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Chapter 1

1. General Introduction

Textile materials (natural and synthetic) used to be coloured for value addition, look, and the desire of the customers. Anciently, this purpose of colouring textiles was initiated using colours from natural sources until synthetic colours and dyes were invented and commercialised. Due to the ready availability of pure synthetic dyes of different types and classes and their cost advantages, most textile dyers and manufacturers shifted towards the use of synthetic colourants. Almost all the synthetic colourants being synthesised from petrochemical sources through hazardous chemical processes pose a threat to their eco-friendliness. Hence, worldwide, growing consciousness about the organic value of eco-friendly products has generated renewed interest among consumers in the use of textiles (preferably natural fibre products) dyed with eco-friendly natural dyes. Natural dyes have been known for their use in the colouring of food substrates, leather, and natural fibres like wool, silk, and cotton as major areas of application since pre-historic times. Although this ancient art of dyeing textiles with natural dyes withstood the ravages of time, due to the wide availability of synthetic dyes at an economical price, a rapid decline in natural dyeing continued.

The consumption of synthetic dyes is more than one million metric tonnes per year, and more than 1000 metric tonnes of natural dyes are required, which is almost 1% of the world's synthetic dye consumption. However, even after a century, the use of natural dyes has never eroded completely, and they are still used in different parts of the world. Thus, natural dyeing of different textiles and leathers has been continued mainly in the decentralised sector for specialty products, besides the use of synthetic dyes in the large-scale sector for general textiles and apparel.(Gulrajani, 2001).

All the local craftsmen/artisans are extracting the dyes themselves and dyeing as per their skills. Besides that, many organizations are producing the dyes. Some Indian companies are: Satal Katha, Sam & Ram, Amma Herbal, D. Manohar Lal, etc.(Gulrajani, 2001).

Natural dyes have a complex chemical constitution. Unlike synthetic dyes, they are usually not a single entity but a mixture of closely related chemical compounds. Natural dyes have been grouped together as a class in the color index. In Volume 3 of the color index, 32 natural reds, 6 natural oranges, 3 natural blues, 5 natural greens, 29 natural yellows, 12 natural browns, 6 natural blacks, and 1 natural white have been listed (Saxena & Raja, 2014). Natural dyes available in primary colours: In the colour index, the natural dyes are classified according to hue, and there are 28 yellow dyes, 3 blue dyes, and 32 red dyes. Red colour dyes: Most red dyes are hidden in the roots or barks of plants or camouflaged in the bodies of dull grey insects. They are almost invariably based on anthraquinone and its derivatives. These dyes are stable to light and washing. Yellow colour dyes: Yellow is the liveliest and perhaps the most abundant of all hues in nature. About 90% of the yellow dyes are flavonoids. Generally, they produce a pale shade with quicker fading, except turmeric, which produces a dull, deep shade but is considered susceptible to light as it emits fluorescence. The wash fastness rating of natural yellow dyes ranges from fair to excellent, e.g., tesu, turmeric, and kapila. Blue dyes, such as indigo and wool, give excellent fastness to light and washing. An attempt will thus be made to find the gamut of suitable natural dyes that are compatible, thus producing spectral data to formulate the recipe by spectrophotometer.

Chapter 2

2.1 Statement of the problem

As the scope of organic and natural products is increasing day by day, the use of natural dyes in textiles is also picking up pace. In this scenario, lots of scientific research is going on to increase the use of natural dyes. Many researchers are trying to simplify the process of natural dyeing in many possible ways. In today's ever-competitive global economy, maximising product output becomes ever more important. For those of us that deal with colour as one of our product's critical specifications, this can be a thorny and time-consuming issue. Manufacturers that produce items such as dyed or printed textiles, paints, plastics, cosmetics, and food will attest to not only the importance of having the correct colour and appearance on every order but also the time it takes to bring the colour of a product within acceptable specification limits. There are a lot of studies available in the literature regarding the extraction, application, dyeing behaviour, antibacterial activities, and others of many individual natural dyes. But the reports on the application of natural dyes in combination are very scanty. For synthetic dyes, there is a well-established method for computerised colour matching, but for natural dyes, such studies are not found in the literature. Readily available reports on compatible dyes will make it easier for natural dye users to produce a variety of mixed shades. Computerized prediction of recipes would further smooth the task of natural dyers. Under this background, it is thought to provide a wide range of information on natural dye compatibility for selected dyes to the people working in large or small sectors and the researchers working in this field so that it may be easier for them to make mixed shades using natural dyes. Combinations of natural dyes in compound shades will provide a variety of newer or less common shades. In this study, therefore, an attempt will be made to find the gamut of suitable natural dyes that are compatible, thus producing spectral data to formulate the recipe by spectrophotometer.

2.2 Objective of the research

- To optimize the extraction process of selected natural colours
- To find the optimal dyeing parameters of selected natural dyes on cotton fabric
- To dye the cotton fabric with binary and tertiary mixture of natural dyes
- Assessment of compatibility for mixture of dyes
- Spectral database creation for the selected dyes using computer aided

spectrophotometer.

