JTATM
Journal of Textile and Apparel, Technology and Management

Volume 7, Issue 4, Fall 2012

Sulfur Dyeing With Non-Sulfide Reducing Agents

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ABSTRACT

Sulfur dyeing realized as the most economical and the promising way to obtain heavy shades on cellulosic in industries. Traditional sulfur dyeing is done with sodium sulfide as reducing agent which is the major reason for effluent. In this study we employed reducing sugars for sulfur dyeing and compared with conventional one. The cotton fabric is subsequently dyed with sulfur black and brown dyes using glucose and fructose reducing sugar. Comparable color strength with good wash fastness is observed with these non-sulfide reducing agents.

Keywords: sulfur dyeing, color strength, wash fastness

Introduction

Sulfur dyes hold promising, in the coloration of cellulosic fibers, particularly for cotton and polyester/cotton blends. Sulfur dyes offer an economical method of obtaining good color strength and acceptable fast dyeing on cellulosic substrate with medium to dark shades. The percentage share of sulfur dye in the cellulosic dyeing is about 70%. These dyes are available in various forms like water insoluble powder, dispersed powder, water soluble form and pre-reduced ready to use form[1, 4, 6, 7].

Sulfur dyes are characterized by the disulfide and polysulfide bonds (- S-S -) n between aromatic residues containing thiazole, thiazone, or thianthrene as the chromophores[1,3,4,7,8]. Initially this is the insoluble (pigment) form of sulfur dyes and the application of these dyes involves the reduction of this disulfide linkage in dye molecules to water soluble leuco form having high substantivity to cellulosic fibers. The substantivity between the dye anion and the substrate arises from hydrogen bonding and ion-dipole and dispersion forces and the different dyes have different exhaustion[4, 12]. The exhaustion of the dye is promoted by addition of electrolyte, usually sodium chloride (NaCl) and high temperature. After complete exhaustion of dye onto the substrate, the reduced, adsorbed dye is reconverted in to insoluble form in situ within the fiber by air or chemical oxidation[7, 8, 9, 10].

In recent years environment concern have brought sulfur dyes in to disrepute because of significant environmental problem with this sulfur dyeing process. Sodium sulfide is the largest consumed reducing agent; around 90% of all sulfur dyes are being reduced by sodium sulfide has adverse effect on environment[3, 11]. A part of sodium sulfide is used for reduction but the excess sulfide remains in discharged effluent, the concentration of which depends on the dyeing method and the applied depth. The discharge of sulfides is only permissible in very small amounts because of the danger to ecological & human health from liberated hydrogen sulfide, corrosion of sewerage systems and is often associated with high pH and unpleasant odours[1, 2, 11].

The modification in the process of application of sulfur dyes to replace the reduction by sodium sulfide plus caustic soda with non-sulfide eco-friendly reducing systems that should give similar color value with economic considerations. Some alternative reducing systems like sodium dithionate, thiourea dioxide, and indirect cathodic reduction have been tried for the reduction of sulfur dyes. These alternative methods cannot be used industrially due to inconsistent results and higher cost[1, 2]. Reducing sugars like glucose with sodium hydroxide or sodium carbonate at high temperature also can sufficiently reduce the sulfur dyes[2]. So, different researchers employed various sugars like glucose, fructose, molasses, invert sugar, arabinose galactose etc. as reducing agent for sulfur dyes. They tried to optimize the sugars in terms of their redox potential with different sulfur dyes[3, 5, 11, 13].

In this paper we employed glucose and fructose as reducing agents on two different sulfur dyes and examined their performance in comparison with traditional sulfide based sulfur dyeing on the basis of color strength and wash fastness. In addition we tried to optimize the sugar concentration and reduction temperature using design of experiment.

Material and Methods

The fabric used was 100% cotton having GSM-146, EPI×PPI-57×33 and 30 Ne warp & weft count. CI Sulfur Black 1 and CI Sulfur Brown M dyes were procured from Clariant. The-non-sulfide reducing agents used for the reduction of sulfur dyes were D (-) glucose and D (-) fructose. Instead of this sodium sulfide, sodium hydroxide, sodium carbonate and sodium chloride were used. All the chemicals used were of LR grade.

The required amount of dyestuff (pigment form) was mixed with varying concentrations of reducing sugar and twice the concentration of sodium hydroxide and then dissolved in 50 ml of water. The solution was heated to 70°C for 15 min to partially reduce the dye. A total of 7 gm of cotton fabric and the reduced dye solution (40ml) were added to the stainless steel, sealed dye pots, and the total volume was made up to a Material to Liquor ratio (MLR) of 1:40. Samples were dyed in a laboratory-scale Innolab water bath dyeing machine. The temperature was raised to 95°C at a gradient of 2.0°C min^{-1}, and after 15 min at 95°C, sodium chloride (20 g/l) was added. The dyeing was then continued for a further 30 min at 98°C. After the hold time of 30 min the samples were taken out and rinsed thoroughly in cold water. Then oxidation is done dried in the open air. After that a soaping treatment was given with 1-2 g/l soap solution at 90°-95°C for 15 mins.

