Review Article

Dyeing of denim with indigo

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Indigo is extensively used for dyeing of denim. Though indigo is a class of vat dye, it cannot be applied following conventional vat dyeing method due to its very little affinity for cotton. This paper reviews proper application of indigo on denim as well as various aspects relating to this application.

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1 Introduction

Natural indigo, known in different names in different parts of the world, has been in use since around 7000 BC for dyeing of cotton in attractive and bright blue shades. Plants belonging to the genus Indigofera are most valuable for producing natural indigo. The colouring matter in the plant is present as a glucoside of indoxyl, known as indican, which is hydrolyzed to the indoxyl by enzymatic action and indigo is then obtained by subsequent oxidation. In ancient times, reduction of indigo was carried out by fermentation technique which included use of ripen fruit and stale urine assisted by wood ash or lime as alkali. The solution prepared in this way was left overnight for reduction and solubilization of indigo. The supernatant liquor was then taken out for colouration through repeated dip-exposure to air sequence at room temperature till a deep shade was produced, a cumbersome as well as time consuming process.

However, extensive work for finding out a suitable alternative of natural indigo to meet growing demand of it gave birth of modern indigotin by Adolf Von Bayer in 1880. Later, BASF AG (Germany) placed commercial synthetic indigo in market in 1897 (refs 4, and 5). Indigo (C1. Vat Blue 1) has the chemical structure as shown below:

Though natural indigo was known since ancient times and the synthetic one was developed more than 100 years back, research work started slowly in various areas of indigo dyeing only in the 60s with an intensification since 80s to cope up with increase in popularity of indigo dyed denim worldwide. Enormous developments were proposed which mainly comprised changes in conventional reduction and application techniques, modification in design of machineries, various ways to enhance indigo uptake and quantitative estimation of indigo on cotton denim. Beside, developments have also been made to improve wash-down property through efficient dyeing. The present paper reviews proper application of indigo on denim as well as various aspects relating to this application.

2 Application of Indigo

Indigo is exclusively used to produce attractive blue shades on denim along with desired wash-down property. However, in its reduced and solubilised form, indigo possesses little affinity for cotton—the
extent of affinity is too less to exercise exhaust dyeing; rather multi dip/nip technique with intermediate air oxidation is followed for gradual build up of shade. A suitable method of dyeing, viz. slasher dyeing (sheet dyeing) or rope dyeing (ball warp dyeing or chain dyeing) or loop dyeing, is followed for dyeing of warp yarn. After dyeing, the dyed warp yarn is woven using white cotton weft to produce mostly a warp faced 3 x 1 twill fabric with blue face and white back. The fabric is then washed through specific techniques to remove a part of dye in order to develop unique fading property.

In slasher dyeing method, denim yarns in the form of a warp sheet are pretreated in earlier compartments followed by multi dip/nip indigo dyeing; the process completes with after-washing followed by drying, sizing and final drying. Handling of yarn is minimum as the warp sheet is directly processed and then sent to weaving section for its subsequent conversion to fabric. A slasher dyeing range may consist of either the indigo dyeing range alone or a continuous indigo dyeing range with an integrated sizing range. In the first type, yarn sheet moves forward through one or two pretreatment boxes with the stages of dipping, squeezing and skying; washing and drying are the only aftertreatments. On requirement, two or more layers of warp sheet may be processed simultaneously. Schematic diagram of a popular slasher dyeing range is shown in Fig. 1. The second type includes the steps followed in first type, extra attachments are the sizing and the washing compartments as shown in Fig. 2. Slasher dyeing is suited for better production schedules with a possible problem of centre to side variation. Superior quality of yarn is needed to minimize breakage problems. Broken end roll wrap ups can cause catastrophic shutdown problem as well as undesired waste. On the other hand, the dipping, squeezing and oxidation require less time as each yarn is independently subjected to treatments.

