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# Eco-Friendly Vat Dyeing of Cotton Using Alkaline Iron (II) Salt as Reducing Agent

Okolju prijazno barvanje bombaža z redukcijskimi barvili z uporabo alkalne železove (II) soli kot redukcijskega sredstva

## Original scientific article/Izvirni znanstveni članek

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## Abstract

Sodium hydrosulphite is used commercially as the reducing agent for vat dyes in the dyeing of cotton. Large amounts of sodium sulphate, sulphur oxyanion and toxic sulphite are produced during the dyeing due to the dissociation of sodium hydrosulphite leading to severe air and water pollution. This research focuses on the use of alkaline iron (II) salt as the reducing agent for vat dyeing on cotton fabrics through a complete replacement of hydrosulphite. The 3<sup>4</sup> Box-Behnken design was used to achieve optimum parameters and statistically analyse the performance of the new reducing system. The results showed that the alkaline iron (II) salt system was relatively effective in developing a comparable dyebath reduction potential, surface colour strength of cotton and colourfastness, if compared to the hydrosulphite-based reducing system. The dyebath stability in the presence and absence of the dye also showed superior results compared to that of the hydrosulphite system. Hence, it can be said that a complete substitution of sodium hydrosulphite with alkaline iron (II) salt is possible. Keywords: cotton, vat dyes, hydrosulphite, ferrous sulphate, solubility, colour strength

## Izvleček

Natrijev hidrosulfit se tržno uporablja kot redukcijsko sredstvo za redukcijska barvila, ki se uporabljajo za barvanje bombaža. Velika količina natrijevega sulfata, žveplovih oksianionov in toksičnega sulfita, ki nastane pri disociaciji natrijevega hidrosulfita, med barvanjem vodi do močnega onesnaženja zraka in vode. Ta raziskava se osredinja na popolno zamenjavo hidrosulfita z alkalno železovo (II) soljo kot redukcijskega sredstva za barvanje bombažne tkanine z redukcijskimi barvili. Za doseganje optimalnih parametrov in statistično analizo učinkovitosti novega redukcijskega sistema je bila uporabljena metoda 3<sup>4</sup> Box-Behnken. Rezultati so pokazali, da je v primerjavi z redukcijskim sistemom na osnovi hidrosulfita sistem z uporabo alkalne železove (II) soli učinkovitejši pri razvijanju primerljivega redukcijskega potenciala barvne kopeli, jakosti obarvanja bombaža in obstojnosti barv. Stabilnost barvalne kopeli v prisotnosti barvila in njeni odsotnosti je bila v primerjavi s hidrosulfitnim sistemom prav tako boljša. Zato lahko rečemo, da je mogoča popolna zamenjava natrijevega hidrosulfita z alkalno železovo (II) soljo.

Ključne besede: redukcijsko barvilo, hidrosulfit, železov sulfat, topnost, jakost obarvanja

# 1 Introduction

Dyeing cellulosic fibres with vat dyes provides excellent colourfastness properties in terms of washing, rubbing and light [1–2]. Vat dyes are practically insoluble in water; dyeing is a somewhat complicated procedure, involving reduction and solubilisation steps to attain the water-soluble form of the dye molecule that has high substantivity on cotton. For the reduction of dyes, a reduction potential from around -750 mV to -1000 mV is required for a proper reduction and to retain the reduced form of the dye throughout the dyeing [3–4]. Sodium hydrosulphite is commercially used as the reducing agent in the dyeing of cotton with vat dyes [5]. During the dyeing, large amounts of sodium sulphate, sulphur oxyanion and toxic sulphite are produced, leading to severe air and water pollution. It is also worth emphasising that sodium hydrosulphite cannot be recycled as it mostly gets dissociated in the bath, and the disposal of exhausted dyebaths and rinsing water causes high costs and various problems with the effluent, viz. high salt load, depletion of dissolved oxygen, problems with nasal nuisance etc [6]. To overcome these problems, attempts have been made to develop alternative eco-friendly reducing systems [7]. Such new systems include electrochemical reduction [8], organic reducing agents such as hydroxyacetone [9], iron (II) salt complexes [10], and natural reducing agents such as sheghar [11], orange peel extract [12] and palm wine [13]. In the electrochemical reduction method, a reducing agent must be added to the reduced dyestuff in order to ensure corresponding stability of the reduced liquor. However, the dyestuff requirement to produce a specific shade is higher [14]. Sodium dithionite can be completely replaced with hydroxyacetone and is biocompatible, yet costlier. Iron (II) salts were widely used in ancient times to reduce vat dyes through the technique known as the "copperas method", where ferrous sulphate and calcium hydroxide were used. However, the dyebath resulted in bulky sediments due to the poor solubility of Fe(OH)<sub>2</sub>. It was found that Fe(OH)<sub>2</sub> produced via the reaction of iron (II) salts with sodium hydroxide can be complexed and taken back into the solution to obtain the desired reduction potential value. Iron (II) salts along with the gluconic acid and NaOH at 60 °C, iron (II) salts in combination with the tartaric or citric acid, triethanolamine and NaOH at room temperature and alkaline enzymes are capable of generating the required reduction potential by solubilising Fe(OH), generated from iron salts [15–19].

The basic problem associated with use of sodium dithionite as the reducing agent can hence be eliminated by introducing alkaline iron (II) salts. In the case of a natural reducing alternative, it is not possible to use sheghar, orange peel extract and palm wine commercially due to their inherent problems such as extraction via steam distillation plant; furthermore, their huge quantity required for the reduction may rise to additional costs [20].

