses combination due to under reduction of the vat dyes and some yellowish spots or stains are showed on the dyed fabric surface and in dye solution due to precipitation out of ferrous sulphate.

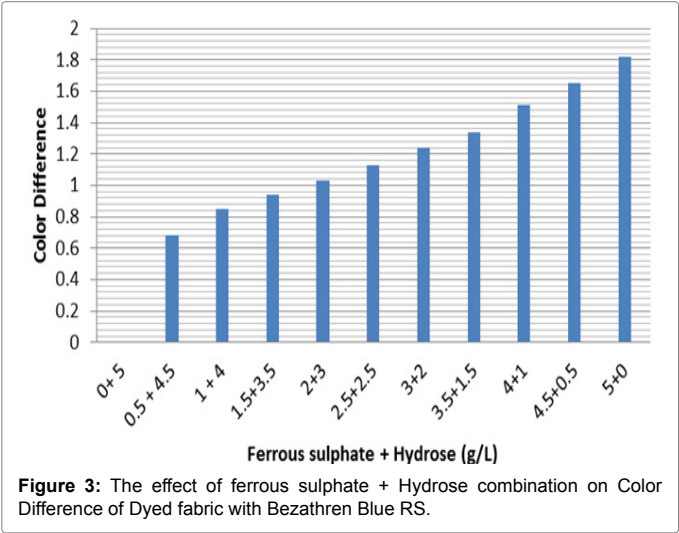
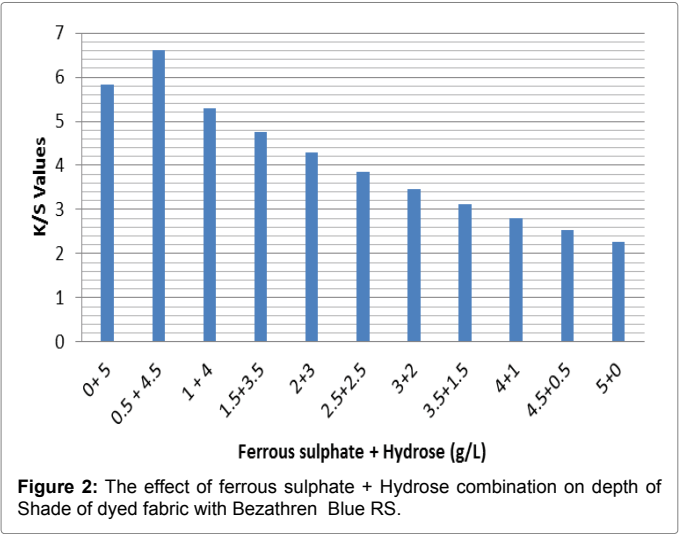
The color difference of cotton fabric dyed with Bezathren Blue RS vat dye using different ferrous sulphate and hydroses combinations as reducing agents is shown in Figure 3. The color difference was determined by comparing with 5g/L hydroses (K/S=5.82). The color difference between the dyed fabric with Bezathren Blue RS using 0.5g/L (10%) ferrous sulphate + 4.5g/L (90%) hydroses combination as reducing agent and 5g/L hydroses is 0.68. According to the International Commission on Illumination (CIE), the color difference <1.0 is not perceptible by human eyes. Thus, the color of the dyed fabric with Bezathren Blue RS vat dye using 0.5g/L (10%) ferrous sulphate + 4.5g/L (90%) hydroses combination as reducing agent and 5g/L hydroses are the same. The color difference increases when the concentration of ferrous sulphate increases and hydroses decreases in the ferrous sulphate and hydroses combination due to under reduction of the vat dyes and some yellowish spots or stains are showed on the dyed fabric surface and in dye solution due to precipitation out of ferrous sulphate.

This result shows, when ferrous sulphate is combined with hydroses (FeSO_4 + hydroses), the dyeing effect is good with appreciable uniformity. The reducing agents such as hydroses, zinc and ferrous sulphate respectively in the individual application do not give uniform dyeing and the deposits of insoluble dyes are more on the cotton fabric after dyeing as reported by Santhi P (Figures 2 and 3) [3].