In rope dyeing method, yarns from creel are pulled by a ball warping machine and then passed through a lease stand consisting of a special comb and lease rods to ensure proper registration of ends. These drawn ends then pass through a condenser tube assembly to merge these into a bundle followed by passing the latter to form a rope comprising 350-400 ends. Ropes are then wound on drums. Once the beam has been fully wound, it is unloaded and mounted on dye range creel. Dyeing is done by passing ropes, up to 12 at a time, through pretreatment bath followed by multiple dipping in separate indigo baths with intermediate squeezing and skying, as done in slasher dyeing. Schematic diagram of a rope dyeing unit is shown in Fig. 3 (ref. 48). Rope dyeing method is important for higher production rate with better
quality dyeing and better fastness to wet/dry rubbing as well as colour wash down. It includes less breakage of ends and better shade consistency but in contrast more handling of yarn to open ropes before sizing. However, the efficiency of slasher and rope dyeing methods depends on back feed to dyebaths to maintain concentration of indigo and other chemicals at a constant rate, which is a cumbersome work. Moreover, consumptions of chemicals and dye remain on higher side with greater chance of uneven/tailing effect.

In loop dyeing, problems associated with slasher and rope dyeing were solved through the development of a new dyeing technique, known as "loopdye 1 for 6", by Eckhardt Theodor Godau. In comparison with other indigo dyeing methods with six colour troughs, in loop dyeing there is only one brief indigo dyebath with one squeezing unit. The process, offered by Looptex SA(CH) and under licence by Intes(I) and Texima SA(Brazil), is of modular construction. It comprises 8-16 warp beams (threading in feature), pre-wetting or pre-mercerising unit, twin-pad colour applicator, an integrated skying passage, two rinsing sections and an accumulator scray. Fig. 4 shows the sequence of operation used in this new technique.

3 Reduction of Indigo

3.1 Conventional Reducing Agents

Sodium hydrosulphite reduces indigo at 30-50°C depending on type of indigo used, resulting in formation of biphenols (leuco-indigo). The reduced form is quite stable in presence of NaOH to carry out dyeing at room temperature. However, hydrosulphite is very unstable. At the time of reduction of dye, it gets decomposed thermally, oxidatively and in various other ways, requiring 2-3 times higher amount over the stoichiometric requirement. Attempts have been made to keep control over its use through scientific analysis in course of dyeing.

Other reducing systems, viz. fermentation technique, copperas method, zinc-lime method, bisulphite-zinc-lime vat method, thiourea dioxide method, and sodium borohydride method have fallen out of use due to limitations associated with their applications.

3.2 Ecofriendly Reducing Agents

In recent times, the use of ecofriendly reducing systems for indigo has attracted attention of researchers. These new reducing systems include hydroxyacetone, iron-pentacarbonyl compounds,
electrochemical reduction, glucose-NaOH and iron (II) salt along with a suitable ligand.

Hydroxyacetone when used as a reducing agent (reduction potential \(-810\) mV) in refined dyeing\(^{29}\) process results in 20% higher dye uptake along with less consumption of auxiliary chemicals. Other advantages are higher quality dyeing, better ring dyeing effect, better elasticity of yarns, increased productivity, higher dye uptake and less dyestuff in effluent. However, in this method the required reduction potential for vatting is obtained at 100°C with higher concentration of NaOH and the produced shade does not correspond with that obtained with hydrosulphite. Hydroxyacetone is found to be more suitable for pad - steam method\(^{75}\).

The detailed report on the use of iron-pentacarbonyl compounds, though suggested as reducing agent, has not been disclosed so far\(^{76}\).

In electrochemical reduction technique, vat dye is directly reduced by making the contact between dye and electrode. A reducing agent at lower concentration must be added to the reduced dyestuff to ensure corresponding stability of reduced dye liquor. However, the dyestuff requirement for a specific shade is too high\(^{77-80}\).