The reduction of vat dyes using iron (II) salt was earlier attempted by many researchers with no practical success due to the very poor solubility of  $Fe(OH)_2$ in water, resulting in an inadequate reduction potential, making the reduction of vat dyes impossible. However,  $Fe(OH)_2$  can be solubilised to a higher extent by increasing the concentration of NaOH to generate a very high reduction potential. Only iron (II) salt and NaOH were used in this study, and for a comparison in performance,  $Na_2S_2O_4$  was used, which is applied in practice in industries. While iron (II) salt is eco-friendly, NaOH at a higher concentration is not as eco-friendly as iron (II) salt, but is still far better than hydrosulphite. In the conventional  $Na_2S_2O_4$  reduction system, NaOH is used as well.

In the present work, the effectiveness of alkaline iron (II) salt was studied regarding the reduction and solubilisation of vat dyes, attempting to substitute sodium hydrosulphite in the vat dyeing technology to formulate a green and eco-friendly process. The extent of the dissolution of the formed  $Fe(OH)_2$ , the reducing agent which is directly proportional to an increase in the reduction potential of the dyebath at various concentrations of alkali was studied and the relationship of the soluble Fe(OH), with a reduction potential of the bath was explored. The solubility pattern of Fe(OH), was studied with a rise in temperature to study the rise in the reduction potential of the bath as well. The dyeing performance in terms of the reduction potential at different stages of the dyeing, change in pH, stability of dyebaths in the presence and absence of the dye and the colourfastness of dyed cotton were studied through a statistical analysis.

# 2 Experimental

## 2.1 Materials

A commercially scoured, bleached cotton fabric (34.5 ends/cm, 27.4 picks/cm), warp and weft yarn linear density 20.3 tex and 30.2 tex, respectively, was used for the purpose of the research.

Sodium hydroxide (AR, 98%), ferrous sulphate (AR, 98%), hydrogen peroxide (30%),  $K_2Cr_2O_7$ , diphenylamine, concentrated  $H_2SO_4$  and distilled water were procured from SD Fine chemicals Limited, Mumbai. Ten different vat dyes of commercial grade were obtained for this study from ATIC and Indian Dyestuff Industries, i.e. Green XBN (Vat Green 1, C.I. 59825), Brown BR (Vat Brown 1, C.I. 70800), Yellow 5G (Vat Yellow 2, C.I. 67300), Gold Orange 3G (Vat Orange 15, C.I. 69025), Red 6B/UD (Vat Red 10, C.I. 67000), Grey M (Vat Black 8, C.I. 71000), Brown R (Vat Brown 3, C.I. 69015), Indigo (C.I. Vat blue 1), Blue BC (Vat Blue 6, C.I. 69825) and Olive Green B (Vat Green 3, C.I. 69500).

#### 2.2 Methods

#### 2.2.1 Dyeing of cotton using sodium hydrosulphite

The dyebaths were prepared with a vat dye (1% on the weight of fabric, owf) pasted with T R oil, hot water being added as well. Sodium hydrosulphite (10 g/l) for the reduction and sodium hydroxide (10 g/l) for the solubilisation were added and stirred well until the vatting of the dye took place over a period of about 15 to 20 min at 60 °C. Cotton was dyed for 60 min at 60 °C at 1 : 25 liquor ratio. The bath was then dropped, dyed cotton was cold washed and oxidised with hydrogen peroxide (1–2 g/l) at 50–60 °C for 20–30 min, followed by soaping and a final wash. This was the so-called control sample.

#### 2.2.2 Dyeing of cotton using alkaline iron (II) salt

The dyebaths were prepared with a vat dye (1% owf), iron (II) salt (1–50 g/l) and sodium hydroxide (5–40 g/l) at 80 °C for 90 minutes at 1 : 25 liquor ratio. In this method, NaOH of specific concentration was dissolved in 100 ml of water in a glass beaker to make an alkaline solution followed by the pouring of NaOH to ferrous sulphate (FeSO<sub>4</sub>) to form insoluble Fe(OH)<sub>2</sub> and the bath turned turbid. The quantity of the dye required to get 1 wt% dye was added in this bath to produce 1% shade. Vatting and dyeing were carried out at 80 °C, keeping two parameters constant with varying iron (II) salt and NaOH concentrations. The dyed fabrics were cold washed thoroughly and oxidised with hydrogen peroxide, followed by soaping and washing.

#### Deciding concentration of FeSO<sub>4</sub> and NaOH

 $FeSO_{4} + 2NaOH = Fe(OH)_{2} + Na_{2}SO_{4}$ (1) Molecular weight of  $FeSO_{4} \cdot 7H_{2}O = 278.08 \text{ g/mol}$ Molecular weight of NaOH = 40 g/mol Equation 1 shows that the reactant 1 mole of ferrous sulphate and 2 moles of NaOH were combined together to form 1 mole of ferrous hydroxide and 1 mole of sodium sulphate. This equation is balanced for the stoichiometric requirement.

278.08 g of  $FeSO_4$  require 80 g of NaOH. Similarly, 1 g of  $FeSO_4$  requires 0.28 g of NaOH. This means that 0.28 g of NaOH is required for the stoichiometric balance, which has no effect on the alkalinity in the dyebath. The addition of extra NaOH into the dyebath increases alkalinity, which is the major requirement in the alkaline iron (II) salt system. Iron (II) salt (1–50 g/l) was selected based on our previous investigations of iron (II) salt along with enzymes, ligand and sodium hydroxide used in vat dyeing.