- To predict the recipe for certain standard shades using spectral database in spectrophotometer
- To analyse the fastness properties of selected dyed samples

2.3 Delimitation of the study

- The study was limited to only 8 natural dyes namely: Marigold, Pomegranate, Madder, Sappanwood, Rhubarb, Annatto, Catechu and Acacia Nilotica
- The study was limited to cotton and the use of alum mordant using pre-mordanting method
- The study was limited to exhaust method of application

2.4 Scope of the Study

- The study attempts to find out the optimized extraction conditions for selected dyes and optimized dyeing condition for them on cotton fabric.
- The study will attempt to find out the compatible/ non-compatible set of dyes from a set of dyes using different methods. This will give rise to the possibility of new shades production using compatible set of dyes.
- This study will attempt for the prediction of recipe using spectrophotometer. The dyer can predict the recipe for a particular standard as done in the case of synthetic dyes.

Chapter 3

Literature Review

3.1 Application of selected natural dyes on textiles

Davulcu *et al.* (2014) experimented on dyeing of cotton fabric with pomegranate peel. The fabric was pre-mordanted with alum. The dyeing parameters were temperature 100 °C, pH 7, and time 60 min. The K/S for the mordanted fabric was significantly higher than the unmordanted fabric, with a similar effect on L*a*b*h* values. Anti-bacterial activity tests showed a 90% reduction in bacterial activity on unmordanted cotton dyed fabric with pomegranate.

Tutak, Acar and Akman (2014) showed that the waste pomegranate peel extract can dye the wool fabric properly. Pomegranate dyed fabric had a K/S in the range of 6.63 to 23.05, and the colour fastness results obtained were moderate to high. Samples dyed using iron sulphate mordant gave good light fastness properties (5-6 rating). Mordant iron sulphate was found to give good light fastness (rating 5-6). The SEM images of the dyed fabrics demonstrated a smooth surface profile.

The findings of Farooq *et al.* (2013) indicate that the parameters involved in the processes of extraction and dyeing have a noteworthy impact on the colour attributes and overall quality of cotton textile materials. The study determined that the optimized conditions for the marigold flower extraction were M:L ratio of 1:20, an extraction time of 90 minutes, and a temperature of 100°C. Similarly, the optimized parameters for dyeing were found to be a M:L ratio of 1:30, a dyeing time of 1 hour, a temperature of 90°C, and a salt concentration of 60 g/L of Na_2SO_4.

Jothi (2008) worked on the cotton and silk fabrics and pre-mordanted using alum and other metallic mordants. The samples were dyed using marigold flower and colour parameters & fastness properties were measured. Dyeing was done using conventional method at neutral pH for cotton and pH 4 for silk fabrics. Moderate to good colour fastness properties are obtained using aluminum, copper and iron mordants.

Devi Priya and Siril (2022) studied the effect of mordants and mordanting methods on bleached cotton poplin fabric using Rubia cordifolia, where the extraction was done using an aqueous method. Different mordants, including alum, at 5% owf, were applied using methods of pre-mordanting, simultaneous mordanting, and post-mordanting. The dyeing was done at pH 7.5 and 95 degrees C for 45 minutes. Various hues of red were obtained using alum mordant in three mordanting methods. The dye uptake on cotton fabric was highest using alum in pre-mordanting and myrobalan in post mordanting methods, while it was lowest in the simultaneous mordanting method for all the mordants. The colour fastness rating shows an average to good rating for all the mordants except copper sulphate for wash colour fastness.

Dhanania, Singhee and Samanta (2021) optimised the conditions reported in the literature were employed to perform aqueous extraction of babul bark powder. The extraction was carried out using an MLR of 1:30, a temperature of -60 °C, a time of 45 minutes, and a pH of 6. Cotton fabric pre-mordanted with gallnut was subjected to dyeing using an aqueous extract of babul bark under different dyeing conditions, including variations in dye concentration, pH, FLR, time, and temperature, among others. The optimal conditions include a dye concentration of 40%, a FLR of 1:20, a dyeing time of 30 minutes, and a dyeing temperature of 100 °C. These conditions result in the highest surface colour strength and satisfactory colour fastness to light, washing, rubbing/crocking, and perspiration.

A study by Zerin and Foisal (2016) involved the dyeing of woven fabrics made of 100% cotton using Acacia catechu, a natural dye. The extraction of catechu was done using 10% w/v catechu and water and boiling for 2 hours. The process of mordanting involves three distinct methods, which include pre-mordanting, post-mordanting, and simultaneous mordanting during the dyeing process. The mordants employed in the process were alum and copper sulphate. In this investigation, a mordant solution with a concentration of 3% was employed at a liquor ratio of 1:40. The process involves subjecting the material to mordanting at a temperature of 80 °C for a duration of 30 minutes in all stages of pre-mordanting, post-mordanting, and simultaneous dyeing-mordanting. This study demonstrates that Catechu produces a variety of brown tones on cotton that can appeal to a large number of discerning consumers. On cotton that has been catechu-dyed, it has been discovered that mordanting processes can affect the intensity of brown colours. Reflectance was found to be larger when no mordanting was conducted, whereas the K/S value was found to be greater when mordanting was performed beforehand. In Catechu dyeing, the refraction percentage, K/S, and colour fastness values for alum and copper sulphate are very similar.