The fastness properties: The fastness properties of dyed fabric with Bezathren Blue RS vat dye using different combination of ferrous sulphate + hydroses are given in Table 2. There is an overall good fastness properties (rubbing, light and wash fastness) on the cotton fabric dyed with Bezathren Blue RS vat dye using different form of reducing agents in hydroses (5g/L) and its combination with ferrous sulphate. As the result shows, the rubbing fastness of vat dyed cotton fabric obviously gives good rating of fastness in the dry state (range 4) as compared to the

Ferrous sulphate + Hydroses (g/L)	Reduction Potential (mV)	
	Before Dyeing	After dyeing
0+5	-867	-425
0.5+4.5	-410	-330
1+4	-493	-360
1.5+3.5	-580	-420
2+3	-650	-495
2.5+2.5	-700	-570
3+2	-545	-385
3.5+1.5	-480	-320
4+1	-463	-280
4.5+0.5	-430	-225

Table 1: Reduction potential of vat dye bath using hydroses and its combination with FeSO_4 as reducing agent.



No. of Sample	Ferrous sulphate +hydrose (g/L)	Fastness properties			
		Rubbing Fastness		Washing Fastness	Light Fastness
		Dry	Wet		
1	0+ 5	4	3	5	5
2	0.5 + 4.5	4	3	5	5
3	1 + 4	4	3	5	5
4	1.5+3.5	4	3	5	5
5	2+3	4	3	5	5
6	2.5+2.5	4	3	5	5
7	3+2	4	3	5	5
8	3.5+1.5	4	3	5	5
9	4+1	4	3	5	5
10	4.5+0.5	4	3	5	5
11	5+0	4	3	5	5

Table 2: The effect of ferrous sulphate + Hydrose combination on Fastness properties of Dyed fabric with Bezathren Blue RS dye.

wet state (range 3) for all the reducing agent combination. As understood, the wash and light fastness properties of vat dyed cotton fabric obviously give excellent (rating 5) for all combination of reducing agent [12].

Tensile strength of cotton fabric: The tensile strength both in warp

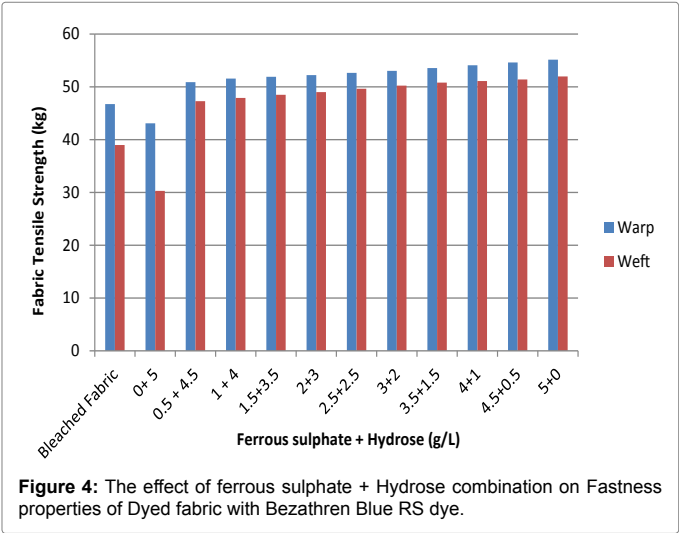
direction and in weft direction of cotton fabric after bleaching and dyeing with Bezathren Blue RS vat dye using different ferrous sulphate and hydrose combinations as reducing agents is given in Figure 4. The ferrous sulphate and hydrose combinations such as 0.5g/L (10%) ferrous sulphate + 4.5g/L (90%) hydrose combination shows good average fabric strength both in warp and weft directions (50.9Kg and 47.3Kg respectively) compared with 5g/L hydrose (43.1kg and 30.3kg in warp and weft directions respectively). The tensile strength in both warp and weft direction is reduced after dyeing with Bezathren Blue RS vat dye using 5g/L hydrose compared with that of Bleached cotton fabric (46.74kg and 38.99Kg in warp and weft directions respectively); while it is increased in both weft and warp directions after dyeing with Bezathren Blue RS vat dye using the ferrous sulphate and hydrose combination such as 0.5g/L (10%) ferrous sulphate + 4.5g/L (90%) hydrose combination compared with that of Bleached cotton fabric. Thus, the fabric strength of cotton fabric dyed with Bezathren Blue RS vat dye using ferrous sulphate and hydrose combinations is greater than that of bleached fabric and those of the hydrose assisted dyed fabric. The tensile strength of cotton fabric in both warp and weft direction increases when the amount of ferrous sulphate increases and the amount of hydrose decreases in the ferrous sulphate and hydrose combination [12].

