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Effect of Indigo Dye Bath Variables on Dye Affinity, Color Uniformity and Ring Dyeing of Dyed Cotton Yarn

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Abstract

This study explores the dyeing of 100% cotton yarn with indigo, focusing on the effects of temperature, pH level, and reducing agent ratio using a Box-Behnken statistical design. The findings reveal that increasing caustic concentration rapidly raises pH levels, which then stabilize. The study highlights the critical role of pH in determining the ionization and dyeing behavior of indigo, with lower pH favoring higher affinity and strike rate due to the dominance of the mono-phenolate form. Elevated pH levels, however, reduce dye affinity and cause uneven dyeing due to ionic repulsion. Additionally, sodium hydrosulfite concentration and temperature significantly influence redox potential, dye strength (K/S values), and color yield. The CIE*Lab values are impacted by alkali concentration, reducing agent ratio, and temperature, affecting the hue and darkness of the dyed yarn. Finally, pH levels play a crucial role in ring dyeing, with lower pH levels resulting in more uniform surface dyeing, while higher pH levels enhance dye penetration but reduce surface ring dyeing.

Introduction

Indigo stands as one of the most ancient textile dyes globally, maintaining its significance as a key industrial chemical to this day [1, 2]. However, the application of indigo to cotton requires a complex dyeing process involving several steps. Indigo, categorized as a vat dye, demonstrates high insolubility in water when in its solid blue pigment state due to robust hydrogen bonding between adjacent molecules. Furthermore, it displays minimal affinity for cellulosic fibres [3-6]. In order to facilitate dyeing on cellulosic materials, indigo is reduced to leuco indigo which exhibits affinity for cellulose fibres due to van der Waals and dipole forces [7]. Subsequently, the leuco indigo form is further converted to mono- and bi- sodium phenolate forms in the presence of alkali to enhance water solubility [8, 9]. However, a significant challenge arises due to low substantivity of indigo's oxidized forms for cotton fibres. Therefore, to achieve proper dyeing on the cotton yarn continuous rope and Slasher (sheet) dyeing methods are used. Both dyeing methods entail multiple steps, including dipping, padding, and oxidation, to achieve comprehensive layer-by-layer surface dyeing [10-12]. This encapsulation (ring dyeing effect) of yarn by the indigo dye is responsible for the gradual shaded effects in garments, which are in high demand among consumers [13]. Several variables influence the quality and consistency of encapsulation, as well as the shade, color yield, color build up and hue of dyed yarn. These include pretreatment, dye bath temperature, immersion and oxidation duration, padding expression and the concentration of caustic and sodium hydrosulfite [5-9, 13-15]. Ensuring the desired quality of shade and encapsulation of indigo is a challenging endeavor, demanding extensive expertise and technical proficiency. In the past the studies have been conducted on the effects of pretreatment and it has been reported that pretreatment has significant effects on the shade depth and hue [16-19]. The studies on immersion time and the number of dips suggest that prolonging the duration and increasing the number of dips both improve dye penetration and deepen shade intensity. Similarly, longer oxidation times also result in greater shade depth [11, 20]. The dyeing temperature has a notable impact on dyeing characteristics. The temperature above 40°C adversely affects color yield of indigo dye [6]. Research indicates that at temperatures 40°C and above hydrosulfite becomes more reactive, leading to a faster rate of reduction and transforming indigo dye into a soluble leuco form. However, at higher temperatures, sodium hydrosulfite oxidizes quickly in the presence of atmospheric oxygen, gradually losing its reduction capacity. Consequently, an excess amount of stoichiometric solution of dithionite and sodium hydroxide is needed for the reduction process [3, 15, 21, 22].The pH level of the dye bath is crucial, as it controls the ionization of leuco indigo and the formation of mono- and bi-sodium phenolate forms, which consequently affects the strike rate and affinity of dye to cotton fibres. These different forms of indigo govern color yield, dye accumulation, and the distribution of indigo within the cross-section of yarn [9, 11, 23]. The excess amount of sodium hydrosulfite in the dye bath solution governs the physical morphology, degree of aggregation and hue of indigo dye molecules. The researchers have studied the individual effects of pH level, redox potential, free hydro and temperature on the dyeing characteristics of indigo on cotton yarn. However, the mutual effect of all these parameters has yet to be investigated. Hence, it becomes imperative to investigate the effect of pH level and the excess amount of hydrosulfite in the dye bath along with dye bath temperature for consistent dyeing yarn with indigo. In the present work the combined effects of pH level, sodium hydrosulfite concentration (Redox potential) and temperature on dyeing characteristics of indigo dyed cotton yarn samples have been studied.

Materials and Methods

In the present study the pH level with the increasing concentration of NaOH in the solution was determined using an automatic potentiometric titrator, Metrohm (Switzerland) 905 Titrando apparatus available at Oswal Denim Ltd. Bhopal. Caustic lye (50% w/v solution with water) was prepared and added in one litre of distilled water to record the pH level at the intervals of 0.2 g/l caustic concentration in the solution. Furthermore, the dye bath solutions containing indigo and sodium hydrosulfite in a ratio of 1:1.2 was titrated with caustic solution at intervals of 0.2 g/l to determine the pH level of dye bath solution. In order to investigate the additional amounts of sodium hydrosulfite and leuco indigo present in the dye bath, potential curve was generated by titrating the dye bath solution with potassium ferricyanide ($K_3[Fe(CN)_6]$) using a Metrohm potentiometric titrator equipped with an mV meter. Initially, a 50 ml solution of conditioner composed of 6 g/l caustic and 3 g/l dispersing agent, was prepared in a beaker and treated with nitrogen gas for 5 minutes to remove oxygen. Subsequently, a 10 ml indigo dye bath sample of 1 g/l indigo, at room temperature (30°C) and pH level of 11, was added to the conditioner. The final solution was then titrated with a 0.05 normal (16.46 g/l) solution of potassium ferricyanide to determine the excess amounts of sodium hydrosulfite and leuco indigo in the dye bath. The study involves preparation of indigo dyed yarn samples according to Box-Behnken statistical design with three factors with three levels. Therefore, the potential values of extra amounts of sodium hydrosulfite and leuco indigo in the dye bath were determined for three levels of pH, three stoichiometric ratios of sodium hydrosulfite and three temperatures to prepare dye bath solution for dyeing yarn samples.

To investigate the effect of pH level, hydrosulfite concentration (Redox potential), and temperature on the dyeing properties of cotton yarn by indigo, Box-Behnken experimental design approach was adopted [24, 25]. A Box-Behnken statistical design with three factors with three levels was employed to dye the yarn samples at different temperatures, pH level and hydrosulfite concentration as shown in the Table 1. The actual value of process parameters corresponding to coded levels have been mentioned in the Table 2. Here the concentration of hydrosulfite is given in relation to the concentration of indigo dye in stoichiometric solution.