3.2 Compatibility of dyes

Most of the dye producers are providing the different tones and hues of the three basic colours. They try to provide as many tones as possible by changing the structure of the dye. To dye a piece of fabric for any given colour standard, three colours are generally required. If the dyer is lucky enough, the same tone may be obtained by single dyeing or combining two dyes, but this is a rare phenomenon. Mostly, the dyer would require three primary colours. The dyer's task of mixing the dyes and getting a shade out of them is not an easy one. The dyer has to check the compatibility of the dyes being mixed. The optimum dyeing conditions may be different for different dyes. The fastness properties of the different dyes may be different, or the mixture may change the tone during the dyeing cycle. Reproducibility of the shade is a very crucial matter of concern for the dyer. There is scope for improvement through the use of better compatible dyes (Sivaramakrishnan, 2014). All the dyes in the mixture should have the same rate of dyeing. They should have similar rates of exhaustion when used in mixtures under the given dyeing conditions. During dyeing, the colour of the goods will then gradually become deeper, but, since the dyes are absorbed in the same proportions throughout the process, the hue does not change and the goods will always be on shade (Broadbent, 2001).

In the AATCC technical manual (1989) compatibility is defined as **"the propensity of individual dye components in a combination shade to exhaust at similar rates resulting in a build up of shade that is constant or nearly constant in hue throughout the dyeing process".**

In this way, several dyeing parameters are mentioned in the literature, which defines the compatibility of dyes. Many researchers have attempted to define the qualitative and quantitative methods for compatibility.

3.3 Methods to assess the compatibility of dyes

Sultana and Zulhash Uddin (2007) checked the compatibility of dyes using dip test. In this test, small pieces of cotton of equal weight are dyed in the same bath with a mixture of dyes. At various intervals, a small dyed sample is removed from the bath and replaced by an identical piece of undyed fabric. A series of dyed samples arranged in order of increasing dyeing time will have gradually decreasing colour depth, but the invariant hue, when the dyes used are compatible.

Degree of on-tone build-up, rate of dyeing, half-dyeing time, diffusion coefficient, change in hue angle are also used to check the compatibility of binary and tertiary mixtures of dyes.

Determination of compatibility of reactive dyes was done using the chromatic diagram by (Singh, Bhattacharyya and Gupte (2006). It was assessed qualitatively from the nature of plots of Chromaticity Co-ordinates (y against x). Compatibility is observed if the dominant wavelength of all the dyed samples taken out at various time intervals during dye fixation falls between 10 or less than 10 nm (Singh et al., 2006)

Hoffman (1988) worked on compatibility check by plotting ΔL versus K/S or Δ C versus K/S. It is generally used for compatibility check of two dyes for two sets of the progressive depth of shade developed for a binary mixture of dyes. It is done by varying the temperature and time of dyeing for one set and varying the total dye concentrations of the binary mixtures of dyes in another set to judge whether the two sets of curves for shade buildup run alike or not. A plot of ΔL versus ΔC and/or ΔL versus K/S gives better results than other methods because it assumes that there is no interaction between dyes and no change in the rate of dyeing in the presence of another dyestuff, which is not true. A plot of ΔL versus ΔC and/or ΔL versus K/S would require a precise temperature-controlled machine for progressive shade buildup. This method is time-consuming and subjective.

McLaren (1976) devised an objective method with a view to answer the doubts and disputes caused by the earlier methods of assessing compatibility because of its subjective nature. With the introduction of colour measurement systems, series of compatibility tests can be assessed by measuring for e.g.: the hue angle.

3.4 Research related to the compatibility

Sultana & Zulhash Uddin (2007) studied the compatibility of certain reactive dyes on cotton in the different textile industry in Bangladesh. Three steps process was used which includes the measurement of the extinction coefficient, measuring the concentration at a different stage of dyeing and measuring the colour strength before and after wash.

Haque et al., (2015) conducted a reasearch on the auxiliaries present in the dye bath which may also affect the compatibility of dyes. Compatibility analysis of reactive dyes is done by exhaustion-fixation and adsorption isotherm on knitted cotton fabric. Red RR, Blue RR, and

Yellow RR dyes were analyzed. The exhaustion % of Red RR and Blue RR was uniform but exhaustion % of Yellow RR was decreasing with the increase of shade %. The difference in their fixation was significant in deeper concentrations. Increasing the amount of electrolyte gives better results especially for deeper shades. It was also found that a decrease in alkali amount in a dye bath and reducing the washing temperature increases the compatibility of these dyes.

Shahparvari et al. (2018) studied the compatibility of natural dyes on Aluminum pre-mordanted woolen yarn, diffusion coefficient has been calculated and compatibility was checked. The dyes were a walnut green shell, cochineal, and weld. The following equation has been used to check the compatibility:

$$log \frac{C_{t,1}}{C_{0,1}} = K . log \frac{C_{t,2}}{C_{0,2}}$$

Where, $C_{t,1}$ and $C_{t,2}$ denote the concentration of each dye in the dye bath at time t. Besides, $C_{0,1}$ and $C_{0,2}$ show the concentration of each dye in the dye bath at the beginning of dyeing or time=0, respectively. K is a constant that defines the degree of compatibility and ranges between 0 and 1 with 0 as incompatible and 1 as excellent compatibility. It was found that the exhaustion of each dye in single dyeing is different from the exhaustion in the dyeing mixture. The order for compatibility is as follows: cochineal-weld > walnut green shell-cochineal > walnut green shell-weld.

It was observed by Kumar Samanta & Agarwal (2009) that the use of a mixture of turmeric and madder on cotton in case of simultaneous mordanting shows a synergistic effect in colour development than that for single dye application; 50:50 ratio of turmeric and madder gives the best results. For the combined dye application, it is observed that in the case of simultaneous mordanting method, turmeric when combined with either madder or red sandalwood gives better colour strength, while myrobolan shows the reverse trend.