Glucose in combination with NaOH can be used for the reduction of sulphur dyes [reduction potential \((-550)-(600)\) mV]. Indigo requires \(-700\) mV potential for reduction; hence glucose-NaOH system can also be used preferably at boil, producing reduced indigo baths free from sediments and highly stable for several hours. The problem related to this reducing system is that the padded textile requires more time for oxidation in between two successive dips and the indigo uptake is less\(^{81}\).

It has been reported that ferrous hydroxide is a strong reducing agent in an alkaline medium\(^{72}\). The reducing effect increases even more with the increase in pH value. Ferrous hydroxide is poorly soluble in alkaline conditions and precipitates. It must be complexed\(^{82}\) in order to hold the ferrous hydroxide in solution. Fe\(^+\) has hardly any reducing power as the central ion of complexes has the stable arrangement of krypton shell. However, a stable complex with reducing power is obtained with weaker ligands, e.g. gluconic acid. On dyeing with vat dyes at 60°C, good dye uptake was achieved for optimum concentration of iron(II) salt and molar ratio between this salt and gluconic acid. However, dye uptake decreases with the decrease in concentration of iron salt, even too low concentration of iron(II) salt gives lighter and unlevel dyeings at 1:1 and 1:2 molar ratios of iron(II) salt and gluconic acid due to the insufficient vatting of dye. When molar concentration ratio of iron(II) salt and gluconic acid was reduced to 1:0.5 unlevelled shades were produced with reduced brilliance\(^{73}\). Iron (II) salts in combination with NaOH and a weak ligand, like gluconic acid, tartaric acid citric acid or triethanolamine, at suitable concentrations can produce reduction baths with reduction potential ranging from \(-800\) mV to \(-1000\) mV. These reduction baths are capable of reduction and dyeing with indigo at room temperature. The reduction baths showed superior stability in presence of indigo up to 24 h. Deposition of iron on dyed samples was also assessed and it was found that gluconic acid as ligand causes least deposition whereas citric acid causes maximum deposition. Produced shades were bright with no shifting of \(\lambda_{\text{max}}\). The baths were turbid throughout dyeing\(^{83}\).

It may be summarised here that for quality dyeing, whatever may be the reducing agent the reduction potential and alkalinity of bath should be accurately adjusted for development of true shade of indigo\(^{84-90}\).

### 4 Factors Influencing Indigo Uptake

Reduced and solubilized indigo, though ionic in nature, possesses negligible affinity for cotton; a multiple dip / nip technique is followed with intermediate airing for gradual build-up of shade. Yarn to be dyed is dipped in indigo bath for a specific time followed by a passage through padding unit in order to achieve better penetration as well as distribution at nearly 100% expression, succeeded by air oxidation. This dip / nip followed by airing cycle is repeated till desired depth of shade is produced, succeeded by a final oxidation for 3-5 min for complete conversion of soluble indigo to its insoluble form.

As stated, desired depth of shade is primarily governed by number of dips/nips, but dye uptake during each dip is influenced by a number of other process parameters, viz. pH of dyebath, immersion time, time of intermediate oxidation, concentration of indigo and temperature of dyebath. These parameters affect build-up of indigo on cotton, degree of penetration and various fastness properties.

The crucial factor is \(\text{pH}\) of indigo bath\(^{54,91-95}\). Depending on dyebath \(\text{pH}\), indigo may exist in following four different forms as shown in Fig. 5:

\[\text{Indigo Blue} \quad \text{Reduction Bath} \quad \text{pH} = 4 \quad \text{pH} = 7 \quad \text{pH} = 9 \quad \text{pH} = 12\]

\[\text{Indigo Blue} \quad \text{Indigo Yellow} \quad \text{Indigo Green} \quad \text{Indigo Orange} \quad \text{Indigo Red}\]
Solubility of mono-phenolate form in this pH range. Rate on cotton at pH and fibre, resulting in reduced dye uptake. Charge on fibre and more is the repulsion between dye and fibre, resulting in reduced dye uptake.