To study the effects of various parameters mentioned earlier, 100% cotton 9 Ne open-end yarn samples with 1900 CSP were received in kind from Oswal Denims Ltd., Punjab. Initially, the cotton yarn was treated with a sodium hydroxide solution, as detailed in Table 1, to eliminate impurities. Subsequently, these yarn samples were dyed in Paramount dyeing pots available in the laboratory, following the recipe provided in Table 4, with a material-to-liquor ratio of 1:20.

Traditionally, the dipping time is 10-20 seconds for slasher dyeing and 20-30 seconds for continuous rope dyeing [26]. However, to enhance dye penetration and adsorption on the yarn surface, the dipping time was extended to 60 seconds. In this process, the yarn samples were dyed in hank form rather than as individual yarns. After dyeing, the yarn samples were squeezed using padding mangles at the same pressure applied in continuous dyeing to ensure consistent and precise results. The dyed yarn samples were then exposed to atmospheric air to convert the water-soluble leuco form of indigo into its insoluble form, ensuring it adheres to the yarn surface. The oxidation time was increased compared to the method typically used in the industry. To achieve optimal dye fixation, the samples were exposed to atmospheric air for 3 minutes for oxidation. The yarn samples were dyed in subsequent four baths to achieve the similar results as continuous dyeing process where the yarn samples are dipped, nipped and oxidized in subsequent eight baths. After completing the experimental design process, 15 samples of indigo-dyed yarn were produced according to the specifications outlined in Table 1 & 2, covering lighter and darker shades of indigo. These dyed yarn samples were then tested to analyze the effects of pH levels and hydrosulfite concentration in conjunction with temperature on the dyeing parameters such as, color yield, color tone and ring dyeing effect on yarn.

The dyed yarn samples were tested for their K/S value (color strength) and CIE Lab* values (color tone) using the American Association of Textile Chemists and Colorists (AATCC) test method (173-2005) with a Datacolor Spectrophotometer 600 at BPL Ltd., Bhilwara. Reflectance values were measured across the visible spectrum (400nm to 700nm) and transformed into absorption (K) and scattering (S) coefficients using the Kubelka-Munk function [27].

The ring dyeing effect produced by multiple consecutive nip and dip cycles was investigated by analyzing the cross-sections of yarn samples. To prepare the yarn cross-section samples, a bottle cap cork was used, through which the yarn samples were threaded using a needle. Subsequently, these corks, containing the yarn samples, were sliced in fine cross-section with a sharp blade. The resulting cross-sections were examined under a Nikon Eclipse E200 microscope at 50x magnification.

Results and Discussion

In this study, the effect of caustic concentration on the pH levels of distilled water, initial dye bath was investigated using a Metrohm potentiometric titrator. The results, illustrated in Figure 1, indicate that in distilled water, the pH level rapidly increases to 11.32 at a caustic concentration of 0.6 g/l, after which it gradually becomes saturated. In general, indigo is dyed at a pH above 12 because maintaining this pH level is easily achieved using a safe concentration of NaOH. The dye bath containing indigo and sodium hydrosulfite in a ratio of 1:1.2 was titrated with 2% (W/V) NaOH solution and it has been found that initially the dye bath exhibits an acidic pH due to presence of leuco vat acid. Upon adding the caustic solution, the pH level initially remains acidic and increases gradually as the alkali neutralizes the acidic products. However, with further addition of the caustic solution, the pH rises sharply and eventually levels off once the alkali concentration reaches 1.2 g/l. Interestingly, another significant increase in pH is observed at an alkali concentration of 5.2 g/l, which then levels off again beyond 5.6 g/l.

In the absence of alkali in dye bath, sodium hydrosulfite reduces indigo to its acid leuco form which is acidic in nature as shown in Figure 1. The reduced form of indigo undergoes a two-step ionisation to produce two ionic species: mono-ionic and di-ionic; the relative amount of each species is governed by the pH of the dye bath. The acid leuco form is gradually converted to the mono sodium phenolate form of indigo and further addition of alkali causes the mono-sodium phenolate form converted to the bi-sodium phenolate form. Figure 2 illustrates the visual depiction of indigo and its different derivatives undergoing reactions with sodium hydrosulfite and sodium hydroxide.

The different fractions of various forms of indigo at various pH levels of dye bath can be calulated based on the following equations [3]:

$$Acid\ Leuco\ Fraction = \frac{1}{1+10^{(pH-pK_1)}+10^{(2pH-pK_1-pK_2)}} \quad \ldots\ldots (1)$$

$$Mono-Sodium\ Phenolate\ Fraction = \frac{1}{1+10^{(pK_1-pH)}+10^{(pH-pK_2)}} \quad \ldots\ldots (2)$$

$$Bi-Sodium\ Phenolate\ Fraction = \frac{1}{1+10^{(pK_1+pK_2-2pH)}+10^{(pK_2-pH)}} \quad \ldots\ldots (3)$$

where,

pH is the pH value of dye bath
pK_1 is first step equilibrium ionisation constant in logarithmic term
pK_2 is second step equilibrium ionisation constant in logarithmic term

Using equations (1) to (3), the fractions of various forms of indigo were plotted at different pH levels as shown in the Figure 3. It was observed that at the initial pH level, only the acid leuco form is present. Further addition of alkali to the dye bath decreases the fraction of acid leuco, while there is a sharp increase in the fraction of mono-sodium phenolate. As more alkali is added, the pH level of the dye bath rises, and the fraction of mono-sodium phenolate reaches unity at a pH level of 10.5. However, with continued addition of alkali, the mono-sodium phenolate form of indigo converts to the bi-sodium phenolate form.

The affinity of indigo dye to cotton fibres is influenced by the different forms of indigo present in the dyebath. The oxidized and acid leuco forms of indigo exhibit very low water solubility and low substantivity for cotton fibres. However, the physicochemical properties of these two sodium phenolate forms of indigo differ significantly. The mono-sodium phenolate form has a higher striking rate and greater substantivity to cotton fibres. In contrast, the bi-sodium phenolate form is more soluble in water but has lower substantivity to cotton fibres.

Interestingly, it has been reported that the pH level of the dye bath significantly influences the ionization of cotton fibre (cellulose), as shown in Figure 4. At higher pH levels (above 11), the ionization of the alcoholic OH groups in cellulose occurs similarly to the ionization of the second OH group in the indigo molecule [5, 28]. Additionally, the affinity and strike rate of the indigo dye molecule to cotton fibre are negatively affected at higher pH levels due to ionic repulsion between the di-ionic form of indigo and the ionized fibre. Although, the strike rate and affinity of indigo to cotton fibre is high at pH level 11 however, it is quite difficult to maintain pH level at 11, because the dye bath pH is easily fluctuated in this range and gives uneven dyeing, shade variations and streaking [14].