Samanta^ et al. (2009) studied the single and binary mixture of aqueous extract of red sandalwood with aqueous extract of the other five natural dyes in different proportions are applied on bleached jute fabric. The other five dyes used are Manjistha (MJ), Jackfruit wood (JFW), Merigold(MG), Sappan wood (SW) and babool(BL). These were used in different proportions with Red Sandalwood (RSW). Colour parameters, colour fastness, and compatibility were checked for these combinations of dyes. In this study, the author has not used the conventional methods of compatibility check but has formulated a newer method of assessing then compatibility using a newer index called CDI. On application of different proportion of binary mixtures of dyes on the same fabric, magnitude of respective ΔE, ΔC, ΔH and Metamerism Index (MI) values irrespective of their sign and direction have been utilized to obtain an empirical index called 'CDI' for the samples dyed with different proportions of binary mixture of dyes by the following relationship.

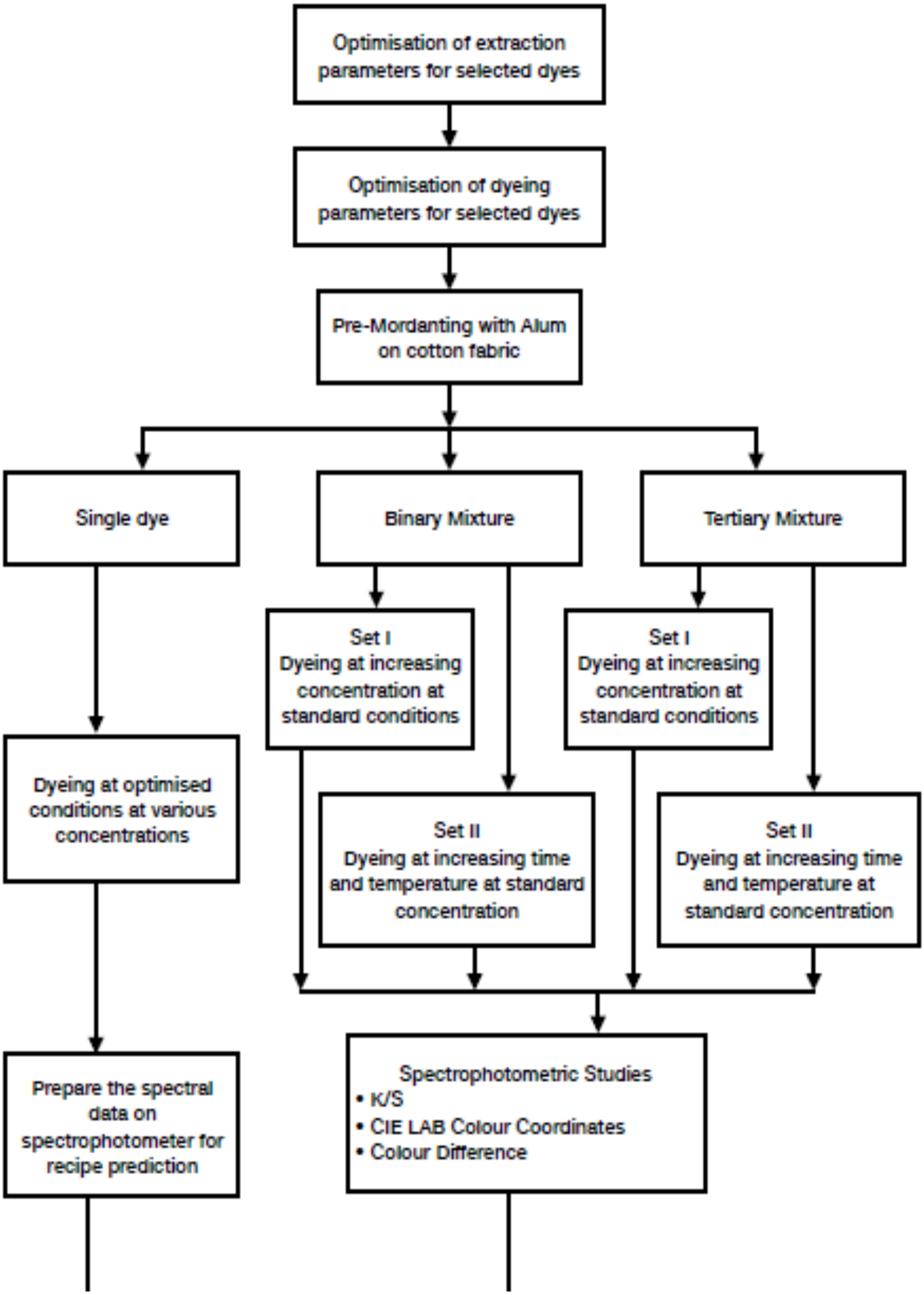
$$CDI = \frac{\Delta E \text{ x } \Delta H}{\Delta C \text{ x MI}}$$