#### 2.3 Statistical analysis of dyeing process

The Box-Behnken design was used to study colour strength (K/S) as a response for cotton dyed with alkaline iron (II) salt for the optimisation of process parameters. Colour strength (K/S) is expressed in terms of the Kubelka-Munk equation as follows:

$$\frac{K}{S} = \frac{\text{Co} - \text{efficient of absorption}}{\text{Co} - \text{efficient of scattering}} = \frac{(1 - R)^2}{2R}$$
(2),

where *R* stands for the reflectance of the specimen. The Box–Behnken design optimises the number of experiments to be performed to ascertain possible interactions between the studied parameters. This included identifying the best suitable combinations of the levels and parameters to achieve a better response equivalent to that obtained in the conventional vat dyeing system. Four factors, i.e. concentrations of iron (II) salt (A), NaOH (B), dyeing temperature (C), time (D), with respective coded values are shown in Table 1.

Using these four factors, each with three levels, the  $3^4$  Box-Behnken design was run to obtain a set of data, consisting of 27 runs with three replicates at the central point. The Response Surface Methodology (RSM) was applied to the experimental data using statistical software, Design Expert 7. The results were analysed using response surface plots and equations were formed for a response at 95% confidence level. Response surface figures were analysed to understand the effect of each parameter (factor) on colour strength (*K*/*S*). A regression equation was formed accordingly. A quadratic model with four independent factors was used to analyse

0.1.14		Levels					
Coded factor	Factors (Independent variables)	(low)	(medium)	(high)			
А	Ferrous sulphate	-1	0	+1			
В	Sodium hydroxide	-1	0	+1			
С	Temperature	-1	0	+1			
D	Time	-1	0	+1			

Table 1: Input with coded value

the relationship of colour strength (*K*/*S*). Model accuracy was verified to measure the goodness of fit to the model using the coefficient of determination ( $\mathbb{R}^2$ ). When  $\mathbb{R}^2$  approaches unity, the empirical model fits the actual data. P-values lower than 0.05 were considered statistically significant. The lack of fit was analysed to check the model accuracy. The regression equation and response surface figures were used to predict the optimised combination of factors that result in maximum colour strength (*K*/*S*) at optimised values.

#### 2.4 Evaluation of dyebath and dyed samples

The status of the dyebath reduction was evaluated for the reduction potential as well as for pH at various stages of dyeing, i.e. in a blank reduction bath, after the reduction of the dye and at the end of dyeing, using a digital pH metre and a digital combined oxidation reduction potential (ORP) metre (Century Instruments, India), respectively. Cotton samples dyed in both the hydrosulphite- and alkaline iron (II) salt-based dyebaths were evaluated for colour strength (K/S) using Datacolor Check Spectrophotometer (Data-colour International, US). Wash- and lightfastness of dyed cotton were assessed according to respective AATCC standards, i.e. AATCC TM61-2007 (wash) using a wash-fastness tester (RBC Electronics, Mumbai) and AATCC TM16-2004 (light) using an ATIRA lightfastness tester (Paresh Engineering Works, Ahmedabad). The tensile strength of dyed fabrics was assessed according to ASTM D5035 using a universal testing machine (Aimil, Delhi).

#### 2.5 Evaluation of dyebath stability

Reduction baths were prepared with hydrosulphite along with NaOH and alkaline iron (II) salt separately. To study bath stability in the absence of the dye, blank reduction baths were stored for 0 h, 1 h, 2 h, 4 h, 8 h, 12 h and 24 h. The reduction potential of these baths was evaluated after specific time of storage followed by the addition of a Vat Green XBN dye (1% owf) and the dyeing of cotton in these baths. The changes in the reduction potential and pH at each stage were noted. To study the reduction potential of stored reduced dyebaths towards successful dyeing, hydrosulphite- and alkaline iron (II) salt-based reduced dyebaths along with the dye were prepared and stored for up to 24 h prior to the dyeing.

# 2.6 Estimation of colour strength after HCl treatment

The surface colour strength (*K*/*S*) of the control sample was evaluated as usual. In iron (II) salt-based baths, iron precipitated on dyed cotton during the dyeing and the hues changed. Precipitated iron was removed from the dyed samples with a treatment with HCl (10% w/v) at 60 °C for 10–15 min. The surface colour strength (*K*/*S*) was analysed before and after the removal of iron using a computer colour matching spectrophotometer.

## 2.7 Analysis for solubility of Fe(OH),

Ferrous hydroxide,  $Fe(OH)_2$ , is a strong reducing agent; however, it remains mostly insoluble in water [21]. It can be partly solubilised in an alkaline medium though not adequately for the reduction of the dye as the desired solubility can be achieved with an increase in temperature and concentration of alkali. The solubility of ferrous iron present in the reduction bath can be evaluated with titration with a standard solution of potassium dichromate [22].

In titration with a standard solution of  $K_2Cr_2O_7$ , the volume of the oxidant ( $K_2Cr_2O_4$ ) completely oxidises ferrous iron Fe<sup>2+</sup> to ferric iron (Fe<sup>3+</sup>) and  $K_2Cr_2O_7$  itself undergoes a reduction due to a high reduction potential, gets converted to  $Cr^{3+}$ , which is green in colour even after the equivalence point. To identify the equivalence point, 3–5 drops of diphenylamine (E<sup>0</sup>Red = 760 mV were added as an internal indicator [23]. In order to prevent the oxidation of diphenyl-

amine prior to the oxidation of  $Fe^{2+}$ , phosphoric acid was added, which reduces the reduction potential of iron couple from 770 mV to 440 mV. Diphenylamine was used as an indicator. At the end, the addition of excess dichromate oxidised diphenylamine to diphenyl benzidine, which developed a deep bluish violet colour.