The concentration of sodium hydrosulfite in the dye bath determines its redox potential, which is crucial for proper vatting of indigo molecules and maintaining the stability of leuco indigo. Typically, the sufficiency of sodium hydrosulfite is assessed by observing the dye bath's color. However, this study examines the effects of sodium hydrosulfite concentration on the reduction of indigo molecules (leuco indigo) and the presence of excess hydrosulfite (free sodium hydrosulfite) using a Metrohm potentiometric titrator with an mV meter. A potential curve resulting from the titration of indigo dye bath solution in ratio of 1:1:1.2, Indigo: NaOH: $Na_2S_2O_4$ with potassium ferric cyanide ($K_3[Fe(CN)_6]$) an oxidizing agent, has been shown in the Figure 5. Initially, the potential of the dye bath was recorded at -750 mV. Gradually, potassium ferricyanide solution was added to the dye bath, causing the potential to suddenly rise to End Point-1 (EP1) at -670 mV, where it remained constant for a while. However, further addition of the oxidizing agent (2.0 g/L) rapidly increased the redox potential to EP-2. This indicates that at EP1, all the available free sodium hydrosulfite was consumed, leading to a sudden increase in potential. Further addition of oxidizing agent oxidizes the leuco indigo to insoluble indigotin at level 'EP-2' leading to the second peak of sudden rise in potential.

The oxidation equation of sodium hydrosulfite in basic medium is given by the following equations:

$S_2O_4^{-2} \rightarrow 2SO_3^{-2}$..(1)

$S_2O_4^{-2} + 2H_2O \rightarrow 2SO_3^{-2} + 4H^+$.......................(2)

$S_2O_4^{-2} + 4OH^- \rightarrow 2SO_3^{-2} + 2H_2O + 2e^-$.........(3)

The reduction equation of potassium ferric cyanide is given by the following equation:

$Fe(CN)_6^{-3} + e^- \rightarrow Fe(CN)_6^{-4}$..........................(4)

The balanced redox equation for sodium hydrosulfite and potassium ferric cyanide is given by combining equation (3) and (4).

$S_2O_4^{-2} + 2Fe(CN)_6^{-3} + 4OH^- \rightarrow 2SO_3^{-2} + 2Fe(CN)_6^{-4} + 2H_2O$.................(5)

Based on the molecular weight, molar solution and purity of sodium hydrosulfite the weight of excess amount of sodium hydrosulfite and leuco indigo present in the dye bath solution were calculated as shown in the Table 5, using the potential curve shown in the Figure 5.

he results obtained from the potentiometry titration of dye bath solution with potassium ferric cyanide are presented in Table 5. It has been noted that as the temperature of the dye bath increases, the amount of free sodium hydrosulfite decreases significantly, leading to a corresponding drop in redox potential. This effect can be attributed to the rapid oxidation of sodium hydrosulfite by atmospheric oxygen at higher temperatures, which over time reduces its ability to act as a reducing agent.

In order to study the effect of alkali concentration (pH level) and sodium hydrosulfite ratio in conjunction with temperature in dye bath, the yarn samples were dyed at different dye bath parameters, according to Box-Behnken experimental design approach mentioned in the Table 1. Furthermore, these yarn samples were tested for their dye strength (K/S values). The results of K/S values of lighter and darker shades of indigo, at different parameters are shown in the Figures 6.

The effects of alkali concentration and temperature on the K/S values are shown in the Figure 6. It has been observed that K/S value significantly affected by alkali concentration in dye bath. Initially the shade depth of yarn sample increases from low level of pH to medium pH level and then after it reduces at high pH level of dye bath. The reason can be attributed to the mono and bi-phenolate forms of indigo. At lower level of pH, indigo molecule exist in mono-phenolate form and it has higher striking rate and good affinity towards cotton fibres. In contrast, at higher pH level bi-phenolate form of indigo exist and it has high solubility in water, however has lower strike rate because of ionic repulsion between the bi-phenolate form of indigo molecule and anionic cellulose molecule of cotton fibre, as shown in the Figure 7.

The ratio of the reducing agent significantly affects the K/S values of dyed yarn samples, especially in conjunction with dye bath temperature. It has been observed that increasing the reducing agent ratio initially leads to higher K/S values. However, further increases in the reducing agent ratio cause a decrease in K/S values. At higher reducing agent ratios and elevated dye bath temperatures, moderate K/S values are achieved. At higher values of reducing agent ratio in dye bath, the oxidised indigo dye molecules again reduced to soluble form and results in low K/S values.

In addition to evaluating the color yield (K/S value) of indigo-dyed yarn samples prepared using the Box-Behnken design, the CIE*Lab values were also tested. The resulting surface plots are presented in Figure 8.

It has been observed that increasing the alkali concentration initially causes the CIE L value to decrease, followed by a sharp increase. Similarly, the reducing agent ratio affects the L values in the same manner, with an initial decrease followed by an increase. However, temperature negatively impacts the L values, leading to a decrease in the darkness of the samples. The similar trend has been observed in L values of dyed yarn samples dyed with 2% and 3.5% shade depth.

The alkali concentration has minimal impact on the CIE a value of indigo-dyed yarn samples. Initially, the CIE a value decreases, then increases, indicating a shift in the hue of the dyed samples towards a redder tone. This effect was consistent across both shade depths.

The effect of temperature on the CIE a value was also measured, and it was observed that with an increase in temperature, the hue of the dyed yarn samples shifted towards a greener tone in both shade depths. The ratio of reducing agent significantly affects the CIE a value, causing the hue of the dyed yarn samples to shift towards a redder tone as the reducing agent ratio increases.

No significant effect of temperature, alkali concentration, or reducing agent ratio was observed on the CIE b values of the dyed yarn samples.

To investigate the impact of pH on the layering of indigo dye on cotton yarn, the cross-sections of yarn dyed with 2% and 3.5% shade depth at different pH levels were examined under a microscope, as shown in Figure 8& 9. The results indicate that pH significantly affects the ring dyeing of the yarn. As discussed earlier, at lower pH levels, the strike rate of indigo molecules is higher, resulting in more uniform and thicker ring dyeing on the yarn's surface. Conversely, at higher pH levels, the solubility of indigo in the dye bath increases, allowing deeper penetration of dye molecules into the yarn cross-section, though the strike rate and dye affinity decrease. These effects are evident in the cross-sections at various dye bath pH levels.

Conclusions

This research investigates the dyeing of 100% cotton yarn with indigo, focusing on the effects of temperature, pH level, and reducing agent ratio using a Box-Behnken statistical design. The experimental results were analyzed through response surface curves to understand how these factors influence color strength (K/S values) and color tone.