The estimation of color values (K/S value) was done using the D65 source and a 10° observer angle on a computerized Premier Colorscan Spectrophotometer. The tensile strength of sample was tested by ASTM D5034-95 using Digital Tensile Strength Tester of Paramount (Maximum Capacity-250 kg) based on uniform rate of loading. After dyeing, the wash fastness was tested in Innolab Washing Fastness Tester by AATCC test method no. 61 and graded according to the AATCC grey scale using spectrophotometer[14].

The Cumulative effect of different reducing agents with concentration and temperature was studied using three variables: type of reducing agent, concentration, and temperature. To minimize the number of trials and to derive maximum significant information, Box Behnken method was used with these three variables at 3 different levels. The effect of these variables was interpreted in terms of color strength (K/S Value) and tensile strength. The experimental design and the 3 levels of three variables are shown below:

Variable	Coded Levels		
	-1	0	+1
Reducing Agent Type	Fructose	Glucose	Na_2S
Concentration(g/l)	0.5	2	3.5
Temperature(°C)	50	70	90

Experimental Design of Box Behnken method

Sample No.	Reducing Agent Type	Concentration(g/l)	Temperature (°C)
S1	-1	-1	0
S2	1	-1	0
S3	-1	1	0
S4	1	1	0
S5	-1	0	-1
S6	1	0	-1
S7	-1	0	1
S8	1	0	1
S9	0	-1	-1
S10	0	1	-1
S11	0	-1	1
S12	0	1	1
S13	0	0	0
S14	0	0	0
S15	0	0	0

The reducing agents are arranged in these three levels according to increasing order of their redox potential[3, 5].

Results and Discussion

Effect of Glucose as Reducing Agent

The glucose was used at different concentrations for the reduction of sulfur dye. Keeping the shade percentage fixed (5%) for both dyes the concentration of glucose was varied from 0.5 g/l to 5 g/l and the results were evaluated in terms of K/S values, tensile strength and wash fastness shown in Table 1.

Table 1. Effect of Glucose sugar

Sample Name	Concentration (g/l)	K/S (600nm)	Tensile Strength (Kg)	Wash Fastness Rating (AATCC)
Na_2S	2	16.89	12.7	1
Na_2S	4	18.52	11.3	1-2
GB1	0.5	10.75	12.7	1-2
GB2	1	13.28	12.4	1-2
GB3	1.5	15.49	12.2	2
GB4	2	16.67	11.7	2
GB5	2.5	17.39	11.3	2-3
GB6	3	17.80	11.5	2-3
GB7	3.5	18.24	11.3	1-2
GB8	4	18.63	11.1	2-3
GB9	4.5	18.78	11.4	1-2
GB10	5	18.81	11.2	2
		K/S (440nm)		
Na_2S	2	13.66	12.9	2
Na_2S	4	15.63	11.5	2
GBN1	0.5	5.33	13.6	3-4
GBN2	1	5.67	12.8	2-3
GBN3	1.5	7.36	13.6	3
GBN4	2	8.77	11.8	3
GBN5	2.5	10.75	12.2	3-4
GBN6	3	12.85	11.8	3
GBN7	3.5	14.41	11.4	2-3
GBN8	4	15.59	11.5	2-3
GBN9	4.5	15.91	11.9	2-3
GBN10	5	16.12	11.7	2

GB-Glucose Sugar Black Dye, GBN-Glucose Sugar Brown Dye

In Table 1 upper part we compared the conventional BLACK dyed samples (Sodium Sulfide as reducing agent) with sample dyed using Glucose as reducing agent.

It can be observed that the color strength is more or less comparable with glucose and sodium sulfide without any significant difference in their tensile strength. Also the washing fastness is some better with the non-sulfide reducing agent as compared to the conventional ones.

The effect of glucose on BROWN dye is shown in lower part of Table 1, comparable and in many cases superior color strength and wash fastness was observed with respect to traditional sulfide based reducing agent.

Effect of Fructose as Reducing agent

Similar to glucose the fructose concentration was varied from 0.5 g/l to 5 g/l for the reduction of both the sulfur dyes. Keeping the shade percentage fixed (5%) the results were evaluated in terms of K/S values, tensile strength and wash fastness shown in Table 2.