Importance of pH is also related to ease in washing. Indigo shows maximum affinity as well as higher strike rate on cotton at pH 10.5-11.5 due to the lower solubility of mono-phenolate form in this pH range.

Structures (i) and (ii) exist below pH 9-9.5; their relative fraction depends on exact pH of bath. With slow increase in pH structure (i) collapses and gets converted to either (ii) or (iii) or mixture of both. Further increase in pH above pH 10 slowly converts all (ii) to (iii). At around 11.5 pH almost all indigo molecules are in their mono-phenolate form. Any further addition of alkali beyond pH 11.5 slowly attacks second C=O group of indigo in presence of excess hydrosulphite, resulting in the conversion of mono-phenolate form (iii) to bi-phenolate form (iv). The extent of conversion strictly depends on exact pH and excess hydrosulphite in dyebath. As the presence of excess hydrosulphite is must for successful indigo dyeing, if alkali is added in excess above pH 12.5, the structure (iv) predominates. Indigo in the form of structure (iv) shows reduced affinity for cotton and thus dye uptake falls. Structure (i) shows no affinity whereas structure (ii) has negligible affinity, as both these structures are non-ionic forms of indigo. Mono-phenolate form is the desired structure which possesses highest affinity as well as strike rate to give higher dye uptake. In this context it is also to be noted that cotton when dipped in alkaline bath acquires negative charge. The higher the pH, the higher is the charge on fibre and more is the repulsion between dye and fibre, resulting in reduced dye uptake.

This hinders penetration inside cotton and gives more intensive surface dyeing, achieving better wash-down effect.

It was mentioned earlier that the relative fraction of mono-phenolate and bi-phenolate forms of indigo can be positively controlled by adjusting the dyebath pH\[^{54,87,91,92,94,95,97-104}\]. pH is such a crucial factor in dyeing with indigo that it not only controls dye uptake but also distribution of indigo on cotton yarn through control over strike rate and hence wash-down properties with removal of unfixed dyes\[^{87,105}\].

Out of two soluble forms of indigo viz. mono-phenolate and bi-phenolate, the former has relatively lower water solubility and higher strike rate, just opposite to that of bi-phenolate species (Fig. 6). Hence, if pH can be kept within a range of 10.5-11.5, most of indigo molecules will exist in bath in their mono-phenolate form, showing higher strike rate for cotton, resulting in poor penetration and higher surface deposition of dyes—the so called ring dyeing effect\[^{87,91,105}\]. In ring dyeing, only a few surface layers are dyed leaving interior of yarn undyed due to the absence of adequate time for penetration as well as thorough distribution\[^{105}\] (Fig. 7). If pH is raised above 11.5, the relative fraction of mono-phenolate form

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(i) indigotin structure at lower alkaline pH,
(ii) reduced but non-ionic form at moderate alkaline pH,
(iii) mono-phenolate form at relatively higher pH, and
(iv) bi-phenolate form at very higher pH.
gets reduced with instant increase in that of bi-phenolate form, lowering the strike rate. This consequently increases time for absorption, resulting in dyeing of few more layers than that obtained with mono-phenolate form. With the further increase in pH, mono-phenolate form goes on diminishing with a substantial rise in bi-phenolate form and thorough dyeing of cotton occurs.

Efficient wash-down property of indigo dyed yarn depends on the amount of dye present on yarn surface. It is the 10.5-11.5 pH range which gives dyeings with desired washing performance and a deeper shade with less amount of indigo. Dyeing at higher pH range gives relatively lighter shades and lower wash-down property.

Ionic nature of cellulose also affects indigo uptake. With the increase in alkalinity of indigo bath ionisation of cellulose (expressed in g-ions / litre) increases with development of more anions, e.g. concentration of Cell-O' at pH 10 is 3 \times 10^3 g-ions/litre, which increases to 1.1 g-ions/litre at pH 13. This, in turn, suppresses substantivity of indigo, finally lowering the dye uptake. Calculation of different forms of indigo in bath, though cumbersome, can be made through the study of equilibrium ionisation constant values.