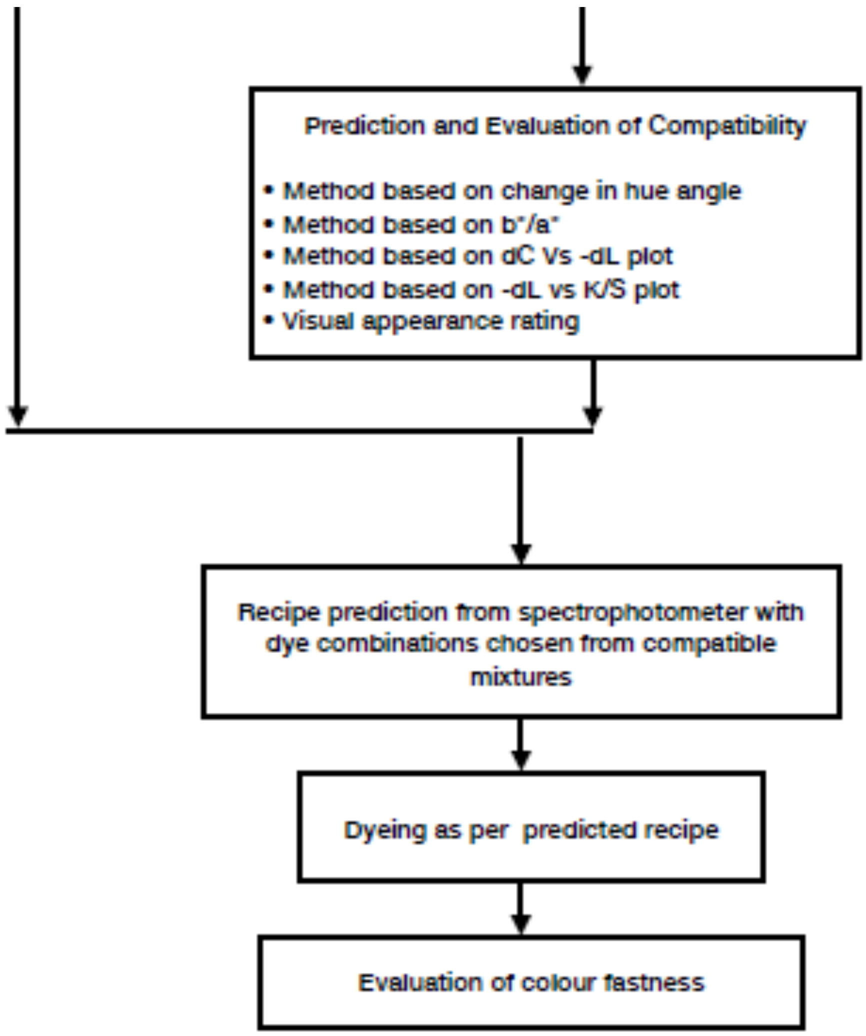
The closer the CDI values for a different proportion of mixture of dyes applied on the same fabric under the similar condition of dyeing, the higher is the compatibility. A relative compatibility rating (RCR) is proposed in accordance with CDI values. The scale of compatibility (RCR) is 0-5, zero is the least compatible and 5 is excellent compatibility. As per RCR system, the order of compatibility was found to be as RSW:MJ>RSW:MG>RSW:JFW>>>RSW:BL>>>RSW:SW.

In a similar study as above by Samanta et al. (2008), varying proportion of binary mixtures of aqueous extracts of jackfruit wood (JFW) with other natural dyes, like manjistha (MJ), red sandal wood (RSW), mariegold (MG), sappan wood (SW) and babool (BL), have been used to dye bleached jute fabric pre-mordanted with 20% myrobolan followed by 20% aluminium sulphate. The compatibility was found by conventional as well as the newer method (by finding RCR). The order of relative degree of compatibility of these binary pairs of natural dyes applied on pre-mordanted jute was found to be JFW:RSW ≥ JFW: BL ≥ JFW : MJ >>> JFW: MG >>> JFW : SW.

Chapter 4

Research Design




Prediction and Evaluation of Compatibility
• Method based on change in hue angle
• Method based on b*/a*
• Method based on dC Vs -dL plot
• Method based on -dL vs K/S plot
• Visual appearance rating
Recipe prediction from spectrophotometer with dye combinations chosen from compatible mixtures
Dyeing as per predicted recipe
Evaluation of colour fastness

Chapter 5

Materials and Methods

5.1 Materials

1. Cotton Fabric

Ready for dyeing (R.F.D.) bleached 60s cotton cambric fabric, obtained from R.M.P. Fab Sourcing Pvt. Ltd., Faridabad, Haryana, India, was used for the present study.

2. Chemicals, Dyes and Auxiliaries

Citric Acid, Sodium Carbonate, Alum (Aluminium Potassium Sulphate), and Non-ionic detergent were used in this present work. All these were laboratory grade chemicals from Fisher Scientific and Loba Chemie Pvt. Ltd. Dye material for Marigold, Pomegranate, Madder, Annatto, Acacia Nilotica, Sappanwood, Rhubarb and Catechu dye material were procured from the Jaipur.

3. Instruments and Apparatus

Electronic pH meter, Electronic Weighing Scale, HTHP Beaker Dyeing Machine; Make- R. B. Electronic & Engineering Pvt Ltd., Laundrometer and Crock meter; Make-Ramp Impex Pvt Ltd., Light fastness tester, Konica-Minolta Spectrophotometer, model-3600d.