Table 2. Effect of Fructose sugar

Sample Name	Concentration (g/l)	K/S (600nm)	Tensile Strength, Kg	Wash Fastness Rating (AATCC)
Na_2S	2	16.89	12.7	1
Na_2S	4	18.52	11.3	1-2
FB1	0.5	11.81	12.8	1-2
FB2	1	14.04	12.7	1-2
FB3	1.5	15.67	13.6	2
FB4	2	17.89	13.1	2
FB5	2.5	18.85	12.8	1-2
FB6	3	20.08	12.7	2-3
FB7	3.5	18.97	12.1	1-2
FB8	4	19.34	12.5	2
FB9	4.5	18.90	12.1	1-2
FB10	5	19.10	12.3	2
		K/S (440nm)		
Na_2S	2	13.66	12.9	2
Na_2S	4	15.63	11.5	2
FBN1	0.5	5.66	11.9	3
FBN2	1	6.89	11.1	1-2
FBN3	1.5	7.36	12.5	1-2
FBN4	2	8.39	11.5	2-3
FBN5	2.5	10.22	12.2	3
FBN6	3	13.33	12.2	3
FBN7	3.5	16.55	11.3	2-3
FBN8	4	17.16	12.1	2
FBN9	4.5	17.48	12.1	1-2
FBN10	5	18.75	11.3	1-2

FB-Fructose Sugar Black Dye, FBN-Fructose Sugar Brown Dye

For both sulfur dyes Fructose also gave comparable color strength in comparison to sulfide based reducing agent. Also a superior wash fastness property without any significant change in tensile strength can be observed with fructose.

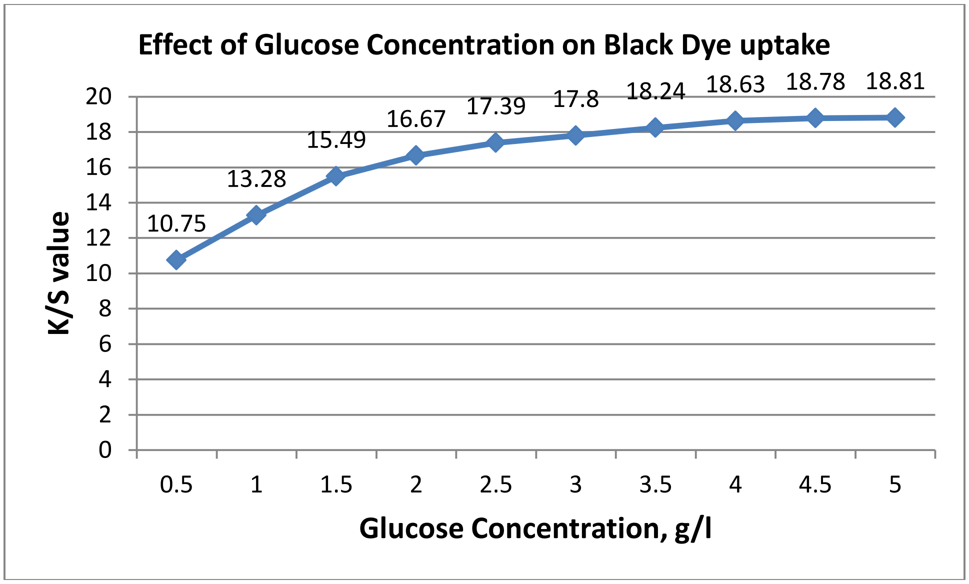


Fig. 1. Effect of Glucose sugar on Sulfur Black Dye

K/S versus reducing sugar concentration plot for glucose and fructose with both sulfur dyes in Fig. 1 to 4 yield similar results; color strength increases with reducing sugar concentration and maximum around an optimum concentration. Further increase in concentration of reducing sugar yield no significant change in color strength.