A standard potassium dichromate solution was prepared by weighing out potassium dichromate (2.45 g)into a 500 ml standard flask and dissolved in a small volume of distilled water to make 0.1 N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution. An acid mixture was prepared by mixing up 100 ml of phosphoric acid with 300 ml of conc.  $H_2SO_4$  in a reagent bottle. Diphenylamine solution was prepared by dissolving 1 g of diphenylamine in 100 ml of conc.  $H_2SO_4$ . Ferrous iron can be standardised by rinsing the burette with a K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution and taking the K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution up to the zero mark of the burette. 10 ml of the ferrous solution was pipetted out into a 250 ml conical flask, 2.5 ml of acid mixture and 1-2 drops of the diphenylamine indicator were added. The resulting solution was titrated with 0.1 N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> until a blue violet colour was obtained.

## 3 Results and discussion

## 3.1 Dyeing of cotton with sodium hydrosulphite

Cotton was dyed with ten different vat dyes (1% owf) using hydrosulphite and NaOH (10 g/l each), followed by the oxidation with  $H_2O_2$ . The *K/S* of dyed cotton was found to be 22.7 at the maximum wavelength ( $\lambda_{max} \sim 630$  nm). The range of pH and reduction potential were found to be 12.2–12.8 and –780 to –880 mV, respectively, at various stages of dyeing.

3.2 Dyeing of cotton with alkaline iron (II) salt To study the reduction potential of the new alkaline iron (II) salt system for successful dyeing of cotton, dyeing factors were initially kept within a certain range in terms of the  $FeSO_4$  and NaOH concentration, temperature and time. Colour strength (*K/S*) values were fed into to the Box-Behnken design against different factor-level combinations.

#### 3.2.1 Selection of factors and levels for statistical analysis

To decide on the effective FeSO<sub>4</sub> and NaOH concentrations, dyebaths were prepared with a Vat Green XBN dye (1% owf), FeSO<sub>4</sub> (1–50) g/l, NaOH (8–50) g/l, temperature of vatting and dyeing remaining constant at 80 °C with the dyeing time of 1 hour. The combined effect of FeSO, and NaOH on K/S is shown in Table 2; temperature and time were kept constant. The starting NaOH concentration was 8 g/l. The increase in the alkali concentration was responsible for the solubilisation of Fe(OH), in the dyebath, which in turn caused an increase in the colour yield (K/S). However, beyond the concentrations of sodium hydroxide and FeSO<sub>4</sub> at 30 g/l each, there was no further improvement in the colour strength of dyed cotton. Therefore, the FeSO<sub>4</sub> concentration at 30 g/l was selected for a further study with a variation in the alkali concentration from 20 to 40 g/l.

To initially assess the effective NaOH concentration, dyebaths were prepared in the same way, i.e. Vat Green XBN dye (1% owf),  $FeSO_4$  (30 g/l), NaOH (20–40 g/l), temperature of vatting and dyeing remaining constant at 80 °C with the dyeing time of 1 hour. The effect of the NaOH concentration on *K/S* is shown in Table 3, where it can be seen that the NaOH concentration (level) showed a positive response in a statistical analysis within the range from 26 g/l to 28 g/l.

$N_{2}OH(\alpha/l)$		<i>K/S</i> at various concentrations (g/l) of $FeSO_4$											
NaOH (g/l)	1	5	10	20	30	40	50						
5	-	-	-	-	-	-	-						
10	-	-	-	2	2.4	2.8	2.2						
20	-	-	2	5	6	6.5	6.5						
30	-	-	2.8	13	16	15.3	13						
40	-	-	2	11	13	12.7	13.2						
50	-	-	2	11	13	12.8	12						

Table 2: Analysis of effective concentration of FeSO, and NaOH on K/S

NaOH (g/l)	Coloure strength ( <i>K</i> / <i>S</i> )
20	6
22	8
24	16
26	17
28	16.7
30	16
32	15
34	15.2
36	14.8
38	14.2
40	13

*Table 3: Influence of effective NaOH concentration on K/S* 

## Influence of temperature

The vatting and dyeing temperatures were maintained at 80 °C to see if this has any influence on K/S. It was observed that the K/S increases with an increase in temperature from 30-90 °C (Figure 1). Dyeing is usually an exothermic process, i.e. heat releasing. The interaction between the dye and fibre is stronger than that of between the dye and water molecules in a solution. As the dyeing temperature increases, aggregates gradually break up through the absorption of heat; hence, more individual molecules are available for a penetration into the fibres. The exhaustion thus increased with an increase in temperature very slowly from 30-40 °C, beyond which the rate of the increase was uniformly high from 40-90 °C. The increase in colour strength with temperature was mainly a consequence of the breaking down of dye aggregates and the increase in the solubility of Fe(OH)<sub>2</sub>.



*Figure 1: Effect of temperature on surface colour strength* (*K*/*S*)

#### Influence of time

The time of dyeing was 30 min, 60 min, 90 min, 120 min, 150 min and 180 min, with other parameters remaining unchanged. The effect of the dyeing time on K/S is shown in Figure 2. It was observed that K/S increased with an increase in the dyeing time up to 60 min beyond which there was no improvement in K/S till 120 min, succeeded by progressive falling probably due to an increase in the stripping of dyes. Consequently, for a further statistical study, the selected range of the dyeing time was 60 min, 90 min and 120 min.



Figure 2: Influence of time on colour strength

#### 3.2.2 Statistical analysis

The Box-Behnken design was run with the factors and levels of different parameters (cf. Table 4), thus generating 27 runs (cf. Table 5). A cotton fabric was dyed in these baths in the same manner as used in the Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> system and the *K/S* of the dyed specimen was evaluated. It was observed that the range of K/S was 12.6–21.8 and the highest K/S was observed if the bath was prepared according to the 27<sup>th</sup> run, i.e. FeSO<sub>4</sub> (30 g/l), NaOH (27 g/l), temperature (90 °C) and time (120 min) as detailed in Table 5.