5.2 Methods

5.2.1 Pilot study

Optimisation of extraction parameters for all the selected dyes

Dye material for Marigold, Pomegranate, Madder, Annatto, Acacia Nilotica, Sappanwood, Rhubarb and Catechu dye material were taken for extraction optimisation. Optimisation was done using a range of temperature, time and MLR as per Table 1

Table 1 **Experimental Setup for optimization of extraction parameter**

Parameter	Values
Control Factors	
MLR	1:10, 1:20, 1:30

Temperature (°C)	60, 80, 100
Time (min)	30, 60, 90
Response Variable	
Absorbance/Optical density	

The measurement of extracted dyed solution was done using the absorbance value (optical density) on spectrophotometer. Optical density was used to find the maximum colour extract from each dye and hence the optimised parameters for extraction were found. The optimised parameters for respective dyes were then used for the extraction and further dyeing of cotton fabric.

Optimisation of dyeing parameters

Ready for dyeing (R.F.D.) Bleached cotton cambric fabric was mordanted using alum with a M.L.R. of 1:60 and a temperature of 90 °C for 60 minutes. After the complete process, the samples were washed twice to remove the excess alum particles on the surface and make them ready for dyeing. The dyeing of pre-mordanted cotton fabric was done at M.L.R. 1:90 with a dye percentage of 30% owf at a range of pH, time, and temperature to find the optimum dyeing conditions for each. Box Behnken Design of Experiment to select the parameters. The details of the experimental setup are indicated in Table 2. 17 samples of each dye were dyed at different dyeing conditions for all dyes, viz., Marigold, Pomegranate, Madder, Annatto, Acacia Nilotica, Sappanwood, Rhubarb, and Catechu dye material.

Table 2 **Experimental Setup for optimization of dyeing parameter**

Parameter	Values
Control Factors	
pH	3,5,7
Temperature (°C)	65, 80, 95
Time (min)	30, 60, 90
Response Variable	
Surface Colour Strength	

All the samples were dyed as per the conditions mentioned above and were repeatedly washed with hot and cold water. Then the samples were subjected to soaping with a 1 g/l soap solution at 60 °C for 15 minutes and then drying. The optimised parameters were then found for individual and all dyes together on the basis of the maximum K/S obtained.

5.2.1 Experimentation

Dyeing of Binary and Tertiary Mixtures (Set I & II)

As per the objective of study, the binary and tertiary mixture is used to dye the cotton fabric after pre-mordanting with alum using the same conditions mentioned above. With the data of optimised dyeing conditions for each dye, common dyeing condition is found for all the mixture of dyes. The common conditions were found using statistical software.

In case of binary mixture for 6 dyes, a total of 12 combinations are possible and in case of tertiary mixture, a total of 8 combinations are possible. For each combination, two set of samples are prepared. For each set I, six samples were dyed at an equal increment of colour percentage up to total depth of shade of dye mixture with equal concentration of the component dyes at common dyeing conditions obtained above. For set II, six samples were dyed with certain time period intervals with corresponding increase in temperature keeping equal concentration of component dyes.

All the samples were dyed as per the conditions mentioned above and were repeatedly washed with hot and cold water. Then the samples were subjected to soaping with 1g/lt. soap solution at 60°C for 15 mins and then drying.

12 samples are dyed for each binary or tertiary mixture. A total of 144 samples were dyed for 12 binary mixtures and 96 samples were dyed for 8 tertiary mixtures.

The compatibility analysis was done using various methods mentioned in next section.

Dyeing of self-shades at various percentages for spectral data

Dyeing of each of the 6 dyes was done at varied percentages to prepare the spectral data on spectrophotometer for recipe prediction. For each dye, 10 samples were made starting from the minimum to maximum possible concentrations. The same procedure of mordanting, dyeing and soaping was done as done for mixture of dyes. The dyeing conditions taken were the same as of the common dyeing conditions obtained for the mixture of dyes.

10 samples were dyed for each dye. A total of 60 samples were dyed for 6 dyes. These samples were scanned using spectrophotometer and served as spectral data for the prediction of recipe.

Prediction of recipe and dyeing of samples as per standard

The recipe was predicted for a number of chosen standards using spectrophotometer and a number of samples were dyed. The same procedure of mordanting, dyeing and soaping was done as done for mixture of dyes. The dyeing conditions taken were the same as of the common dyeing conditions obtained for the mixture of dyes.

5.3 Testing and Evaluation

Optical density measurement

Dye materials for various materials namely Marigold, Pomegranate, Madder, Annatto, Acacia Nilotica, Sappanwood, Rhubarb, and Catechu were taken for extraction. The measurement of extracted dyed solution was done using the transmittance value (optical density) on spectrophotometer. Optical density was used to find the maximum colour extract from each dye and hence the optimised parameters for extraction were found.

Computer color measurement using spectrophotometer

Surface colour strength parameters were determined using Konica-Minolta Spectrophotometer, model-3600d. K/S is the measure of surface colour strength of dyed samples, and CIEL*,a*,b* values signify the lightness/darkness, redder/greener tone, and yellower/bluer tone, respectively. K/S, CIEL*, a*, b*, C* and h* values were obtained with the help of relevant software for all the dyed samples. The undyed white fabric was used as standard and the colour difference values ΔL*, Δa*, Δb* and ΔC*ab were also determined.

Compatibility Evaluation

Binary and tertiary mixture of dyes was prepared for set I & II. Both the set have 6 samples each for respective combination. The compatibility was evaluated using methods as below:

Method based on change in hue angle (h°)

Method based on ΔC vs –ΔL plot

Method based on -ΔL vs K/S plot

Colour Fastness Evaluation

Colourfastnes to washing, light and rubbing tests were conducted on samples from pure dyes, binary and tertiary combinations.