The percent loss in tensile strength of cotton fabric in both warp and weft direction after dyeing with Bezathren Blue RS vat dye using hydrose (5g/L) is 7.79% and 22.29% respectively, while after dyeing with Bezathren Blue RS vat dye using the ferrous sulphate and hydrose combination such as 0.5g/L (10%) ferrous sulphate + 4.5g/L (90%) hydrose combination, it is in the increasing trend of 8.90% and 21.31% in the warp and weft direction respectively. The average tensile strength, both in warp and weft direction of the cotton fabric vat dyeing using hydrose (5g/L) and 0.5g/L (10%) ferrous sulphate + 4.5g/L (90%) hydrose combination is 15.04% loss and 15.11% gain respectively Figure 4.

Effect of ferrous sulphate and hydrose combinations on dye Effluent

The effect of ferrous sulphate + Hydrose combination on Effluent parameters of dyebath with Bezathren Blue RS dye have been listed into the Table 3.

pH of effluent: The pH of effluent obtained from different dye baths



No. of sample	Ferrous sulphate + Hydrose (g/L)	Effluent Parameters			
		pH	TDS (mg/L)	BOD (mg/L)	COD(mg/L)
1	0+5	11.89	7895	480	1590
2	0.5+4.5	12.44	22500	300	950
3	1+4	12.36	21375	279	870
4	1.5+3.5	12.28	20250	258	790
5	2+3	12.25	19500	232	689
6	2.5+2.5	12.20	18000	216	630
7	3+2	12.12	16500	201	570
8	3.5+1.5	12.07	14250	164	428
9	4+1	12.04	13500	152	380
10	4.5+0.5	12.01	12000	127	285
11	5+0	11.95	10,500	102	190

TDS (Total dissolved solids); BOD (Biological oxygen demand); COD (Chemical oxygen demand)

Table 3: The effect of ferrous sulphate + Hydrose combination on Effluent parameters of dye bath with Bezathren Blue RS dye.

involved for vat dyeing with Bezathren Blue RS vat dye using different ferrous sulphate + hydrose combinations as reducing agent such are given in Table 3 and Figure 5. The pH values of effluent are in the range 11.89-12.44 which are alkaline due to nature of dyes, materials used like cotton, NaOH, etc. used for dyeing process.

The acidic and basic nature of the effluent can be identified by pH value and it is also determines the presence or absence of various ionic species of the textile effluent. In general the majority of the chemical reactions are controlled by altering the value of pH. For example most of the metals become soluble in water at low pH and insoluble at high pH. Hence low or high strength of the pH in effluent can affect the quality of clean water and alters the rate of biological reaction with survival of various microorganisms. The strength of the pH also alters the soil permeability which results in contaminating underground water resources. As a result it is necessary to evaluate the effluent with respect to pH value then it can be neutralized with acidic or basic solution as reported by Gomathi et al. [12,13].