The study found that increasing caustic concentration in both distilled water and dye baths containing indigo and sodium hydrosulfite quickly raises pH levels, which then gradually stabilize. Indigo dyeing is typically conducted at a pH above 12, as this is easily maintained with NaOH. Initially, the dye bath exhibits an acidic pH due to leuco vat acid; however, the addition of caustic solution gradually neutralizes the acidity, causing a sharp rise in pH.

Indigo ionizes into mono-ionic and di-ionic species, with their proportions determined by the dye bath's pH. At low pH, the mono-phenolate form dominates, showing greater affinity and strike rate to cotton fibers, whereas at high pH, the bi-phenolate form is more soluble but exhibits a lower strike rate. At higher pH levels, ionic repulsion between di-ionic indigo and ionized cellulose reduces dye affinity and strike rate, leading to uneven dyeing and shade variations. The concentration of sodium hydrosulfite in the dye bath determines the redox potential, which is crucial for proper vatting and maintaining the stability of leuco indigo. Elevated temperatures decrease the amount of free sodium hydrosulfite, thereby reducing the redox potential due to rapid oxidation.

The study also found that alkali concentration, sodium hydrosulfite ratio, and temperature significantly impact the dye strength (K/S values) and color yield of dyed yarn samples. Initially, increasing the reducing agent ratio raises K/S values, but at higher temperatures, this trend reverses, resulting in a decrease in K/S values.

CIE*Lab values are influenced by alkali concentration, reducing agent ratio, and temperature, with varying effects on L and a values, but minimal impact on b values. Alkali concentration and reducing agent ratio initially decrease the CIE L value, followed by an increase, while temperature generally lowers the L value. The alkali concentration and reducing agent ratio shift the hue of dyed yarn towards a redder tone, while temperature shifts it towards a greener tone.
Lastly, pH levels significantly influence the ring dyeing of yarn, with lower pH levels leading to more uniform and thicker ring dyeing on the surface, whereas higher pH levels increase dye penetration but reduce the intensity of surface ring dyeing.

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Table 1- Experimental design for indigo dyeing variables used for yarn samples

Sample No.	Temperature (°C)	Alkali Concentration (pH)	Reducing Agent (Ratio)
1	-1	-1	0
2	1	-1	0
3	-1	1	0
4	1	1	0
5	-1	0	-1
6	1	0	-1
7	-1	0	1
8	1	0	1
9	0	-1	-1
10	0	1	-1
11	0	-1	1
12	0	1	1
13	0	0	0
14	0	0	0
15	0	0	0

Table 2- Actual values corresponding to coded levels

Coded Values	Actual Values		
	Parameters		
	X_1	X_2	X_3
	Temperature (°C)	Alkali (pH)	Reducing Agent (Ratio*)
-1	30	11	1:1.1
0	45	12	1:1.2
1	60	13	1:1.3

*Ratio of Indigo and Reducing agent

Table 3- Recipe for pre-treatment of cotton yarn

Ingredients	Concentration	Temperature (°C)	Time (Seconds)
Sodium Hydroxide (NaOH)	20 g/l	70	30
Wetting agent (C10-14 Ethoxylate Fatty Alcohol 6 EO)	4 g/l		
Sequestering Agent (Acrylic Copolymer)	2 g/l		

Table 4- Recipe and Dyeing Ingredients for indigo dyeing of cotton yarn

Ingredients	Name	Concentration		
Dye Stuff	DyStar Indigo Vat 40% Solution (Blue)	0.9 g/l (2% Shade)	1.65 g/l (3.5% Shade)	
Reducing Agent	Sodium Hydrosulfite ($Na_2S_2O_4$)	Dye Stuff to Reducing Agent Ratio		
		1:1.1	1:1.2	1:1.3
Alkali	Sodium Hydro Oxide (NaOH)	pH Level		
		11	12	13
Dispersing Agent	Sodium Lingosulphonate ($C_{20}H_{24}Na_2O_{10}S_2$)	0.5 g/l		
Sequestering Agent	Acrylic Copolymer	0.5 g/l		

Table 5- Free sodium hydrosulfite, leuco indigo and redox potential present in the dye bath solution

Indigo Shade (%)			**2%**			**3.5%**		
pH Level	**Ratio of $Na_2S_2O_4$**	**Temperature (°C)**	**Free $Na_2S_2O_4$ (gm)**	**Leuco Indigo (gm)**	**Redox Potential (mV)**	**Free $Na_2S_2O_4$ (gm)**	**Leuco Indigo (gm)**	**Redox Potential (mV)**
11	1.1	30	0.55	0.99	-751	0.75	1.45	-760
		45	0.31	0.96	-700	0.55	1.42	-752
		60	0.15	0.98	-690	0.39	1.51	-749
	1.2	30	0.64	0.98	-735	0.88	1.52	-756
		45	0.43	0.96	-729	0.68	1.55	-752
		60	0.21	0.91	-701	0.49	1.56	-742
	1.3	30	0.78	0.98	-743	0.98	1.5	-762
		45	0.61	0.95	-732	0.71	1.56	-759
		60	0.36	0.92	-720	0.59	1.49	-754
12	1.1	30	0.58	0.99	-765	0.74	1.5	-774
		45	0.34	0.97	-732	0.56	1.45	-765
		60	0.2	0.89	-715	0.35	1.52	-758
	1.2	30	0.67	0.95	-751	0.92	1.49	-783
		45	0.44	0.92	-729	0.71	1.52	-770
		60	0.29	0.9	-720	0.5	1.56	-745
	1.3	30	0.8	0.95	-770	1.11	1.53	-773
		45	0.63	0.9	-730	0.72	1.49	-763
		60	0.37	0.88	-720	0.61	1.51	-762
13	1.1	30	0.59	1.01	-766	0.75	1.51	-771
		45	0.32	0.98	-730	0.52	1.49	-762
		60	0.19	0.96	-720	0.39	1.53	-750
	1.2	30	0.66	0.98	-750	1.16	1.53	-779
		45	0.41	0.96	-725	0.78	1.5	-767
		60	0.33	0.92	-719	0.63	1.49	-746
	1.3	30	0.71	0.96	-761	1.09	1.5	-770
		45	0.55	0.91	-745	0.72	1.48	-765
		60	0.29	0.89	-729	0.58	1.5	-760

Table 6. Regression coefficient and p-Value of effects and their interactions

	2% Shade		3.5% Shade	
Effect	**Coefficient**	**p-Value**	**Coefficient**	**p-Value**
Constant	14.850	0.000	31.703	0.000
Temperature	-1.171	0.015	-2.360	0.010
Alkali Concentration	-1.211	0.014	-2.640	0.006
Reducing Agent Ratio	-0.832	0.050	-1.607	0.041
Temp*Temp	-0.832	0.142	-1.567	0.129
Alkali* Alkali	-1.957	0.009	-4.317	0.004
Red. Ratio* Red. Ratio	-2.340	0.004	-5.652	0.001
Temp * Alkali	0.185	0.704	0.215	0.806
Alkali * Red. Ratio	0.468	0.355	1.565	0.118
Temp* Red. Ratio	1.168	0.052	2.145	0.049
Coefficient of Determination (R^2)	0.95		0.96	