The dyed specimen obtained through the run no. 27 showed the maximum K/S value at higher temperature and longer time, whereas the run no. 10 showed a slightly lower K/S value at shorter time, which would be preferred from the economical point of view. Obviously, the parameters of the run no. 10 were selected for a further study.

Coded factor	T (I	Level					
	Factors (Independent variables)	Low (-1)	Medium (0)	High (+1)			
А	FeSO <sub>4</sub> (g/l)	25	30	35			
В	NaOH (g/l)	26	27	28			
С	Temperature (°C)	60	75	90			
D	Time (min)	60	90	120			

Table 4: Factors and actual levels for dyeing with alkaline iron (II) salt

Table 5: Box-Behnken experimental design	$layout\ and\ observed\ response$
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Run	FeSO <sub>4</sub> (g/l)	NaOH (g/l)	Temperature (°C)	Time (min)	K/S	Standard deviation
1	30	28	75	120	14.2	0.2
2	35	28	75	90	15.2	0.264
3	30	27	75	90	17.2	0.264
4	30	27	60	120	13.9	0.251
5	35	27	75	120	18.6	0.152
6	30	26	60	90	13.8	0.173
7	35	27	60	90	12.9	0.208
8	25	27	60	90	14.5	0.1
9	25	27	75	120	16.5	0.2
10	30	27	90	60	21.2	0.115
11	30	27	75	90	18.6	0.288
12	30	27	75	90	18.8	0.1
13	30	28	60	90	14.8	0.3
14	30	28	90	90	19.6	0.1
15	35	26	75	90	20.2	0.1
16	25	27	75	60	14.6	0.173
17	30	26	90	90	21.4	0.351
18	35	27	75	60	17.4	0.152
19	25	28	75	90	16.8	0.4
20	25	26	75	90	15.4	0.3
21	30	28	75	60	14.9	0.1
22	30	27	60	60	12.6	0.2
23	35	27	90	90	21.6	0.3
24	25	27	90	90	20.1	0.057
25	30	26	75	60	13.6	0.1
26	30	26	75	120	19.6	0.3
27	30	27	90	120	21.8	0.2

## 3.3 Influence of dyeing parameters on K/S

ANOVA is a statistical technique that subdivides the total variation in a set of data into component parts associated with specific sources of variation to test hypotheses on the parameters of the model. The Box-Behnken design was used to analyse the effect of process parameters, i.e. concentrations of FeSO<sub>4</sub>, NaOH, and temperature and time, on K/S. All main effects, two factors interaction and the cubic effect with R<sup>2</sup> ~ 0.94 obtained using ANOVA are presented in Table 6. R<sup>2</sup> represents the proportion of variation in the response data that can be explained by the fitted model. Therefore, the higher the R<sup>2</sup>, the better the model. The model was significant at 95% confidence level, when the value of probability > F' was less than 0.05. The ANOVA table also shows a term of residual error, which measures the amount of variation in the response data left unexplained by the model. The lack of fit term in the residual indicates the variation due to model inadequacy. All p-values for the lack of fit (larger than 0.05 for all responses) indicate that the model adequately fits the data. In other words, the form of the model chosen to explain the relationship between the factors and the response is correct and all the prerequisites associated with the use of ANOVA are met as well. The concentrations of

 $FeSO_4$ , NaOH, temperature and time were significant model factors, the model equation in coded form being shown in equation 3.

$$\begin{split} K/S &= -1248 + 9.32 \times A + 73.89 \times B + 1.19 \times C + \\ 1.82 \times D - 0.32 \times A \times B + 0.01 \times A \times C - \\ 1.16 \times A \times D - 0.04 \times B \times C - 0.05 \times B \times \\ D - 3.88E - 004 \times C \times D - 0.02 \times A^2 - 1.04 \\ \times B^2 - 1.85E - 004 \times C^2 - 1.24E - 003 \times D^2 \end{split}$$

where different values of A, B, C, D are presented in Table 4. A is the dimensionless number taken from Table 4 neglecting the unit, i.e. considering the absolute minimum values, A = 25, B = 26, C = 60 and D = 60. The same is true for the intermediate and maximum dimensionless values of A, B, C and D as shown in Table 4.

This equation can predict the theoretical *K/S* of dyed specimens for given dyeing parameters. Subtracting non-significant factors from equation 3 having p-value beyond 0.5, i.e. AD, CD and C<sup>2</sup>, the final equation stands to:

$$K/S = -1248 + 9.32 \times A + 73.89 \times B + 1.19 \times C$$
  
+ 1.82 × D - 0.32 × A × B + 0.01 × A ×  
C - 0.04 × B × C - 0.05 × B × D - 0.02 ×  
A<sup>2</sup> - 1.04 × B<sup>2</sup> - 1.24E-003 × D<sup>2</sup> (4).