As results shown in Table 2 and Figure 4 the pH value is sophisticated for combined FeSO_4 with hydrose from 0.5g/L-5g/L in vat dyeing of cotton fabric. This indicates the FeSO_4 is slightly strong basicity than hydrose because the pH value of pure reducing agent hydrose has slightly less than the combined pH of FeSO_4 and hydrose. In Table 2 the pH of (0.5g/L) FeSO_4 + (4.5g/L) hydrose combination is 12.44 that shows high basicity of dye bath and the least pH is 11.95 obtained during the use pure 5g/L FeSO_4 as reducing agent. This value indicates that the FeSO_4 itself does not increase the pH in the vat dyeing effluent because other components are responsible for increasing the pH in the effluent like dye, NaOH and hydrose (Figure 5).

Total dissolved solids (TDS): The TDS of effluent obtained from different dye baths involved for vat dyeing with Bezathren Blue RS vat dye using different ferrous sulphate + hydrose combinations as reducing agent such as 0.5g/L (10%) ferrous sulphate + 4.5g/L (90%) hydrose combination as reducing agent are given in Table 3 and Figure 6. The parameter TDS is very high in the effluent of dye baths. The parameter TDS in the dye bath of 0.5g/L (10%) ferrous sulphate + 4.5g/L (90%) hydrose combination as reducing agent (95,000mg/L) is higher than hydrose (5g/L) (8895mg/L) because in the dye solution with 0.5g/L (10%) ferrous sulphate + 4.5g/L (90%) hydrose combination as reducing agent, all dyestuff molecules are dissolved properly. However, the TDS decreases when the amount of ferrous sulphate increases and the amount of hydrose decreases in the ferrous sulphate and hydrose

combination due to under reduction of the vat dyes.

Total Dissolved Solids (TDS) combined content of all inorganic and organic substances contained in a liquid which are present in a molecular, ionized or micro-granular (colloidal solution) suspended form. A certain level of these ions in water is necessary for aquatic life. However, if TDS concentrations are too high or too low, the growth of many aquatic lives can be limited, and death may occur. TDS can be eliminated by adding alum salt in the effluent and other treatment systems (Figure 6) [14].

Biological oxygen demand (BOD): The BOD of effluent obtained from different dye baths involved for vat dyeing with Bezathren Blue RS vat dye using different ferrous sulphate + hydrose combinations as reducing agent are given in Table 2 and Figure 7. Among the different ferrous sulphate + hydrose combinations as reducing agent, the ferrous sulphate and hydrose combination such as 0.5g/L (10%) ferrous sulphate + 4.5g/L (90%) hydrose combination as reducing agent shows good average BOD values (300 mg/L) compared with vat dyeing using 5g/L hydrose (480 mg/L). The BOD values in the dye bath using 0.5g/L (10%) ferrous sulphate + 4.5g/L (90%) hydrose combination as reducing agent is less than that of hydrose (5g/L). The BOD value decreases when the amount of ferrous sulphate increases and the amount of hydrose decreases in the ferrous sulphate and hydrose combination in the ferrous sulphate and hydrose combination due to under reduction of the vat dyes.

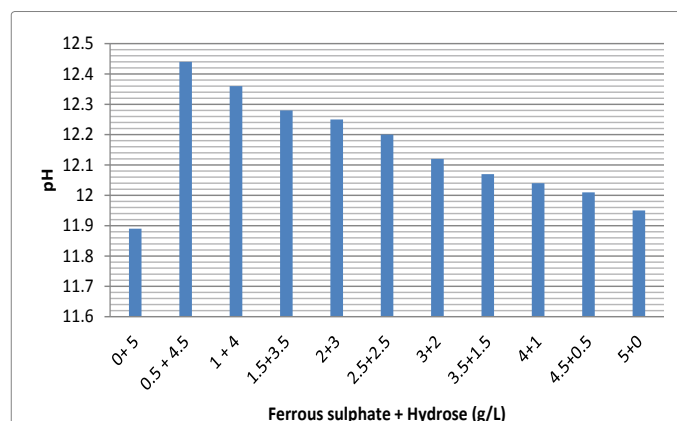


Figure 5: The effect of ferrous sulphate + Hydrose combination on Effluent pH of dye bath with Bezathren Blue RS dye.