Colourfastnes to washing was done using test method AATCC 61-2009

Colourfastness to light was done using test method AATCC 16

Colourfastness to rubbing was done using ISO 105/X-1984 method.

Chapter 6

Results and Discussion

6.1 Pilot study

Optimisation of Extraction

Dye material for Marigold, Pomegranate, Madder, Annatto, Acacia Nilotica, Sappanwood, Rhubarb and Catechu dye material were taken for extraction optimisation. Optimisation was done using a range of temperature, time and concentration of material using optical density method using spectrophotometer. The optimised parameters for respective dyes were then used for the extraction and further dyeing of cotton fabric.

Optimisation of dyeing parameters

The dyeing of pre-mordanted cotton fabric was done at a range of pH, time and temperature to find the optimum dyeing condition for each dye. Box Behnken Design of Experiment was used to select the parameters. 17 samples of each dye were dyed at different dyeing conditions for all dyes, viz., Marigold, Pomegranate, Madder, Annatto, Acacia Nilotica, Sappanwood, Rhubarb, and Catechu dye material.

The colour parameters were measured using Konica-Minolta Spectrophotometer, model-3600d. The measurement was done in common used Daylight (D-65) illuminant with 10° standard observer over the 400-700 nm range. CIELAB coordinates L*, a*, b*, h* and K/S values were obtained with the help of relevant software for all the dyed samples. CIEL*,a*,b* values signify the lightness/darkness, redder/greener tone, and yellower/bluer tone, respectively. K/S is the measure of surface colour strength of dyed samples, and h*, the hue angle was measured for all the samples.

Effect of dyeing parameters

The dyeing parameters of pH, temperature and time effected the K/S of the fabric. The effect of pH was significant on the K/S. In some cases the samples showed very low colour strength in acidic pH and gradually increased with increase in pH towards neutral. In few pH sensitive dyes like madder, the tone changes significantly with change in pH. For example for madder, on visual examination, it found that the madder produces different colour/hues at different pH and other dye conditions. The samples at pH 3 were creamish colour with no red tint and almost no effect of time and temperature. At pH 5, the dye produces peach colour in initial temp 65° C, 30 minutes; turns to light purple at 80° C, 60 min and the turns complete red at

95° C, 90 mins. In other cases, the pH had non-significant role in tone of but effecting the overall colour strength of the dye. It was observed that the highest K/S was near pH 7 for most of the dyes.

It was found that the effect of temperature and time on tone was not very significant. The tone was not changing in most of the cases except one to two dyes. The effect of temperature and time has been significant for colour strength in many dyes. It was seen that the trend was not same for all the dyes but was varying. In case of annatto, the K/S increased with increase in temperature and time. The effect was sharp for temperature in comparison to time. At pH 5 and time 60 minutes, the K/S increases sharply from temperature 65° C to 87° C and then decreases slightly till 95° C. At pH 5 and temperature 80° C, the K/S increases slightly from time 30 minutes to 80 mins. The range of optimum temperature was from 65° C to 95° C and optimum time range was 60 minto 90 mins.

Optimum dyeing conditions, graphs of K/S Vs. pH, K/S Vs. Temperature and K/S Vs. Time were obtained using the Box-Behnken Design of Experiment for all the dyes under analysis.

Common dyeing conditions for combination dyeing

As per the objective of the study, the dyes were mixed as binary and tertiary combinations for dyeing. For this objective to accomplish, one common set of dyeing conditions need to be find out for all the dyes. All the binary and tertiary combinations were dyed using the common set of dyeing conditions. The common conditions obtained were pH – 7, temperature- 82.8°C and time – 88 mins. The nearest dyeing conditions were used for the ease in practical dyeing which is pH – 7, temperature- 85°C and time – 90 mins.

6.2 Experimentation

Dyeing of Binary and Tertiary Mixtures (Set I & II)

The binary and tertiary mixtures were used to dye the cotton fabric after pre-mordanting with alum using the same conditions mentioned above. In case of binary mixture for 6 dyes, a total of 12 combinations are possible and in case of tertiary mixture, a total of 8 combinations are possible. For each combination, two set of 12 samples are prepared. All the dyed samples were visually checked in colour matching box. Slight, average and major tonal variation was observed in the set I and II samples of compound shades samples.

Surface colour strength parameters were determined using Konica-Minolta Spectrophotometer, model-3600d. K/S, CIEL*, a*, b*, C* and h* values were obtained with the help of relevant software for all the dyed samples. The undyed white fabric was used as standard and the colours difference values ΔL*, Δa*, Δb* and ΔC*ab were also determined.

The visual analysis for the samples was done for each combination. For a compatible mixture the samples should not show tonal variation with gradual colour buildup. It was observed that the samples showed good, average and low compatibility behavior. In some cases where pomegranate and marigold were used, the visual analysis of initial samples of set II showed that the yellow component from marigold and pomegranate has more affinity than other dyes. This behavior was visible in initial samples of set II where sample number 7 and 8 were much yellower than sample number 9 to 12.

In the change of hue angle (h°) method for compatibility check, for a compatible dye combination, the variation in hue angle has to be minimum. The change in hue angle was checked for set I and set II. In some cases, the hue changes to certain extent only and shows good compatibility. For certain combinations, the hue angle for initial samples of set II showed significant variation which may be the cause of low time and temperature conditions provided. This type of behavior impacted the compatibility in the combination.