Effect of immersion time on final colour depth in indigo dyeing shows that with the increase in immersion time, dye uptake increases initially, remains nearly same for little further increase in pH and beyond certain limit falls considerably. An immersion time of 30 s seems to be adequate. Prolonged immersion reduces colour depth mainly due to the re-reduction of oxidised indigo retained by cotton through previous dips and go back to dyebath. To get optimum colour yield oxidation time is fixed at 60 s. Due to very low affinity of solubilised indigo in bath for cotton, the increase in indigo concentration in bath though initially can increase the depth of colour, but beyond certain concentration does not show any remarkable change on dye uptake. Increase in indigo concentration up to 3 g/L in bath increases its uptake on cotton but beyond this concentration it shows little impact on dye uptake. Optimum depth of shade is obtained in as high as ten dips and beyond that no such increase occurs. But keeping in view the limitation in machinery set up and a lengthy process time, generally a 6-dip 6-nip technique is followed. However, it has been reported elsewhere to use the lowest possible concentration of indigo and maximum number of dips. By doing so, colour uniformity, fastness and wash-down properties after dyeing improve. A rule of thumb is that more the number of dips used for a given shade with low concentration of indigo in bath, the better the colour uniformity, fastness and wash-down properties.

Affinity of solubilised indigo for cotton decreases with the increase in temperature, initially at a faster rate followed by very slow decrease. At lower temperature, affinity of indigo is better and also re-reduction of oxidized indigo does not occur typically. Hence, it is better to carry out dyeing without any application of heat. It has been reported that the maximum dye uptake occurs if dyeing is carried out at room temperature. With the increase in dyeing temperature from 40°C to 60°C, dye uptake falls relatively at a slower rate and beyond that it becomes almost parallel.

5 Techniques to Enhance Indigo Uptake

5.1 Alternate pH Control Techniques

Indigo uptake can be enhanced through proper control over pH in the region 10.5-11.5. NaOH, used in indigo dyeing, is a very strong alkali and makes efficient dyeing impracticable due to the wide fluctuation in pH during dyeing. Initially, the pH is highly sensitive to NaOH concentration, a small change in NaOH concentration changes pH remarkably. The normal practice is to add NaOH at higher concentration so that the final dyebath pH does not fall below 10.5 with a result of less dye uptake in initial dips. This is because when less NaOH is used in an attempt to achieve a dyebath pH of 11.0, small changes in NaOH concentration lead to very large changes in dyebath pH. In fact, the dyebath pH may drop suddenly into a range in which mainly non-ionised indigo is formed and superficially deposited onto the denim yarn. Such deposition inhibits sorption of ionised dye, leading to streaking and extremely poor crock fastness. In contrast, the use of excess alkali makes lighter dyeings of higher alkalinity, which creates trouble in finishing.

Attempts to substitute NaOH with other alkalis/bases developed buffered alkali system of undisclosed composition. This was manufactured by Virkler Company, USA, which when applied in indigo bath at recommended concentration produced a stable pH in the range of 11.0 and little fluctuation occurred in dye uptake throughout the period of dyeing.

In another attempt, NaOH was substituted with different organic bases. Before application, alkalinity of these bases was evaluated and then these were
applied in various indigo baths, keeping equivalent alkalinity with that produced with NaOH. It has been reported that the dye uptake with these new systems was on quite higher side than that obtained with NaOH method. Stability of indigo bath was superior to that of NaOH baths even after a lapse of 8 h. Change in pH with time was also studied and it was found that most of the bases are capable of maintaining pH in 10.5-11.5 range up to 4 h (ref. 113).