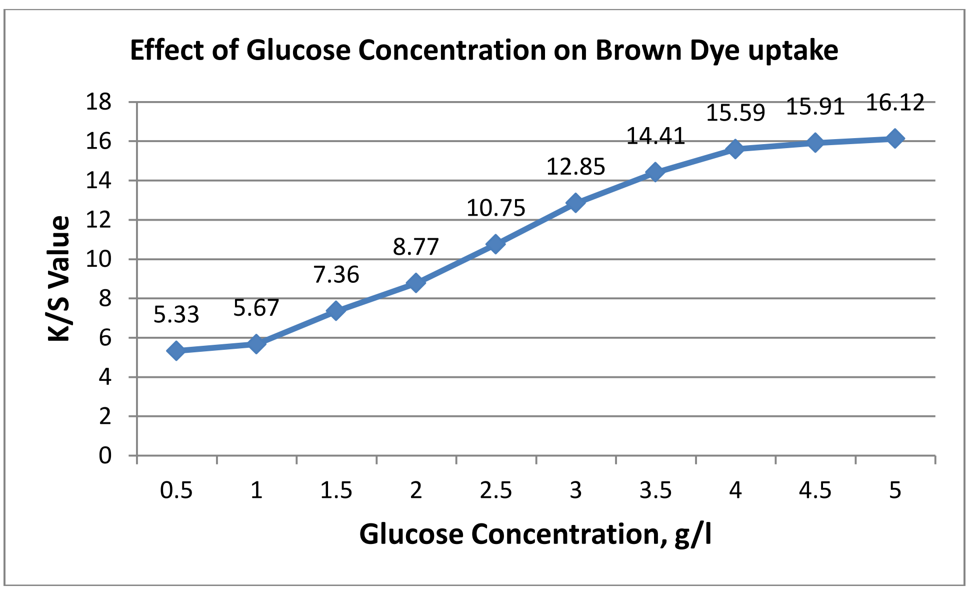


Fig. 2. Effect of Glucose sugar on Sulfur Brown Dye

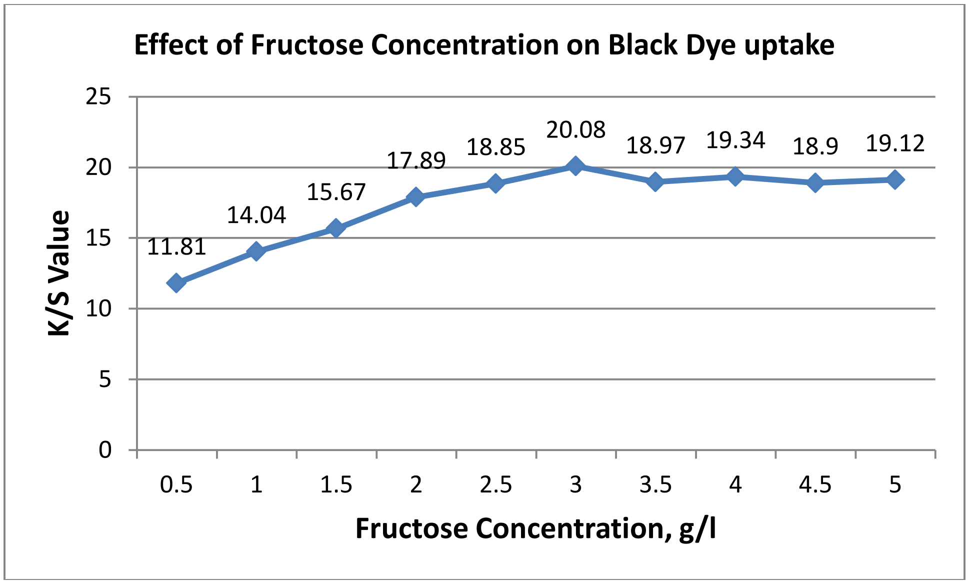


Fig. 3. Effect of Fructose sugar on Sulfur Black Dye

Actually there is an optimum concentration of reducing sugars for dyes where maximum dye uptake achieved, this was discussed by Blackburn and Harvey in terms of optimum redox potential, above and below which the dye molecule is either too large or too fragmented for maximum adsorption and subsequent diffusion. Also the good wash fastness characteristic at similar concentrations support the increased diffusion inside the substrate[3].

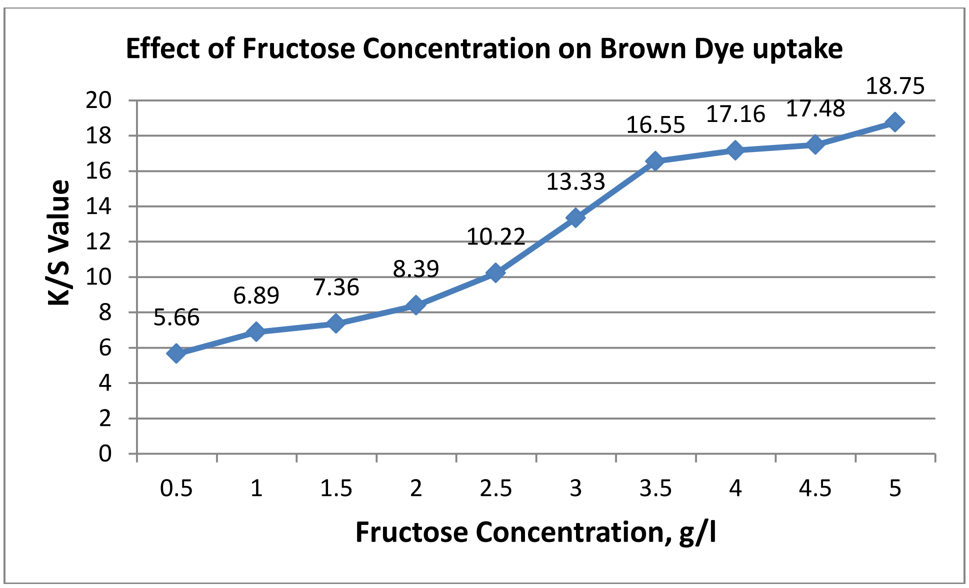


Fig. 4. Effect of Fructose sugar on Sulfur Brown Dye

Cumulative Effect of Reducing Agent, Concentration and Temperature

Design of experiment was used for effective analysis using three variables: Reducing agent type, concentration and reduction temperature. Table-3 shows the experimental results of sulfur black dye with these three different parameters and result was interoperated in terms of K/S value and Tensile Strength.