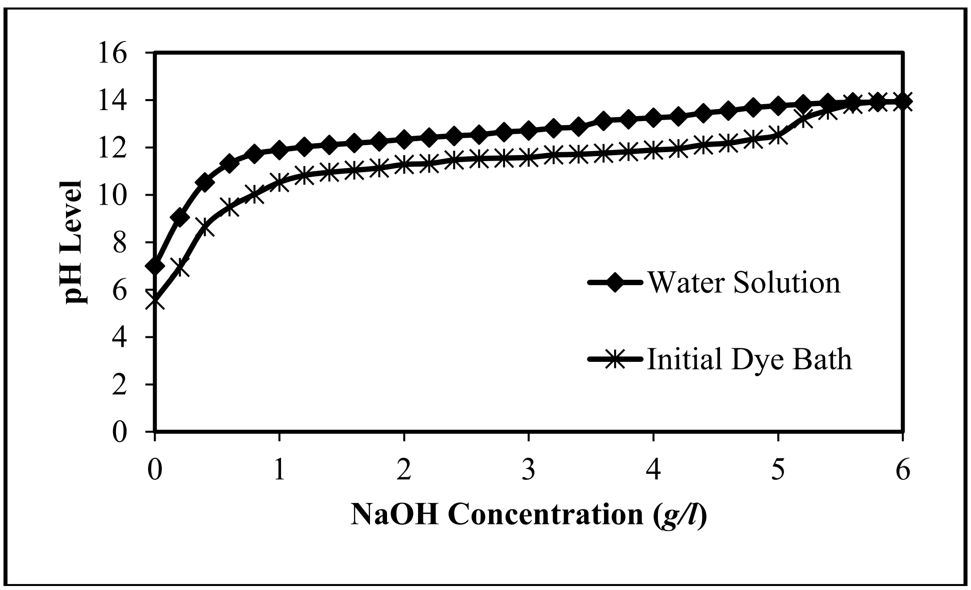


Figure 1: pH level of water and dye bath solution at various NaOH concentrations.

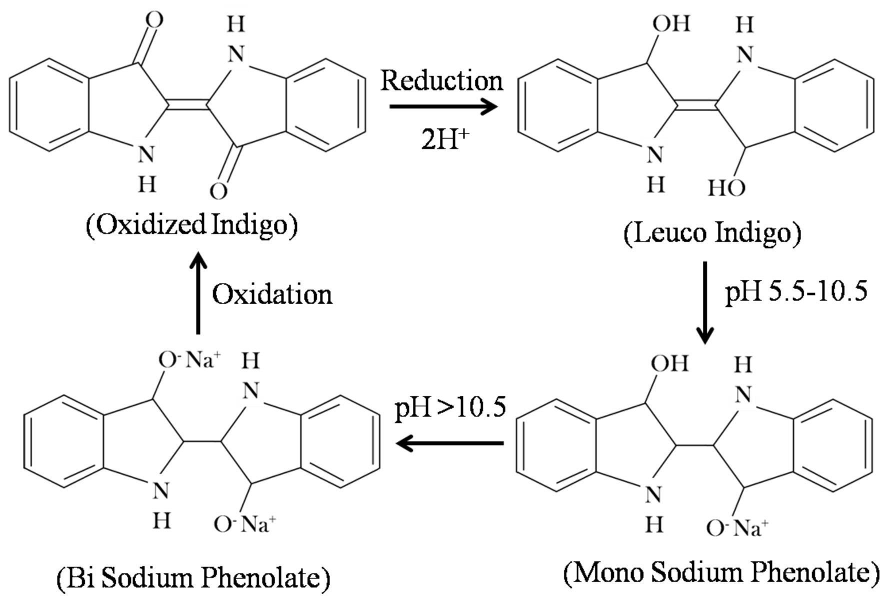


Figure 2. Indigo and its various forms undergoing reactions with sodium hydrosulfite and sodium hydroxide

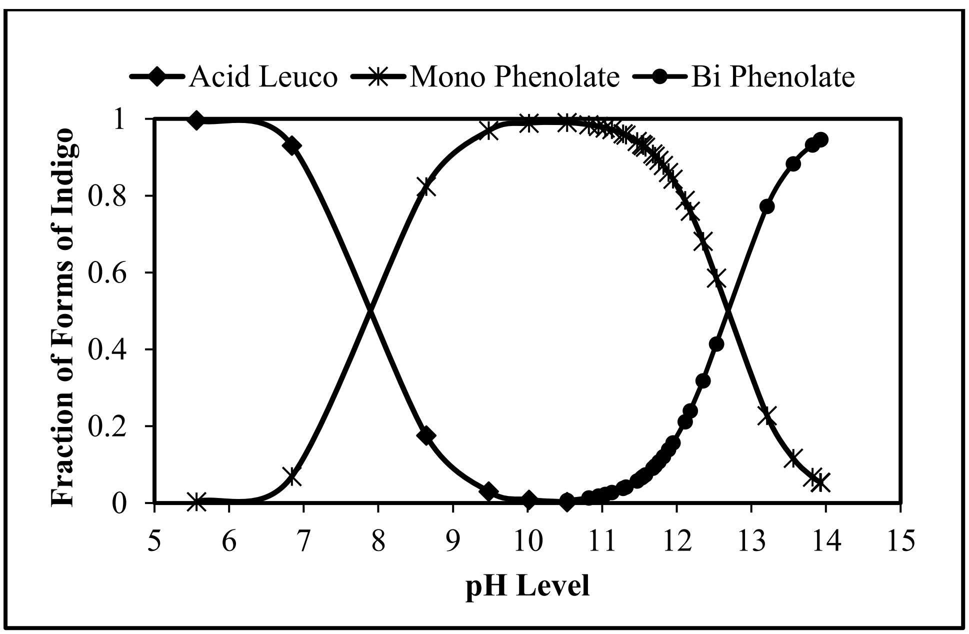


Figure 3. The fractions of various forms of indigo at different pH values include acid leuco, mono and bi-sodium phenolate.