5.2 Pretreatment of Cotton

Indigo in solubilised state is anionic in nature and will be attracted by cotton if the latter is pretreated with cationic compounds. Cotton was pretreated by immersing it in a solution containing 200 g/L of 12% aqueous Hercosett 57 (cationic water soluble polyanime-epichlorohydrin resin) and 10 g/L of Sandozin NI for 5 min followed by squeezing the material in padding mangle to achieve 80% pick-up and drying at 100°C for 3 min. Treated cotton was padded with indigo through 6-dip 6-nip technique. It has been reported that dye uptake on pretreated cotton remain on higher side than that on untreated cotton under identical dyeing conditions.

Pretreatment of cotton with metal salts prior to padding with indigo (which may be done in several ways to synchronize with batch or continuous dyeing methods) results in substantial increase in indigo uptake. It is also observed that iron and cobalt (II) salts are more effective even at very low concentration of 1g/L. Formation of insoluble metallic hydroxides in situ cotton in presence of NaOH and air is responsible for more anionic indigo molecules in bath, causing increase in dye uptake.

Introduction of a mercerizing step prior to indigo padding enhances indigo uptake considerably. A DIMER was shown at ATME-I, Greenville, October 1988, which is basically a loop dyeing system that incorporates real premercerizing in the loop dye process for indigo warp dyeing. The technique was originally developed in Switzerland by Loopdyke, but is now being produced and marketed by Kuesters. The unit simplifies warp production with advantages like improved fabric appearance and handle, higher yarn strength, higher dye uptake and more intensive ring-spun yarn dyeing with shorter stone washing. Even it also possible to bottom with sulphur, indanthrene, reactive and naphthol colours.

6 Cost Effective Production in Indigo Dyeing

Multi-vat machine concept has regained its importance through flexible adaptation of machine technology. Accurate dosing, targeted dyestuff use, low dyestuff and chemical losses are the main aspects of such production system.

According to literature, adequate dwell times in the steeping bath (approx. 6 m/bath) and oxidation zones (>60 s) together with a high circulation rate with low dyestuff concentration have been pursued in order to achieve optimum dyeing. Due to lower dyestuff concentration in the effluent, ultra-filtration device can then be equipped with smaller filter surfaces to reduce investment and operating cost. Washing water consumption can be kept low at 3 L/kg of warp.

Indigo vat, hydrosulphite and NaOH are continuously dosed in proportion to speed of circulation avoiding shade variation. A Semen Op 20 automation unit, confirming a high degree of processing reliability and reproducibility, controls dosing. Dosing of dye is controlled via a special frequency control pump. Measuring systems are available for bath concentration, pH value, redox potential, bath temperature, etc.

Another unique way of cost reduction is ‘zero discharge concept’, which works in ‘loopdye I for 6 process’ using hydroxyacetone as reducing agent to produce waste-free improved quality dyeing at reduced cost through recovery and reuse of unused dye and wastewater.

7 Quantitative Estimation of Indigo

Indigo in dyed textile/dye bath/wash liquor is determined spectrophotometrically at maximum wave length (λmax). When indigo is in solid state, each of its molecules forms H-bonds with 4 adjacent dye molecules (between C = O and NH groups) and makes it insoluble in water as well as in most of the organic solvents. Pyridine acts as a good solvent. For spectroscopic estimation of indigo, a clear and stable solution of indigo is an indispensable precondition for consistent and reproducible results. Alternately, turbidity of oxidised form of indigo may be a measure of quantitative estimation. Several analytical methods have been devised in this context, viz. colorimetry of leuco indigo, turbidity of indigo in oxidised form and colorimetry of sulphonated indigo. In solvent technique, a few methods based on colorimetry of chloroformic, pyridine/water and dimethyl sulphoxide extracts have also been reported.

The colorimetry of leuco indigo method consists of reduction of pure indigo with hydrosulphite in
alkaline medium. Absorbance is instantly observed at 412 nm, as reduced indigo has time-bound stability; its spectrum changes considerably in very short time intervals. This technique lacks reproducibility. However, the technique may be dispensed with other methods if stability of reduced indigo can be increased. It has been mentioned in literature that iron(II) complex with triethanolamine can reduce vat dyestuffs and the reduced dye bath has high degree of stability to temperature, time and atmospheric oxygen. In this technique, iron(II) salt concentration should be kept under control as iron ions below 400 ppm tend to go for self absorption.