Table 3. Cumulative Effect of Reducing agent, Concentration and Temperature

Sample No.	Reducing Agent	Concentration (g/l)	Temperature (°C)	K/S Value	Tensile Strength (kg)
S1	Fructose	0.5	70	9.77	12.9
S2	Na_2S	0.5	70	10.23	12.7
S3	Fructose	3.5	70	9.99	12.6
S4	Na_2S	3.5	70	14.71	10.9
S5	Fructose	2	50	14.86	11.2
S6	Na_2S	2	50	15.51	11.3
S7	Fructose	2	90	14.08	11.3
S8	Na_2S	2	90	9.98	11.2
S9	Glucose	0.5	50	9.06	11.1
S10	Glucose	3.5	50	9.81	10.4
S11	Glucose	0.5	90	18.16	11.4
S12	Glucose	3.5	90	14.11	12.9
S13	Glucose	2	70	12.61	11.1
S14	Glucose	2	70	16.23	12.2
S15	Glucose	2	70	18.21	12.8

Statistical Analysis

The result of K/S values were feed into computer software, Syatat 12 and result obtained was:

Dependent Variable	:	DYE UPTAKE		
N	:	15		
Multiple R			:	0.647
Squared Multiple R			:	0.418

These are co-efficients of response surface equation :

Regression Coefficients for Uncoded Factors	
Effect	**Coefficient**
CONSTANT	-14.121
REDUCING AGENT	10.320
CONCENTRATION	6.236
TEMPERATURE	0.325
REDUCING AGENT*REDUCING AGENT	-1.843
CONCENTRATION*CONCENTRATION	-1.185
TEMPERATURE*TEMPERATURE	-0.001
REDUCING AGENT*CONCENTRATION	0.709
CONCENTRATION*TEMPERATURE	-0.040
REDUCING AGENT*TEMPERATURE	-0.059

The response surface equation for dye uptake was obtained using forward step regression procedure. The negative coefficient of a variable in response surface equation indicates that a particular characteristic decreases with the increase in that variable while positive coefficient of the variable indicates characteristic increase with increase in that variable.