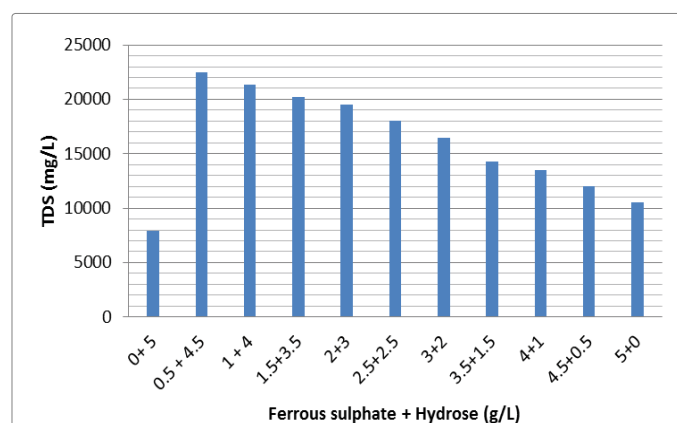


Figure 6: The effect of ferrous sulphate + Hydrose combination on TDS values of dye bath with Bezathren Blue RS dye.

The BOD is due to the presence of organic contaminants of textile effluents in water bodies. The low or nil BOD values shows good quality water, whereas a high BOD indicates the water is highly contaminated and not suggested for drinking purposes. It is suggested that, the effluent water undergoes anaerobic fermentation processes as a result formation of ammonia and organic acids. Hydrolysis of these acidic materials causes a decrease of pH value which in turn changes the water as more acidic. Moreover increase in BOD leads to microbial oxygen demand causes reducing DO which may induce hypoxia conditions with subsequent adverse effects on aquatic biota. BOD, COD and DO are interrelated when higher COD in effluent induces the BOD as a result it consumes more oxygen in the water hence aquatic organisms become suffocate, and die [13].

Chemical oxygen demand (COD): The BOD of effluent obtained from different dye baths involved for vat dyeing with Bezathren Blue RS vat dye using different ferrous sulphate and hydroses combination as reducing agents are given in Table 3 and Figure 7. The ferrous sulphate and hydroses combinations such as 0.5g/L (10%) ferrous sulphate + 4.5g/L (90%) hydroses combination as reducing agent shows good average COD values (950 mg/L) compared with vat dyeing using 5g/L hydroses (1590 mg/L). The COD values in the dye bath using 0.5g/L (10%) ferrous sulphate + 4.5g/L (90%) hydroses combination as reducing agent is less than that of hydroses (5g/L). The COD value decreases when the amount of ferrous sulphate increases and the amount of hydroses decreases in the ferrous sulphate and hydroses combination due to under reduction of the vat dyes.

Higher concentration of COD in water implies toxic conditions and the presence of biologically resistant organic substances. Commonly, organic strength of the effluent can be identified by COD values. Increases in COD can be due to huge amount of industrial wastes such as detergents, softeners, non-biodegradable dyeing chemicals, formaldehyde based dye fixing agents etc. Higher concentration of COD in water implies toxic conditions and the presence of biologically resistant organic substances. Hence the effluent is incompatible for the survival of water living organisms due to the reduction of DO content (Figure 7) [13].

Effect of NaOH on ferrous Sulphate + Hydroses combination with bezathren blue RS vat dye

The depth of shade (K/S) of cotton fabric dyed with Bezathren Blue RS vat dye using 0.5g/L (10%) ferrous sulphate + 4.5g/L (90%) hydroses combination as reducing agent and different amounts of NaOH are given in Table 4 and Figure 8. Among the different amounts of NaOH, the 6g/L NaOH give good dyeing effect on the vat dyed cotton fabric with anticipated uniformity on the vat dyed cotton fabric. The K/S value at 600 nm for dyed fabric with Bezathren Blue RS vat dye using 6g/L and 11g/L NaOH is 4.3 and 3.91 respectively. The depth of shade decrease and some yellowish spots or stains are showed on the dyed fabric surface and in dye solution when the concentration of NaOH increases Table 4 and Figure 8.