Source	Sum of squares	df	Mean square	F value	p-value Prob > F	Significance
Model	213.42	14	15.24	14.69	< 0.0001	Yes
A – Iron(II)salt	5.33	1	5.33	5.14	0.0427	
B – NaOH	6.02	1	6.02	5.80	0.0330	
C – Temp.	155.52	1	155.52	149.83	< 0.0001	
D – Time	8.84	1	8.84	8.52	0.0129	
AB	10.24	1	10.24	9.87	0.0085	
AC	2.40	1	2.40	2.31	0.1541	
AD	0.12	1	0.12	0.12	0.7371	
BC	1.96	1	1.96	1.89	0.1945	
BD	11.22	1	11.22	10.81	0.0065	
CD	0.12	1	0.12	0.12	0.7371	
A^2	1.38	1	1.38	1.33	0.2717	
B^2	5.83	1	5.83	5.62	0.0354	
C^2	9.259E-003	1	9.259E-003	8.920E-003	0.9263	
D^2	6.70	1	6.70	6.45	0.0259	
Residual	12.46	12	1.04			
Lack of fit	10.94	10	1.09	1.44	0.4783	No
Pure error	1.52	2	0.76			
Cor total	225.88	26				

Table 6: ANOVA table for K/S

# 3.3.1 Influence of FeSO<sub>4</sub> and NaOH concentrations on K/S

The combined effect of  $FeSO_4$  and NaOH concentrations on *K/S* at moderate time and temperature is shown in Figure 3a. A lower concentration of NaOH (26 g/l) and high concentration of  $FeSO_4$  (35 g/l) resulted in maximum *K/S*, i.e. 21.8. At a lower concentration of NaOH, decreasing the concentration of  $FeSO_4$  resulted in a decrease in the colour strength (*K/S*) of cotton. At a higher concentration of NaOH, there was an increase in the *K/S* value up to a certain limit after which it decreased with a further increase in the  $FeSO_4$  concentration. An increased concentration of  $FeSO_4$  might decrease the concentration of NaOH in the dyebath due to the formation of insoluble  $Fe(OH)_2$  affecting the

solubility of the reduced vat. A lower concentration of NaOH had a positive effect on *K/S*. Additional NaOH might resist the diffusion of particles through fibre pores.

#### 3.3.2 Influence of FeSO, and temperature on K/S

The combined effect of  $\text{FeSO}_4$  and temperature on K/S at moderate NaOH and time is shown in Figure 3b. A higher  $\text{FeSO}_4$  concentration and temperature resulted in maximum K/S, i.e. 21.8. At lower temperature, decreasing the  $\text{FeSO}_4$  concentration, the K/S value increased, whereas at high temperature, decreasing the  $\text{FeSO}_4$  concentration resulted in decreased K/S. At lower temperature, the activation energy of dyeing was too low to solubilise ferrous hydroxide, resulting in decreased K/S.



Figure 3a: Effect of interaction of iron (II) salt and NaOH on K/S



Figure 3b: Effect of interaction of iron (II) salt and NaOH on K/S

#### 3.3.3 Influence of FeSO₄ and time on K/S

The combined effect of  $FeSO_4$  and time on K/S at moderate NaOH and temperature is shown in Figure 3c. A higher concentration of  $FeSO_4$  and moderate time resulted in maximum K/S, i.e. 21.8. At a higher as well as at a lower concentration of  $FeSO_4$ , the K/S value showed an increasing trend for moderate time and went further on decreasing. At shorter and longer times, the K/S value showed an increasing trend with an increase in the concentration of  $FeSO_4$ . At a higher concentration of  $FeSO_4$ , the vat dye completely diffused into fibre pores at moderate time; additional time may further reduce this effect. Longer dyeing time may possibly reduce the activation energy required for the absorption and fixation of the dye on fibre surfaces.

#### 3.3.4 Influence of NaOH and time on K/S

The combined effect of NaOH and time on K/S at moderate concentration of FeSO<sub>4</sub> and temperature is shown in Figure 3d. A low concentration of NaOH and longer time resulted in maximum K/S, i.e. 21.8. At shorter time with increased NaOH concentration, there was an increase in the K/S value up to a certain limit succeeded by a decrease regardless of a further increase in the NaOH concentration. At longer time, there was a decrease in the K/S value with an increase in the NaOH concentration. At a lower concentration of NaOH, there was an increase in K/S with time and at a higher concentration of NaOH, there was a decrease in K/S with time. A longer time of the dyebath by decreasing the alkali concentration may achieve the desired reduction potential that increases colour strength.



Figure 3c: Effect of interaction of iron (II) salt and time on K/S



Figure 3d: Effect of interaction of NaOH and time on K/S



Figure 3e: Effect of interaction of time and temperature on K/S

#### 3.3.5 Influence of temperature and time on K/S

The combined effect of temperature and time on K/S at a moderate concentration of FeSO<sub>4</sub> and NaOH is shown in Figure 3e. Higher temperature and moderate time resulted in maximum K/S, i.e. 21.8. At higher as well as at lower temperature, there was an increase in the K/S value up to a certain point of time after which it decreased despite a further increase in time. A longer time period at higher temperature may take additional water due to the exhaustion of the dyebath, which changes ferrous iron to ferric iron, resulting in reduced reduction potential. For a shorter as well as a longer amount of time, there was an increase in the K/S value with an increase in temperature.

## 3.4 Influence of NaOH on reduction potential and pH

In the alkaline iron (II) salt system, 0.84 g of NaOH was taken for the stoichiometry requirement. At that time, pH was neutral as well. A further addition of extra NaOH was responsible for an increase in the solubility of ferrous hydroxide, which increased the reduction potential. Fe(OH), solubility increased with an increase in the alkalinity at a certain limit. It was calculated that 3 g Iron (II) salt required 0.84 g of NaOH for the stoichiometric requirement. Additional NaOH was used to maintain the alkaline medium. In this study, 1.8 g NaOH was used for solubilisation. The amount of sodium hydroxide varied in the reaction medium from 0.15 g to 5.65 g. The effect of this variation on the evolution of the redox potential of the medium and pH was investigated. The experimental results are shown in Figure 4.