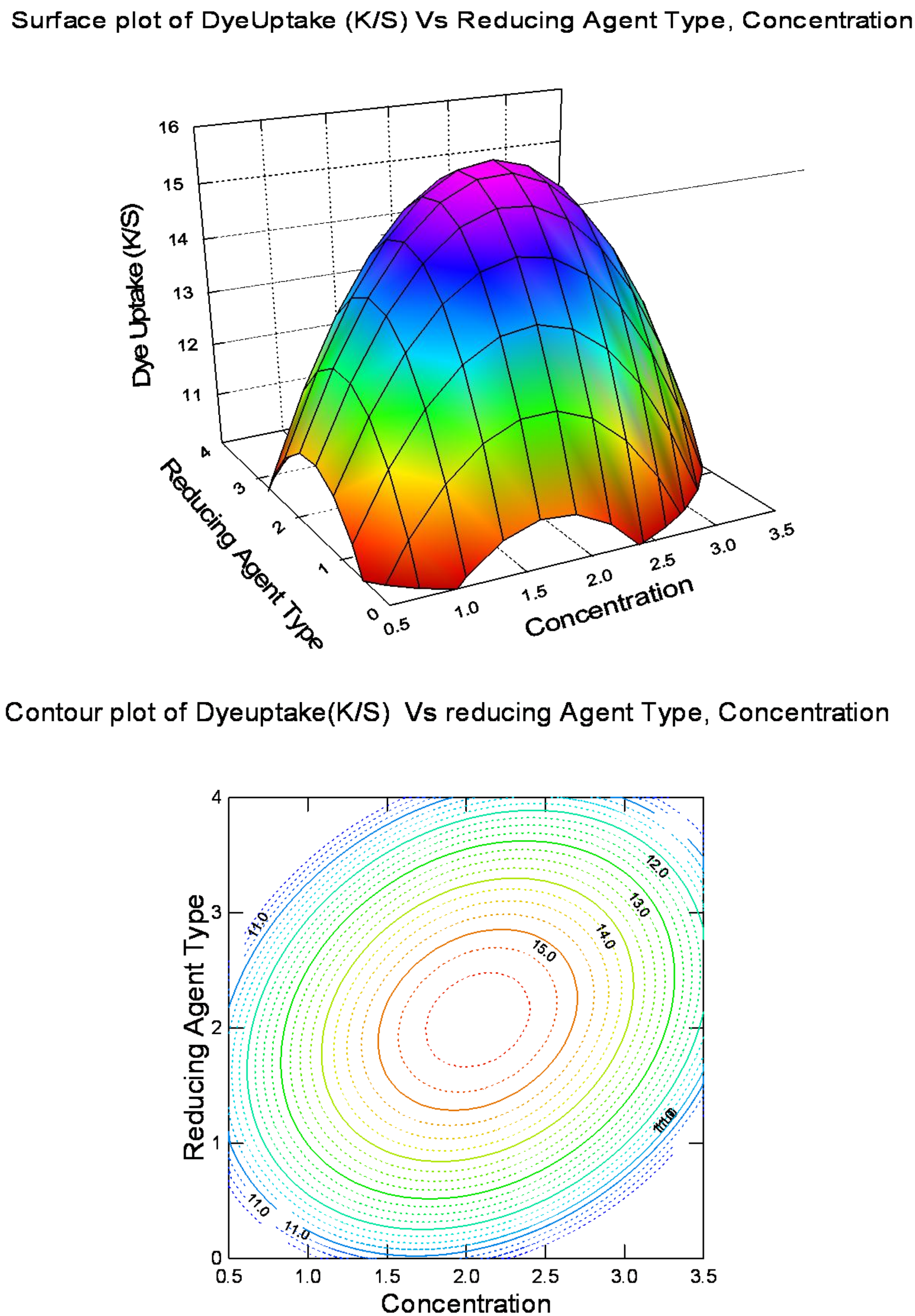
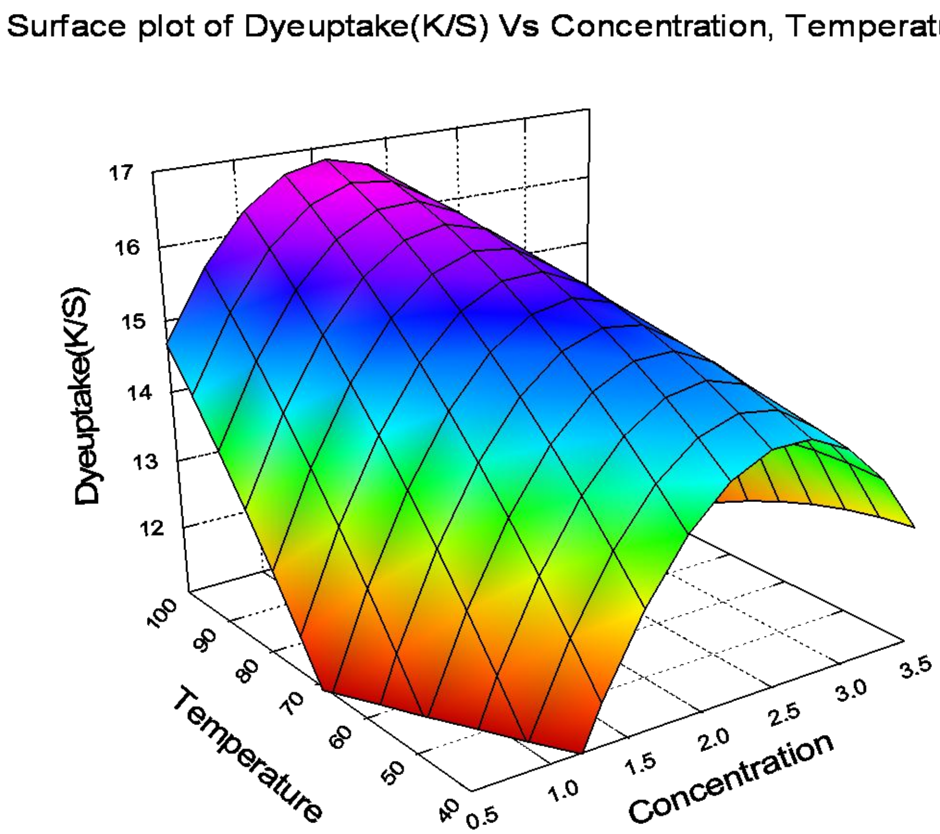


Fig. 5. Surface and Contour plot Dye uptake Vs. Reducing Agent Type, Concentration

The response surface equation of Reducing agent and Concentration on Dye Uptake (K/S) in form of contour and 3-D graph are shown in the Fig-5. The surface and contour plot indicates that with increase in concentration of reducing sugar firstly dye uptake increases and then decreases. Also the dye uptake increase as we move from fructose to glucose and again decrease in conventional Na_2S. Thus, we can conclude that the glucose is effective reducing agent and a concentration of about 1.5-3g/l gives maximum color strength.