The ferrous sulphate and hydroses combinations as reducing agents give very good dyeing effect on the vat dyed cotton fabric depending on amounts of NaOH. However, ferrous sulphate becomes insoluble and then some yellowish spots or stains are showed on the dyed fabric surface and in dye solution when the concentration of NaOH increases. Among the different amounts of NaOH, the 6g/L NaOH give good dyeing effect on the vat dyed cotton fabric with Bezathren Blue RS using 0.5g/L (10%) ferrous sulphate + 4.5g/L (90%) hydroses combination as reducing agent.

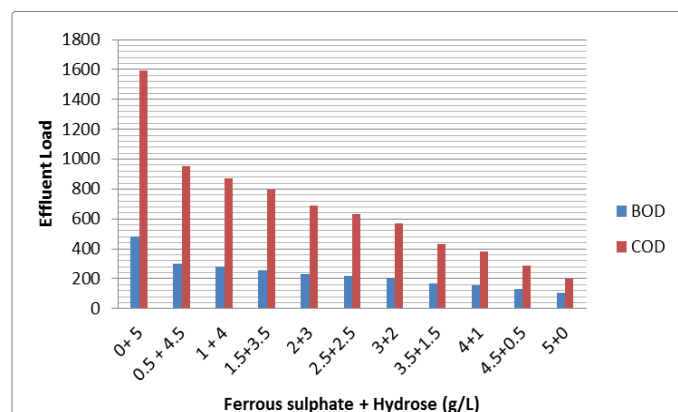


Figure 7: The effect of ferrous sulphate + Hydroses combination on BOD and COD values of dyebath with Bezathren Blue RS dye.

S.No	Ferrous sulphate + Hydroses (g/L)	NaOH (g/L)	K/S at 600nm	Color strength (%)	Color difference
1	0.5 + 4.5	1	0.71	19.12	45.79
2	0.5 + 4.5	2	1.42	38.38	21.08
3	0.5 + 4.5	3	2.14	57.84	13.87
4	0.5 + 4.5	4	2.85	77.03	10.98
5	0.5 + 4.5	5	3.57	96.49	9.05
6	0.5 + 4.5	6	4.28	115.68	0.94
7	0.5 + 4.5	7	4.22	114.05	0.60
8	0.5 + 4.5	8	4.18	112.97	0.561
9	0.5 + 4.5	9	4.02	118.97	0.53
10	0.5 + 4.5	10	3.95	106.76	0.50
11	0.5 + 4.5	11	3.91	105.68	0.48

Table 4: The effect of NaOH on Depth of Shade of Dyed fabric with Bezathren Blue RS using 0.5g/L ferrous sulphate + 4.5g/L Hydroses combination.

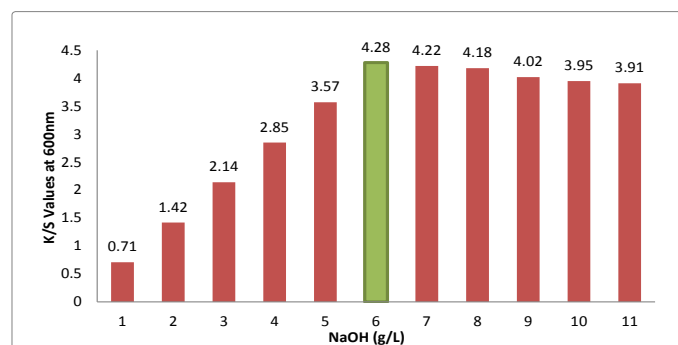


Figure 8: The effect of NaOH on Depth of Shade of Dyed fabric with Bezathren Blue RS using 0.5g/L ferrous sulphate + 4.5g/L Hydroses combination.

On the other hands, the 6g/L and 11g/L NaOH give similar effect on color fastness, effluent parameters and tensile strength of the vat dyed cotton fabric with Bezathren Blue RS using 0.5g/L (10%) ferrous sulphate + 4.5g/L (90%) hydroses combination as reducing agent.