Method based on -ΔL vs K/S plot was used to check the compatibility of combinations. It shows the effect on K/S when the sample is getting darker. For a particular compatible combination, the plot of -ΔL Vs K/S has to overlap for the set I & II. In many cases, the overlap has found in the range of 60-80% and less in other cases. As per this method, many of the combinations are compatible while some are less compatible.

As per above methods, a set of four to six combinations showed good compatibility behavior where Katha/Annatto combination showed the best compatibility. Another set of four to six combinations showed average to good compatibility and remaining set of combinations showed average and below average compatibility.

Dyeing of Self-shades at various percentages for spectral data

Dyeing of each of the 6 selected dyes was done at varied percentages to prepare the spectral data on spectrophotometer for recipe prediction. For each dye, 10 samples were made starting from the minimum to maximum possible concentrations. It was visible from the dyed samples that the colour strength increased with increase in dye concentration and then decreased. The spectral data was created successfully using Konica-Minolta Spectrophotometer. In this process, the samples were scanned and used for recipe formulation software.

Prediction of Recipe and Dyeing of samples as per standard

As per the objective of the study, the recipe was predicted for a number of chosen standards from Pantone swatch book using spectrophotometer. For each chosen standard. A number of recipes were provided by the software with the expected spectral parameters like ΔE, ΔL, Δa, Δb etc. at chosen light source. The most suitable recipe was selected for the dyeing of samples amongst the compatible combinations only. The predicted recipe for each standard was used to dye the samples with the same method used for all combinations. The dyed samples were matched with respective pantone standard and ΔE was calculated. The sample is re-dyed with adjusted recipe in case of certain mismatch.

Colour Fastness Evaluation

Colourfastnes to washing, light and rubbing tests were conducted on samples from pure dyes, binary and tertiary combinations. The pure dyes showed average to good fastness which makes them suitable for combination. It was observed that the dyes in combination also showed similar fastness behavior as of component dye. It was also observed that the dye in combination made them more useful as the lower fastness of one dye may be improved by higher fastness dye in combination.

Chapter 6

Conclusion

In the case of optimization of dyeing parameters for individual pure dyes, it was observed that the highest K/S was near pH 7 for most of the dyes. The range of optimum temperature was from 65° C to 95° C and optimum time range was 60 min to 90 mins. The common dyeing conditions for all the dyes obtained were pH – 7, temperature- 82.8°C and time – 88 mins. The nearest dyeing conditions were used for the ease in practical dyeing of combinations which is pH – 7, temperature- 85°C and time – 90 mins.

In the case of compatibility check for dyes in combination, it was observed that the samples showed good, average and low compatibility behavior. In the change of hue angle (h°) method for compatibility check, for a compatible dye combination, the variation in hue angle has to be minimum. In some cases, the hue changes to certain extent only and shows good compatibility. For certain combinations, the hue angle for initial samples of set II showed significant variation which may be the cause of low time and temperature conditions provided. Compatibility check for the method based on -ΔL vs K/S plot, the overlap was found in the range of 60-80% in many cases and less in other cases. As per above methods, a set of four to six combinations showed good compatibility behavior where Katha/Annatto combination showed the best compatibility. Another set of four to six combinations showed average to good compatibility and remaining set of combinations showed average and below average compatibility.

The recipe prediction was done successfully for a number of pantone standards using the compatible set of dyes combination. The best predicted recipe for each standard was used to dye the samples with the same method used for all combinations. The dyed samples were matched with respective pantone standard and ΔE was calculated.

Endorsement from the Supervisor

Mr. Saurabh Garg has researched extensively on the topic "**Studies on computer aided colour measurement, matching and compatibility for compound shades production on textiles using natural dyes**" vide Registration No. FOTE/984, Dated: 03/11/18. The following papers are published / presented by him:

Sr. No.	**Title of the paper**	**Seminar / Conference / Journal details**	**Presentation/ Published**
1	Study of Compatibility Parameters of Mixture of Natural Dyes	5th International Textiles and Costume Congrees 2019 organized by Department of Clothing and Textiles, Faculty of Family and Community Sciences, The Maharaja Sayajirao University of Baroda, Vadodara, India held from 3rd to 5th October 2019	Oral paper Presentation
2	Study of Compatibility Parameters of Mixture of Natural Dyes	Proceedings of 5th International Textiles and Costume Congrees 2019 organized by Faculty of Family and Community Sciences, The Maharaja Sayajirao University of Baroda, Vadodara, India held from 3rd to 5th October 2019	Paper Publication, ISBN number 978-93-5382-736-6
3	Understanding and Analysis of Three Brown Natural Dyes: Babool, Himalayan Rhubarb, and Catechu	National Conference 'Indian Handloom & Handicrafts: Sustaining Cultural Heritage' organized by National Institue of Fashion Technology, Kangra held from 5th to 6th August 2022	Oral Paper Presentation and Abstract Publication
4	Optimisation and Comparison of Two Yellow Colour Producing Natural Dyes: Pomegranate Peel and Marigold	National Seminar 'Sustainable Textile Processing & Eco-Friendly Chemicals' organised by Department of Textile Chemistry, The Technological Institute of Textile and Sciences, Bhiwani on 6th May 2023.	Paper Presentation and Abstract Publication

5	Optimization of dyeing parameters for Acacia Catechu, Rheum Emodi and Acacia Nilotica natural dyes on Cotton Fabric & their comparative analysis	Asian Dyer (Journal Article)	Paper Accepted, Tentative Publication in October/ November 2023 issue

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