The response surface equation of Temperature and Concentration on Dye Uptake (K/S) in form of contour and 3-D graph are shown in the Fig-6. The surface and contour plot indicates good color strength around optimum concentration of 1.5-3g/l and a reduction temperature above 70°C, because a high reduction temperature reduces dye more effectively.

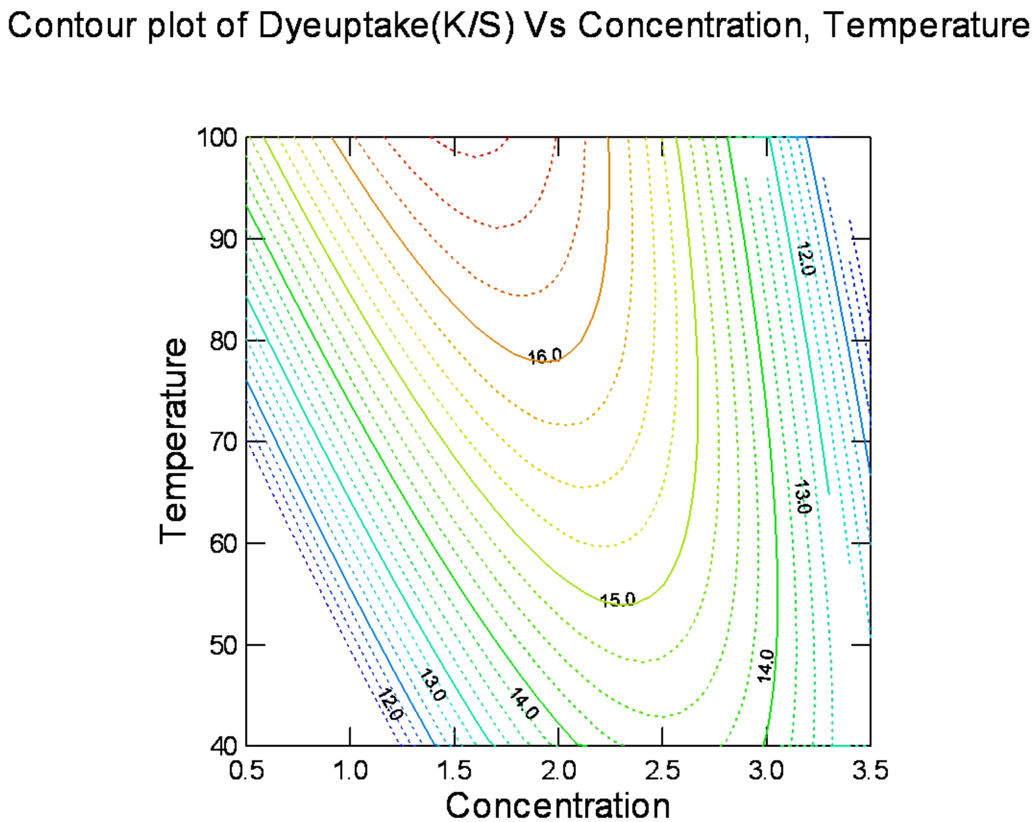
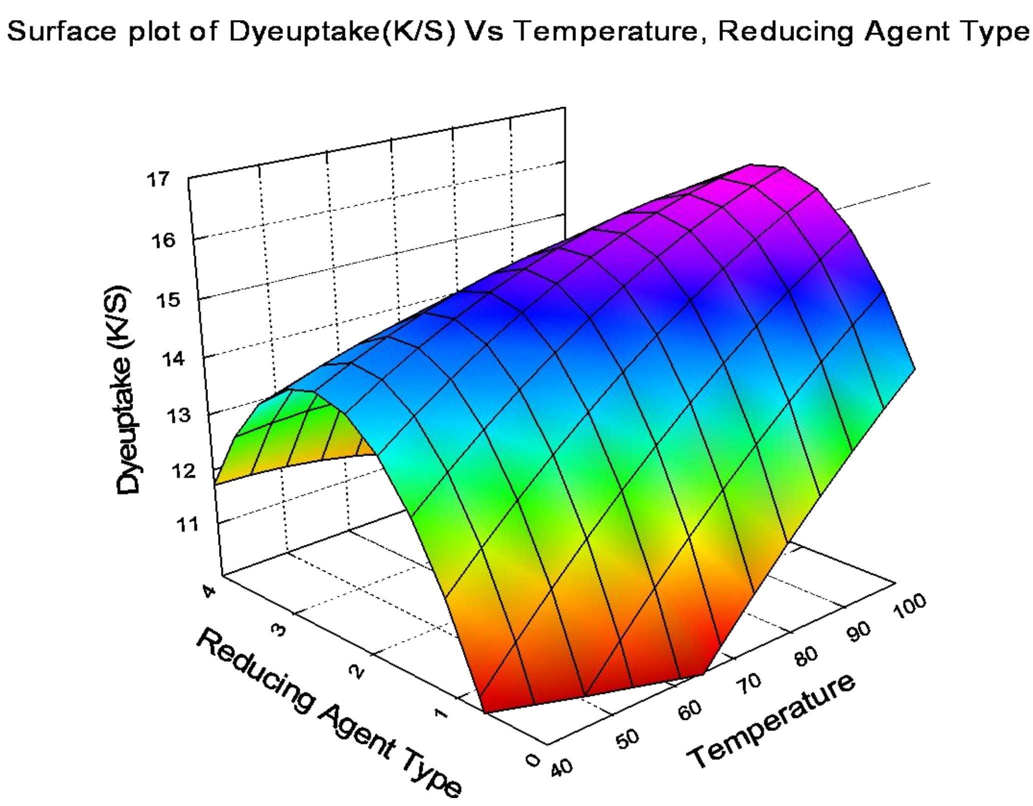