Effect of ferrous sulphate and hydroses combination on bezathren red LGG vat dye

The depth of shade of cotton fabric dyed with Bezathren Red LGG vat dye using different form of reducing agents is shown in Table 5 and Figures 9 and 10. Among the ferrous sulphate + hydroses combinations 2g/L (40%) ferrous sulphate + 3g/L (60%) hydroses combination as reducing agent give very good dyeing effect on the vat dyed cotton

No. Sample	Ferrous sulphate + Hydrose (g/L)	K/S at 480nm	Color strength (%)	Color difference
1	0+5	3.15	100	0.00
2	0.5+4.5	3.17	100.63	0.83
3	1+4	3.20	101.59	0.71
4	1.5+3.5	3.63	115.24	0.85
5	2+3	3.88	123.17	0.95
6	2.5+2.5	2.70	85.71	3.87
7	3+2	2.43	77.14	4.30
8	3.5+1.5	2.18	69.21	4.78
9	4+1	1.97	62.54	5.31
10	4.5+0.5	1.77	56.19	5.90
11	5+0	1.59	50.48	6.56

Table 5: The effect of ferrous sulphate + Hydrose combination on Depth of Shade of Dyed fabric with Bezathren Red LGG.

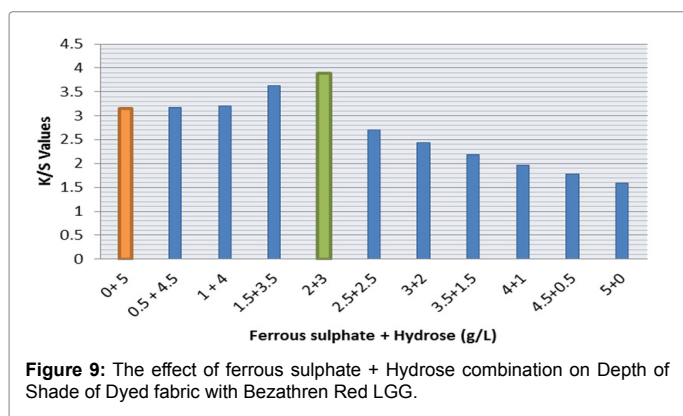


Figure 9: The effect of ferrous sulphate + Hydrose combination on Depth of Shade of Dyed fabric with Bezathren Red LGG.

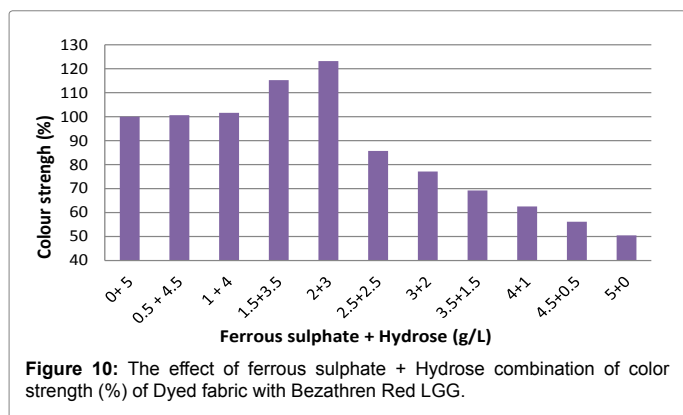


Figure 10: The effect of ferrous sulphate + Hydrose combination of color strength (%) of Dyed fabric with Bezathren Red LGG.

fabric with anticipated uniformity on the vat dyed cotton fabric. The K/S value at 480nm for dyed fabric with Bezathren Red LGG vat dye using 2g/L ferrous sulphate + 3g/L combination is 3.88. Hence, the depth of shade of cotton fabric dyed with vat dye using 2g/L ferrous sulphate + 3g/L hydrose combination shows better dyeing effect than that of the vat dyed fabric using 5g/L hydrose (3.15). The depth of shade decrease and some yellowish spots or stains are showed on the dyed fabric surface and in dye solution when the concentration of ferrous sulphate increases and hydrose decreases in the ferrous sulphate and hydrose combination due to under reduction of the vat dyes.