It can be observed that at sodium hydroxide amounting to 0.15 g to 0.75 g, there was a slow increase in the redox potential and pH, respectively. The increase in the amount of sodium hydroxide led to a rapid jump of the redox potential and pH. At a further addition of 2.25 g of NaOH, the reduction potential and pH remained quasi stable. Therefore, it appears that the alkali addition increased the rate of the vat reduction with iron (II) salt.



*Figure 4: Effect of alkali concentration on pH and reduction potential of dyebath* 

# 3.5 Stability of reduction baths 3.5.1 In absence of dye

The stability of reduction baths was studied in the absence of the dye for up to 24 hours with hydrosulphite and the alkaline iron (II) salt system. Reduction baths were prepared and covered; the reduction potential and pH of the baths were checked after being stored for a specific period of time. Vat

		Reduction potential, U (mV) and pH at various stages											
Time	Be	fore redu	ction of o	dye	After reduction of dye				After completion of dyeing				
(h)	Hy	dro	Iro	n II	Hydro		Iron II		Hydro		Iron II		
	pН	U (mV)	pН	U (mV)	pН	U (mV)	pН	U (mV)	pН	U (mV)	pН	U (mV)	
0	12.84	-872	13.95	-708	12.70	-760	13.83	-705	12.40	-748	13.71	-665	
1	12.84	-865	13.94	-718	12.58	-755	13.85	-705	12.28	-750	13.69	-633	
2	12.83	-870	13.96	-711	12.39	-767	13.84	-648	12.19	-720	13.70	-639	
4	12.82	-782	13.93	-705	12.60	-740	13.83	-646	12.20	-730	13.65	-634	
8	12.80	-706	13.94	-713	12.40	-685	13.84	-660	12.34	-640	13.67	-620	
12	12.82	-680	13.94	-704	12.54	-660	13.82	-655	12.32	-610	13.68	-620	
24	12.86	-655	13.92	-696	12.40	-620	13.81	-641	12.27	-580	13.65	-616	

Table 7: Stability of reduction baths in absence of dye

Green XBN (1%) was then added to the baths. The dyeing was carried out, with the results presented in Table 7. There was a progressive drop in U (mV) and pH in both reduction baths with the passage of time. K/S gradually decreased with an increase in storage time in both reduction systems. Hydrosulphite-based reduction baths retained the required reduction potential for up to four hours compared to the alkaline iron (II) salt-based reduction baths in 24 hours.

#### 3.5.2 In presence of dye

Reduction baths with hydrosulphite and alkaline iron (II) salt were prepared, followed by the addition of Vat Green XBN (1%). The baths were covered and stored for up to 24 hours. The results were noted in terms of pH and reduction potential, and are presented in Table 8.

The rate of the fall in the reduction potential was higher in the hydrosulphite system. In contrast, alkaline iron (II) salt-based systems showed a very slow fall in the reduction potential. However, pH remained in both systems at a higher level. Reduced dyebaths showed the maximum colour strength for dyeing at 0–2 hours (cf. Table 9). The hydrosulphite bath showed stability for up to four hours compared to that in the alkaline iron (II) system for 24 hours with a progressive fall in colour strength with time.

## 3.6 Fastness performance

The colourfastness of cotton dyed in the hydrosulphite and alkaline iron (II) salt systems was evaluated. The results are shown in Table 10. The lightfastness of dyed cotton remained very good to excellent and almost the same in both systems for the ten dyes

	Reduction potential, U (mV) and pH at various stages											
<b></b>	В	Before dye	reductio	n		After dye	reduction	n	Afte	r complet	ion of dy	veing
(h)	Hy	dro	Iro	n II	Hy	dro	Iron II		Hy	dro	Iron II	
	pН	U (mV)	pН	U (mV)	pН	U (mV)	рН	U (mV)	рН	U (mV)	рН	U (mV)
0	12.74	-850	13.64	-780	12.60	-865	13.53	-790	12.30	-810	13.34	-770
1	12.74	-810	13.58	-765	12.38	-825	13.46	-775	12.18	-770	13.26	-760
2	12.73	-770	13.47	-760	12.29	-775	13.40	-760	12.09	-760	13.35	-720
4	12.72	-740	13.55	-740	12.5	-735	13.45	-745	12.10	-640	13.29	-730
8	12.70	-690	13.51	-730	12.30	-670	13.36	-740	12.19	-520	13.32	-697
12	12.72	-500	13.55	-725	12.34	-450	13.48	-735	12.12	-400	13.42	-695
24	12.66	-450	13.50	-710	12.2	-400	13.35	-720	12.05	-350	13.24	-685

Table 8: Stability of reduction baths in presence of dye

under study, except for the Yellow 5G dye. Wash fastness, and dry and wet crock-fastness results showed identical, excellent fastness properties for both the hydrosulphite and alkaline iron (II) salt systems, except for the Brown R dye. Overall, the colourfastness of cotton dyed using the alkaline iron (II) salt systems showed comparable performance with the cotton dyed with the hydrosulphite system.