Fig. 6. Surface and Contour plot Dye uptake Vs. Temperature, Concentration



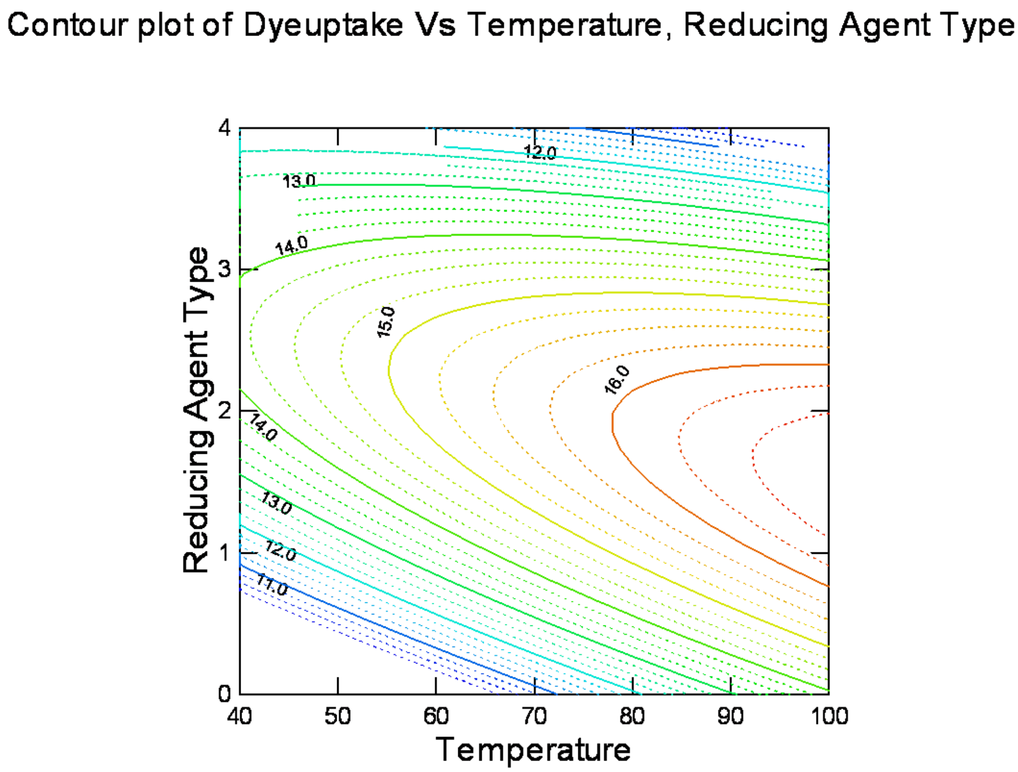


Fig. 7. Surface and Contour plot Dye uptake Vs. Reducing agent type, Temperature

The response surface equation of Temperature and reducing agent type on Dye Uptake (K/S) in form of contour and 3-D graph are shown in the Fig-7. These also support the maximum color strength obtained with glucose as compare to fructose and Na_2S at reduction temperature above 70°C.

Conclusions

Non sulfide reducing agents employed for sulfur dyeing show comparable results in terms of color strength and wash fastness without any significant loss in tensile strength to sodium sulfide. These reducing sugars have an optimum concentration based over their redox potential over which a maximum dye uptake with less color loss is obtained. The reduction temperature beyond 70°C is more effective for the reduction of sulfur dyes using non sulfide reducing agents.

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