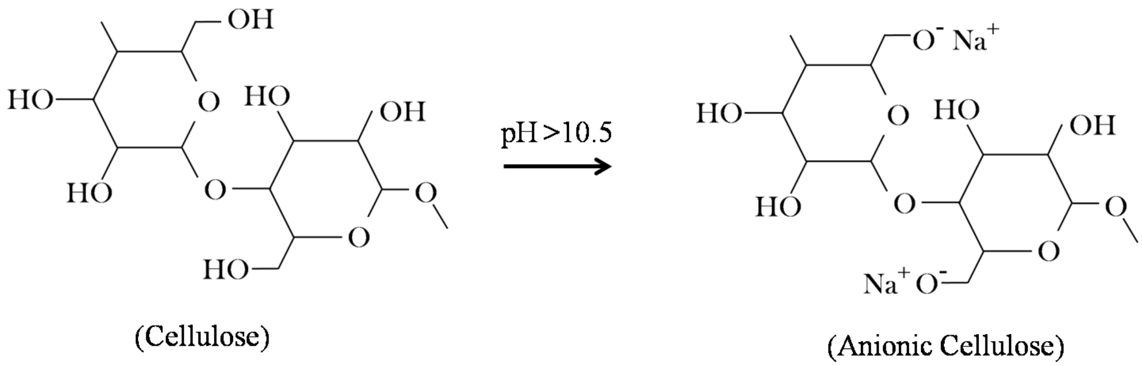


Figure 4. Ionization of cotton fibre (cellulose) in alkaline condition.

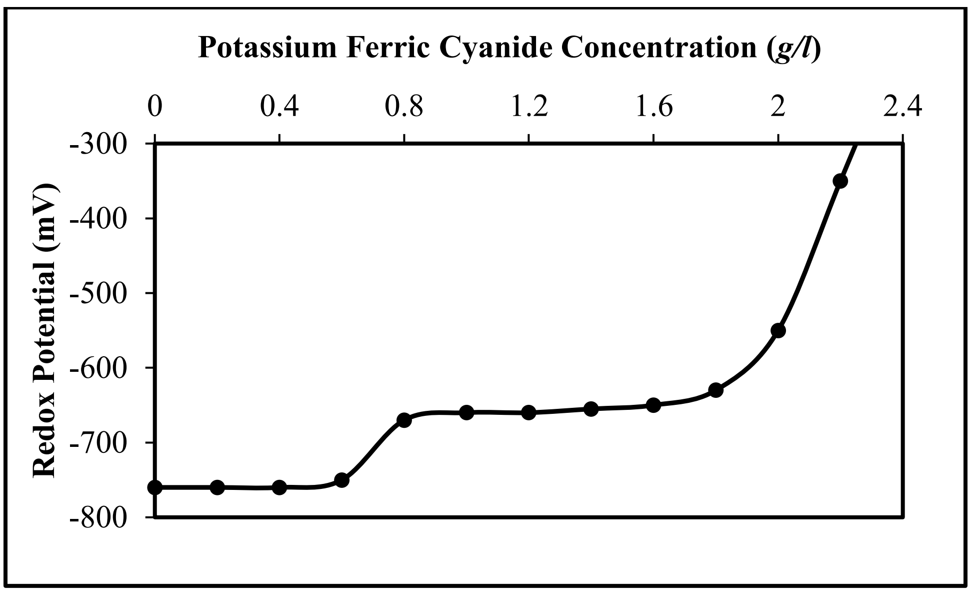
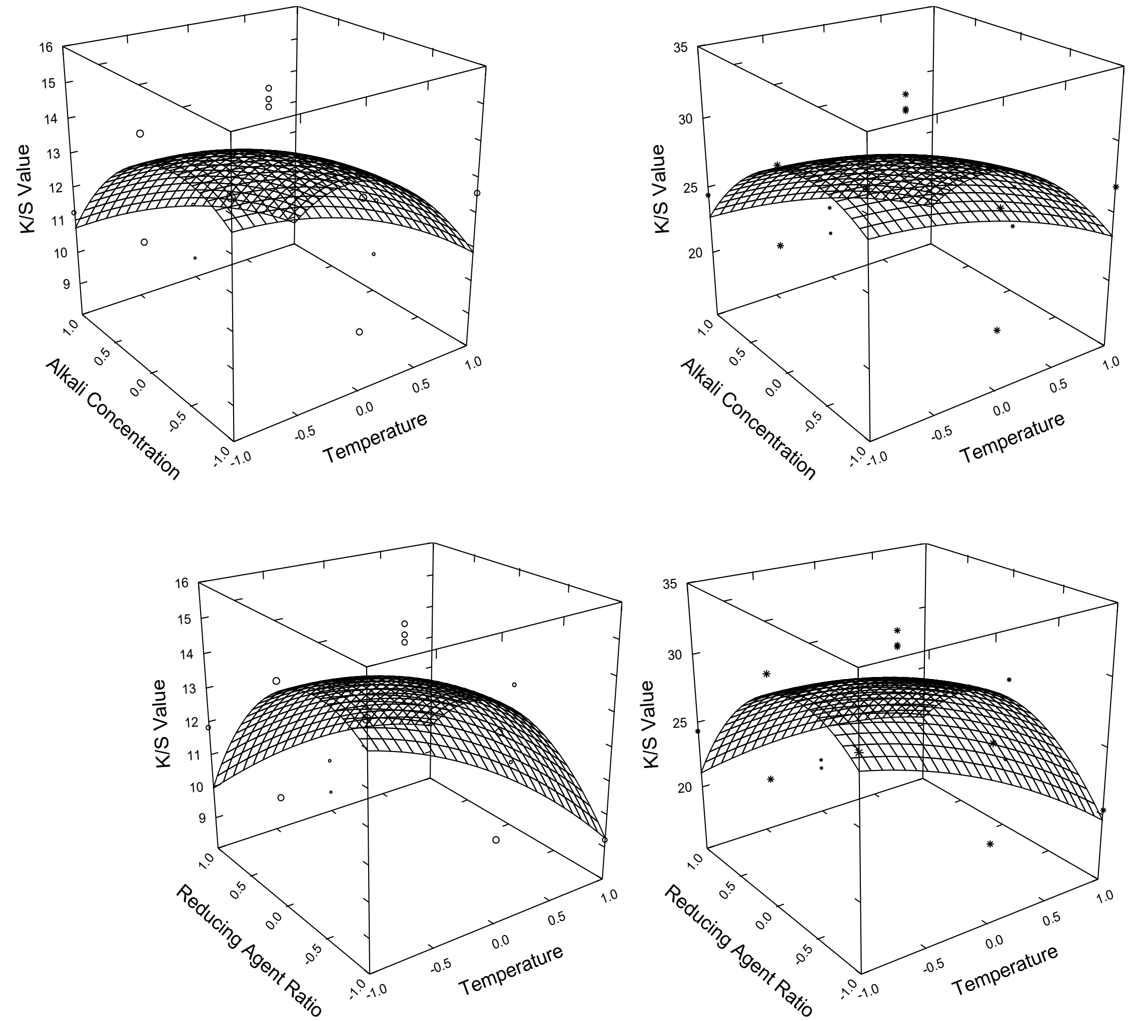


Figure 5. Redox potential curve of indigo dye bath titrated with potassium ferric cyanide using Metrohm potentiometer