Turbidity of oxidized indigo method shows no linear relation between turbidity and concentration. In some cases, the higher values of turbidity were also achieved on reducing the concentration. This behaviour is possibly due to the excessive dimensions of indigo particles as well as distribution of uneven sizes. Addition of glycerine to stabilize the suspension did not improve the results (glycerine increases bath density and retards particle fall). Maximum absorbance was found to be at 666 nm but the slope of the calibration curve varied according to the status of initial dyeing bath.

In sulphonated indigo method, incorporation of solubilizing groups of sulphuric acid in indigo structure makes indigo water soluble, stable and deep blue coloured. The absorbance is maximum at 605 nm (ref. 125). Beer's law is fulfilled up to 15 ppm of concentration and the reproducibility of the method is 0.3-2%. However, before sulphonation, indigo should be in oxidized and dried form otherwise a greenish-brown solution is obtained. Indigo should also be free from hydrosulphite. This analytical technique is hardly suited for instantaneous and continuous control of indigo liquors. Sulphonation of indigo with concentrated sulphuric acid at 75°C is also troublesome.

7.1 Solvent Techniques

The colorimetry of chloroformic extract gives maximum absorbance at 605 nm and good linearity is achieved in the calibration curve up to indigo concentration of 10 ppm. At this concentration solubility limit of dye in chloroform is reached and a blue interphase between the two layers is formed during extraction.

Indigo structure has a similarity with that of pyridine. Solubilization occurs through H-bonding between these two. Oxidized indigo can be dissolved up to a concentration of 40 ppm by boiling in pyridine-water (50:50) solution which is then photometrically measured at 625 nm. Measurement must be done when the solution is hot to avoid precipitation of indigo on cooling the solution. Indigo should be completely free from hydrosulphite; if not, the later decomposes indigo during heating with reagent solution. Presence of NaOH with dye also changes absorbance as aggregation of dye alters with pH. This method has a reproducibility of 2-4% (ref. 125).

A completely new approach has been made by solubilizing oxidized indigo in dimethyl sulphoxide (DMSO). The method does not have any problem as shown with earlier methods. It is time saving, safe, without interference and largely reproducible. Solubility of indigo is excellent even at room temperature; the maximum absorbance is achieved at 619 nm. The solution is highly stable for several days and for indigo concentration of up to 250 μg/ml, complete dissolution takes place. The only problem lies in handling of DMSO is that it is slightly detrimental to health, causes irritation in contact with skin and itching, etc.

In some cases, denim is dyed with a combination of indigo and sulphur or hydron blue dyes. To estimate contribution of these two in the shade developed, indigo is first extracted completely from sample at boil in pyridine-water solution. The dyed sample under test is rinsed with methyl alcohol and dried at 40°C to remove residual pyridine and methyl alcohol. Reflectance of the sample is measured. Colour strength calculated from reflectance value at each wavelength is integrated over the wavelength range, the result is an integrated value.

8 Conclusion

Though indigo is a class of vat dye, it cannot be applied according to conventional vat dyeing techniques due to its negligible affinity for cotton, rather multiple dip/nap with intermediate airing is to be followed. During dyeing, the pH of dye bath plays a crucial role to affect indigo uptake as well as location of dye on cotton structure, though influence of other factors cannot be overlooked. Dyeing mostly takes place in yarn stage, necessitating selection of specific machine depending on form of yarn. Beside dyeing parameters, special techniques through use of buffer/other alkalis/bases, pretreatment of cotton, etc. may be introduced to enhance indigo uptake. As far as quantitative assessment of indigo is concerned,
DMSO method has been found to be the most effective one.

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