The ferrous sulphate and hydrose combinations as reducing agents give very good dyeing effect on the vat dyed cotton fabric depending on the reduction potential of a dye. Among the different ferrous sulphate and hydrose combinations as reducing agents, the 0.5g/L (10%) ferrous sulphate + 4.5g/L (90%) hydrose combinations with Bezathren Blue RS and 2g/L (40%) ferrous sulphate + 3g/L (60%) hydrose combinations with Bezathren Red LGG vat dye give very good dyeing effect on the

vat dyed cotton fabric because Bezathren Blue RS and Bezathren Red LGG have different Reduction potentials (-860mV and -780mV respectively). In the Table 5 and Figure 3, it is clearly seen that color strength of fabric varies with different combination of ferrous sulphate and hydrose. From the result analysis of Figure 9, it is seen that at ferrous sulphate (2g/L) + hydrose (3g/L) combination color strength value is 123.17%. The value normally increases at higher concentration of hydrose and decrease as ferrous sulphate concentration is increase upto 5g/L. On the other hand, color strength steadily increases at the (0+5) g/L, (0.5+4.5) g/L, (1+4) g/L, (1.5 +3.5) g/L, (2+3) g/L of ferrous sulphate and hydrose combination respectively. From industrial point of view (2+3) g/L ferrous sulphate and hydrose combination is suitable for reducing vat dye solution and also suitable for cost minimization.

On the other hands, 2g/L (40%) ferrous sulphate + 3g/L (60%) hydrose combinations with Bezathren Red LGG vat dye give similar effect on color fastness, effluent parameters and tensile strength of the vat dyed cotton fabric with Bezathren Blue RS using 0.5g/L (10%) ferrous sulphate + 4.5g/L (90%) hydrose combination as reducing agent.

Conclusion

The $\text{FeSO}_4 + \text{Na}_2\text{S}_2\text{O}_4$ combinations give very good dyeing effect on the vat dyeing cotton fabric depending on the reduction potential of a dye. Among the $\text{FeSO}_4 + \text{Na}_2\text{S}_2\text{O}_4$ combinations, 0.5 g/L (10%) $\text{FeSO}_4 + 4.5$ g/L (90%) $\text{Na}_2\text{S}_2\text{O}_4$ and 2 g/L (40%) $\text{FeSO}_4 + 3$ g/L (60%) $\text{Na}_2\text{S}_2\text{O}_4$ combinations give very good dyeing effect on the dyed cotton fabric with Bezathren Blue RS and Red LGG vat dyes respectively. The reduction potential of reducing agent has to be matched with the dye for proper dyeing. The $\text{FeSO}_4 + \text{Na}_2\text{S}_2\text{O}_4$ combinations give very blameless dyeing effect on the vat dyed cotton fabric at 6g/L NaOH with Bezathren Blue RS using 0.5g/L (10%) $\text{FeSO}_4 + 4.5$ g/L (90%) $\text{Na}_2\text{S}_2\text{O}_4$ combination as reducing agent. However, FeSO_4 becomes insoluble and then some yellowish spots or stains are showed on the dyed fabric surface and in dye solution when the concentration of NaOH increases.

A ferrous sulphate and hydrose combination as reducing agent in vat dyeing minimizes pollution problem better than hydrose. Especially, the BOD and COD values in the effluent from dye baths are less than dye baths using hydrose. The amount of H_2S is less than that of hydrose assisted vat dye. This combination as reducing agent in vat dyeing increases the color and tensile strengths of the dyed fabric better than hydrose. The color fastness is not inferior to hydrose assisted vat dyeing.

The commercial cost of ferrous sulphate is similar to that of hydrose, and hence the process cost could be affordable to the textile industries. Since, the effluent parameters are within the limit of environmental aspect, the process is not only useful for the textile wet processing industry, but also to the society in general. However, ferrous sulphate is poorly soluble in an alkaline solution and gets precipitated.

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