K/S Value
Alkali Concentration
Temperature
K/S Value
Alkali Concentration
Temperature
K/S Value
Reducing Agent Ratio
Temperature
K/S Value
Reducing Agent Ratio
Temperature

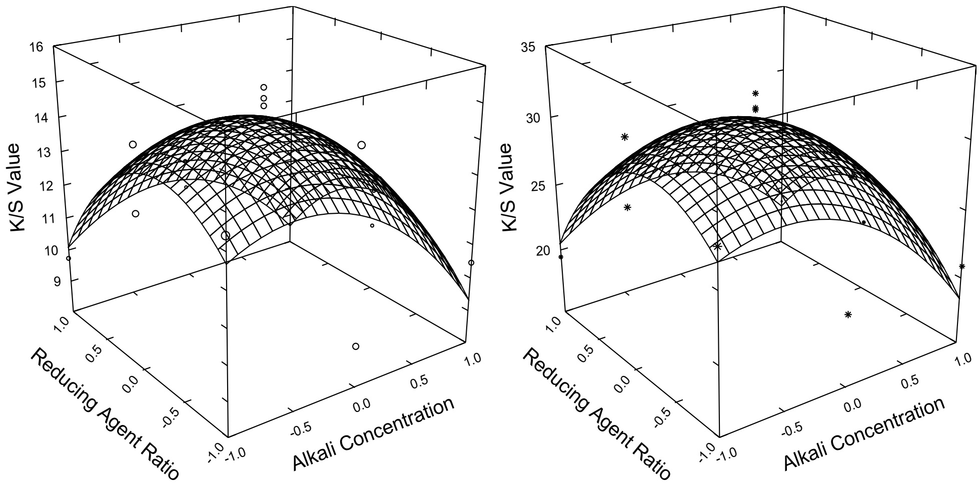


Figure 6. Effect of alkali concentration (pH level), hydrosulfite concentration (Reducing agent ratio) in conjunction with temperature on dye uptake (K/S value) of two different shades (a) Lighter Shade (b) Darker Shade.

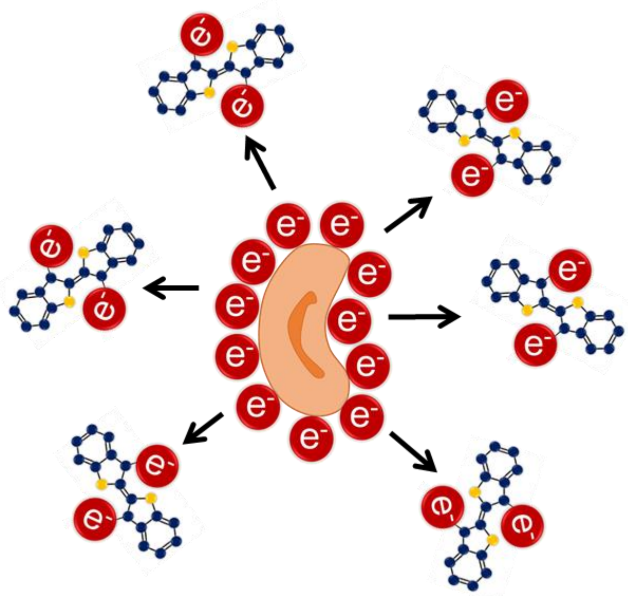


Figure 7. Ionic repulsion between cotton fibre and bi-phenolate form of indigo molecule

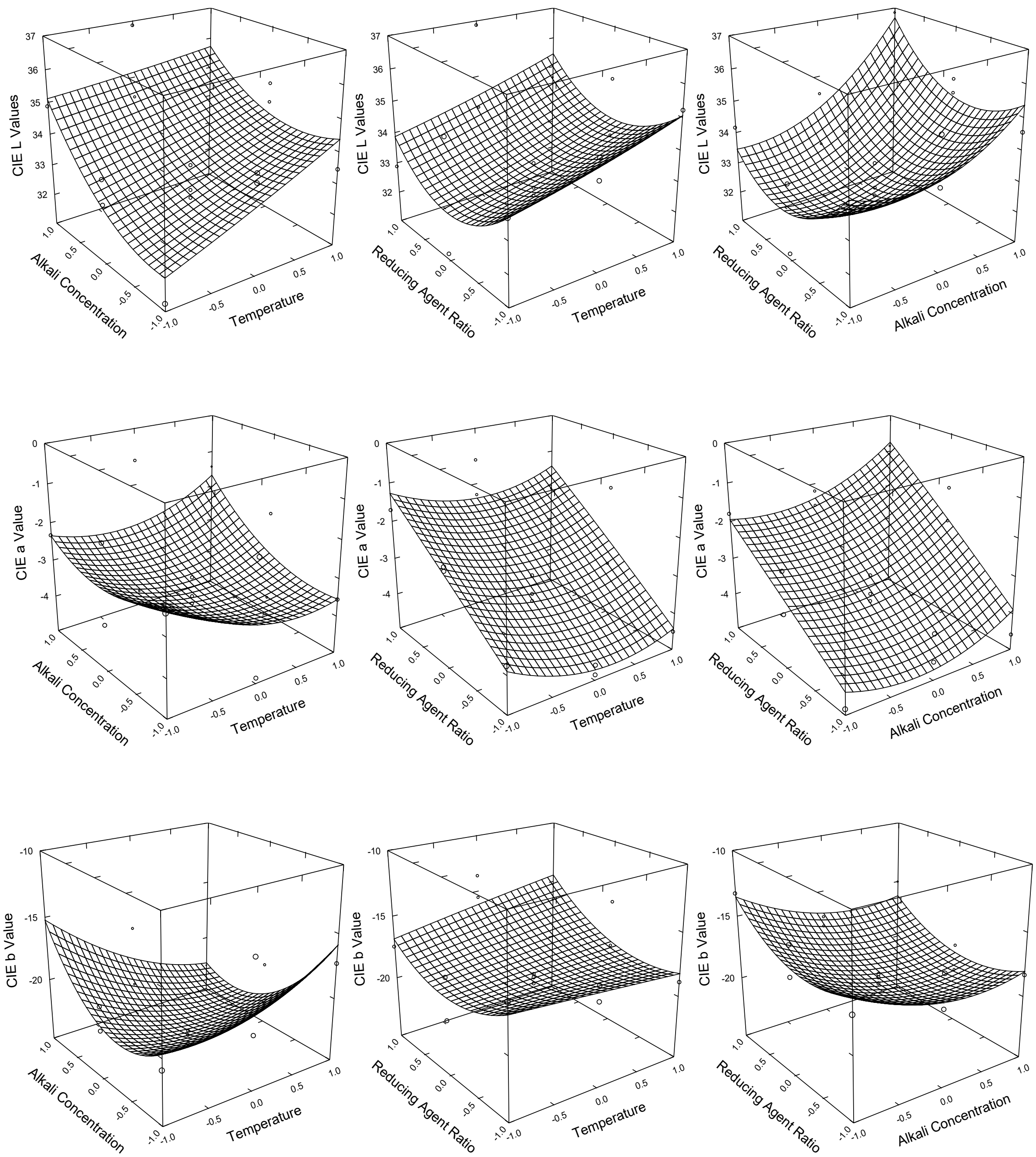


Figure 8. CIE Lab Values of indigo dyed cotton yarn at 2% shade depth.