	Colour strength (K/S)									
Time (h)	Sodium hy	drosulphite	Alkaline iron (II) salt							
	Presence of dye Absence of dye		Presence of dye	Absence of dye						
0	22.7	22.6	21.4	21.2						
1	20.2	22.7	21.4	18.9						
2	18.9	20.8	22.12	18.4						
4	15.9	16.4	20.68	16.43						
8	0	0	19.46	16.2						
12	0	0	17.8	15.9						
24	0	0	14.5	13.4						

Table 9: Effect of storage time on K/S in presence and absence of dye

Table 10: Colourfastness of cotton dyed in hydrosulphite and alkaline iron (II) salt systems

	<b>D</b> 1 ·	V	Vash fastness		Crock	fastness	
Vat dye	system	Colour change	Stain on cotton	Stain on wool	Dry	Wet	Light fastness
Durana DD	Hydrosulphite	5	5	5	5	4-5	7
Brown BR	Alk. iron (II)	5	5	5	5	4-5	7
V-lloss 5C	Hydrosulphite	5	5	5	5	5	5
rellow 5G	Alk. iron (II)	5	5	5	5	5	5
California	Hydrosulphite	5	5	5	5	5	7
Gold Orange	Alk. iron (II)	5	5	5	5	5	7
	Hydrosulphite	5	5	5	5	5	7
Ked 6B	Alk. iron (II)	5	5	5	5	4-5	7
Current M	Hydrosulphite	5	5	5	5	5	7
Grey M	Alk. iron (II)	5	5	5	5	4-5	7
D D	Hydrosulphite	5	5	5	5	5	8
Brown K	Alk. iron (II)	5	5	5	5	4-5	7
T. J.	Hydrosulphite	5	5	5	5	4-5	7
Indigo	Alk. iron (II)	5	5	5	5	4-5	7
	Hydrosulphite	5	5	5	5	4-5	8
Blue BC	Alk. iron (II)	5	5	5	5	4-5	8
Olive Green	Hydrosulphite	5	5	5	5	5	7
В	Alk. iron (II)	5	5	5	5	5	7
Cross VDN	Hydrosulphite	5	5	5	5	4-5	8
Green XBN	Alk. iron (II)	5	5	5	5	4-5	8

# 3.7 Comparison of colour strength of treated samples

A comparison was made of the colour strength of the samples dyed with different vat dyes with hydrosulphite, alkaline iron (II) salt system and HCl-treated after the soaping in the alkaline iron (II) salt system. Figure 5 shows that all these dyes showed comparable colour strength in the hydrosulphite and alkaline iron (II) salt system though the HCl-treated samples showed slightly lower colour strength.



*Figure 5: Comparison of K/S obtained as control, reference and HCl-treated* 

In addition to the result without an HCl treatment, there was a slight difference in colour strength between the control and reference sample. The alkaline iron (II) salt system might be used as an alternative reducing agent; however, it gives a non-uniform deeper shade, indicating the deposition of the insoluble dye and insoluble iron on samples. For a brighter and uniform shade, an HCl treatment is required.

## 3.8 Solubility of Fe(OH)<sub>2</sub> 3.8.1 Effect of pH

The effect of alkali on the solubility of  $Fe(OH)_2$  is determined by titrating the standard dyebath solution with  $K_2Cr_2O_7$ .  $Fe(OH)_2$  is insoluble at pH 7; a gradual addition of NaOH increases pH, resulting in the solubility of  $Fe(OH)_2$ . The optimised concentration of alkaline iron (II) salt was taken and pH varied from 7 to 14 by adding NaOH and increasing the solubility of  $Fe(OH)_2$  by up to 1.95 g/l as shown in Table 11.

pН	Solubility of $Fe(OH)_2$ (g/l)
7	0.0143
8	0.27
9	0.55
10	0.83
11	1.11
12	1.39
13	1.67
14	1.95

#### 3.8.2 Effect of temperature in alkaline medium

The solubility of  $Fe(OH)_2$  only by adding NaOH was not adequate for the reduction of the vat dye. At low temperature, the heat or chemical energy is not sufficient for the diffusion or penetration of the dye into fibre pores. The increase in temperature is essential to synergise the reduction potential. The effect of temperature on solubility in an alkaline medium was hence studied.

In Figure 6, it is shown that with an increase in temperature in an alkaline medium, the solubility of  $Fe(OH)_2$  increased, showing a better result in colour strength. An incomplete vat dye reduction was found at lower temperature and a complete dye reduction at higher temperature. At 30 °C, the solubility of Fe  $(OH)_2$  was 1.95 g/l compared to that at 90 °C, which was 3.07 g/l. The amount of total  $Fe(OH)_2$  at iron (II) salt 30 g/l and NaOH 27 g/l was 23.4 g/l, where the amount of soluble  $Fe(OH)_2$  in the dyebath was 3.07 g/l, the rest remaining insoluble.



*Figure 6: Effect of temperature in alkaline medium on solubility of Fe(OH)*,

## 4 Conclusion

In this study, alkaline iron (II) salt was used to replace sodium hydrosulphite in the vat dyeing of cotton. Iron (II) salt forms Fe(OH), in a reaction with NaOH; the former may act as a strong reducing agent. However, due to a very poor solubility of Fe(OH), in lower alkaline pH, its performance as a reducing agent cannot be realised. An increase in the concentration of NaOH increases the solubility of Fe(OH)<sub>2</sub>, thus approaching to a concentration of both chemicals, i.e. FeSO<sub>4</sub> and NaOH, to attain the reduction potential as high as -780 mV, showing the capability to reduce all vat dyes. An increase in temperature enhances the reduction potential of the bath as well. The surface colour strength of cotton remained almost comparable along with colourfastness. The reduction bath stability in the absence and presence of the dye shows maximum performance of hydrosulphite-based baths up to maximum storage time of 4 hours and no dyeing beyond that compared to the stability of alkaline iron (II) salt-based reduction baths till 24 hours with a slight progressive fall in colour strength after 8 hours. Moreover, after the removal of precipitated iron from dyed cotton, a small drop in surface colour strength was observed. It can be summarised that the alkaline iron (II) saltbased reducing system can be a good replacement for hydrosulphite-based vat dyeing processes.

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