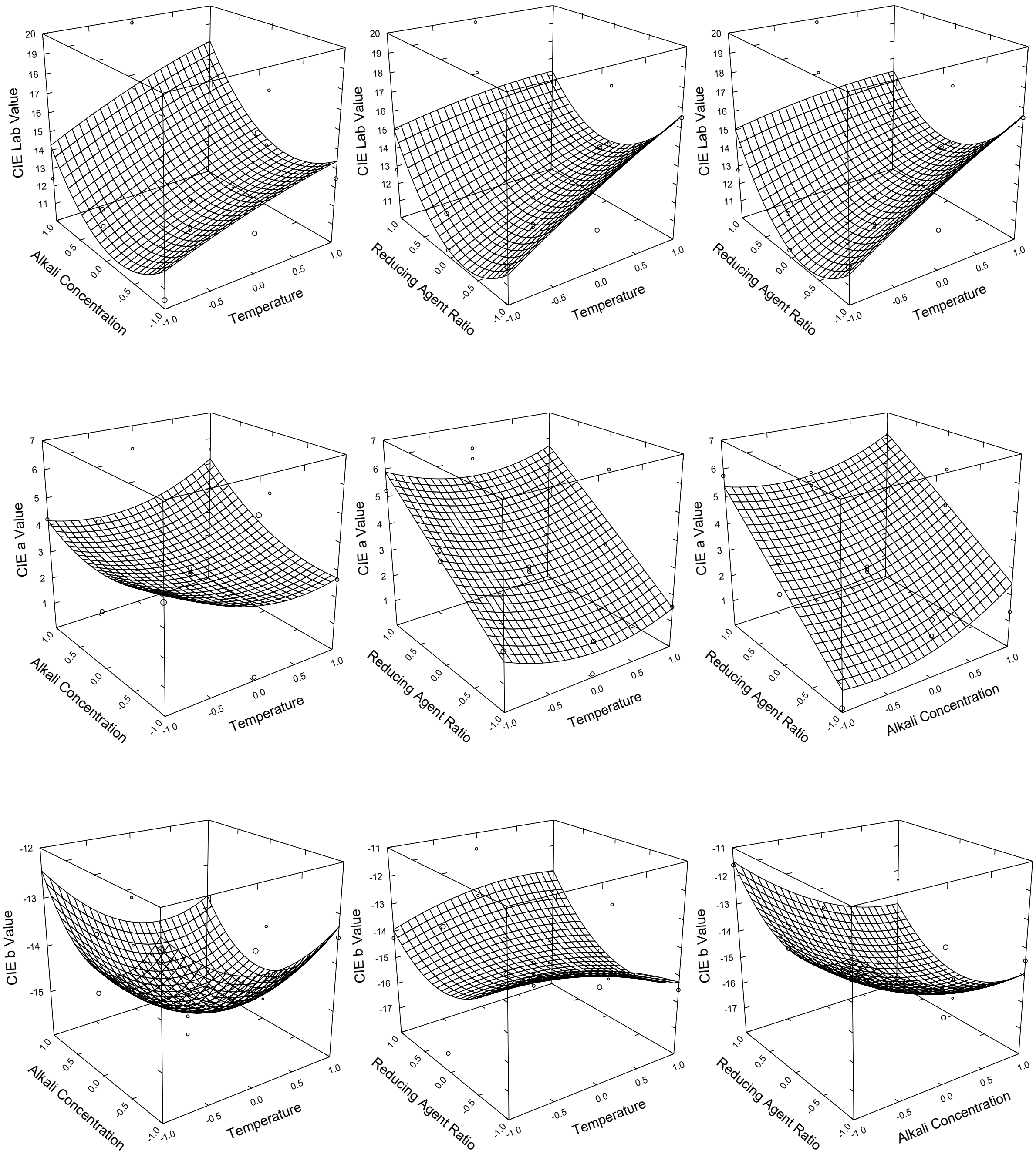


Figure 9. CIE Lab Values of indigo dyed cotton yarn at 3.5% shade depth.

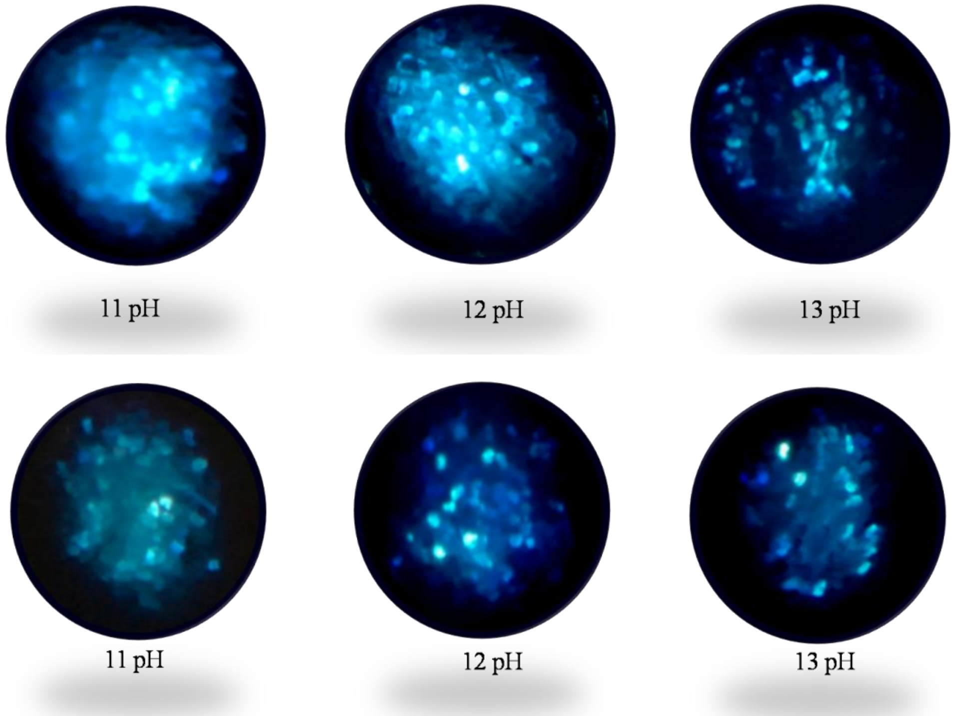


Figure 10. Cross-section of indigo dyed cotton yarn, dyed at various pH level and shade depth.