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A Step-by-Step Chemical Recipe to Dye Commercial Cotton with Natural Indigo Dyes in an Open Bath for the Beginners and Artisans

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Abstract

With the emergence of the need for natural bio-based chemical dyed wearable substrates, such as apparel or textiles, the demand for value-added craftsmanship induced on apparel or textiles is also on the rise. Local artisans are also exporting their value-added apparel products by diversifying their product range creating more local employment. Nowadays global retail fashion houses are also introducing naturally dyed wearable substrates for the increasing consumer demand for eco-friendly green products and concerns with global climate change. Small and medium entrepreneurs (SMEs) or artisans are also keeping pace with this new trend of offering such natural dyed products to the consumers. Therefore, this has created a new space for local artisans to produce various designs using natural dyes. The natural indigo dyed product is in great demand in the high-end fashion retail houses as well as in boutiques. However, little knowledge is available for the artisans to apply indigo vat dyes naturally extracted from the leaves of Indigofera tinctoria plants, because of the lack of technical knowledge, complications of chemical recipe parameters, zero access to expensive heavy industrial machinery.

Therefore, an attempt was taken to formulate an easy chemical recipe to dye cellulosic cotton fabric with natural indigo dyes without the need of any industrial dyeing machinery as well as conforming proper fastness to rubbing and washing, which are basically the major concerns for any vat dyed commercial products to meet the export demand. The chemicals used for this recipe formulation are also commercially available and cheap, making it an appropriate choice for local artisans to use and sell their finished end-product to exportable markets. The most important finding was the effect of vatting temperature to act as a major player to form water-soluble leucoindigo vat dyes from their insoluble solid dye state. Azo test was also conducted to confirm the absence of any carcinogenic amine containing any azo functional group that is harmful to the skin. Additionally, two different temperatures, such as 23ºC and 30ºC was used to produce the vatting recipe required for successful dyeing within 5 minutes at a lower temperature of 40°C, which will not cost any additional expenditure for the local artisans as they can produce this fermented vat on normal atmospheric conditions.

Keywords: Natural indigo dyes; Artisan; Cotton; Chemical recipe; Dyeing; Vat dyes; Beginners

Introduction

Direct extraction of natural indigo vat dyes from the leaves of indigofera tinctoria doesn't disperse in water properly as it is basically stays in water insoluble form [1]. Hence, the industrial dyeing recipe used for synthetic indigo vat dyes for dyeing cellulosic cotton substrate cannot be applied by the local artisans or craftsman to dye because they lack access to the expensive industrial machinery as well as technical chemistry background required for pre-treatment, dyeing and after-treatment of dyed cotton substrate. Local artisans basically purchase pretreated cotton fabric from the local weaving or knitting factories and impart their colorful craftsmanship or design work on them using the available commercial dyes. However, in present world scenario with the drastic climate change as well as threats from global warming, consumers are looking for sustainable wearable products or textiles dyed with natural product [2]. International fashion brands like Blue Blood, Evisu, Kuyichi, Cone Denim USA, Howie's, LEVI'S and Golden Age, etc., have already started offering natural indigo dyed apparels and denims [3-8]. To keep the products more competitive local artisans need to come up with natural dyed products too. Natural indigo dyed products are of great demand all-over the world. If proper quality can be confirmed, natural indigo-dyed products can be also exported by the artisans who will not only diversify the business, create employment but also can earn foreign currency for the country. Indigo being a natural [9] vat dyes, require a reducing agent to solubilize them as they are not readily available in solubilized state or in a state that will directly dissolve in water to form direct fiber-dye particle interfacial bonds. In short, indigo dye requires subsequent reduction and oxidation process (Figure 1) for successful dyeing with cotton. Vat dye is soluble only in reduced (oxygen-free) form and the cotton fibers are immersed into the dye-bath in this reduced state. The reduced form of indigo vat dyes by a reducing agent is called leucoindigo [10], which is soluble in water; followed by oxidizing it in open air or by O_2 to convert the water-

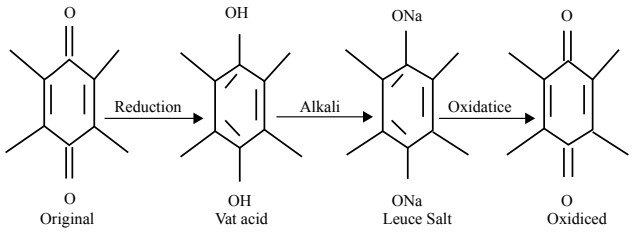

Figure 1: Chemistry of vat dyeing.

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soluble reduced form into water-insoluble form to fix or interlock the dye particle on the fiber substrate.

This research paper discusses the required methodology for successful chemical recipe formulation for cellulosic cotton substrate dyeing using natural indigo vat dyes in conjunction with the available commercial chemical products as well as the confirmation of the optimum fastness property of the dyed substrate surface. Azo test was also conducted to confirm the absence of any carcinogenic amine containing any azo functional group that is harmful to skin [11]. Such application of natural indigo dyes in the apparel, which is also azo free will not only benefit the applicators but also will produce a value added products that is highly demanding by the consumers [12]. For dyeing with indigo dyes many process has been explored, such as fermentation of indigo dyes using recombinant *Escherichia coli* [13], or using dye vats filled with limewater and couched (treated) woad [14]. However, such chemicals are either not readily available in local markets for the artisans to afford; some procedures are also bad-odour creating, such as woads [10], some procedures doesn't discuss the effect of different temperature for leucoindigo production acceleration rate, which has been discussed in this paper as well as a step by step guide with photographic presentation form leucoindigo production to the 5 minute fast dyeing process that can be used as a standard manual for beginners to practice coloration.

Materials and Methods

Materials

An incubator was used to control the temperature of the vat dyes for fermentation or reduction [15] in two different temperatures. Commercially available white colored 100% cotton woven fabric and white colored 100% cotton knit apparel were used in this work as well as commercially available natural indigo dyes extracted from Indigofera tinctoria plants (brand- LIVING BLUE). Both the woven and knit samples were already scoured and bleached. As solubilizing agent NaOH was used. Reducing agent Hydrose [16,17] was used in the fermentation and dyeing of the natural indigo dyes as it maintains the redox potential [10] to ensure the vat dye is maintained in water soluble leucoindigo form. It is to be noted that, hydrose was used only for being industrially available [10] and hydrose is easily oxidized in O_2 that produces a faster dyeing completion [10]. A standard detergent was used for washing the samples. Fastness scales were used for test evaluation of fastness to commercial washing to observe any desorption of indigo dye particles from textile materials into the solutions containing soap and sodium carbonate [17,18]. Crockmeter/ Rubbing fastness tester was used for testing of fastness against rubbing on a gray scale rating ranging from 1-5 [19]. Grinder was used to break down the solid cake form of indigo dyes into powder form. Transparent containers were used to contain vat dyes to notify and observe the visual change of color of the fermented vat dyes forming water soluble leucoindigo as the color of vats is the prime indicator of end-point determination of vat dye fermentation. Open dye bath was used for purpose of demonstrating the dyeing procedure as the local small and medium entrepreneurs or artisans may not have access to complicated closed bath dyeing machinery. For this purpose a hot plate was used to heat the dyeing liquor. Distilled H_2O was used at all level of recipe. A pH meter was used to check the pH level of the liquor. A drier was used to dry the wet samples.

Methods

SMART tactical planning: SMART tactical plan was developed to conduct this research work, as the work was:

- Specific; because the dye samples were sourced from a specific producer.
- Measurable; because the aspect and outcome of the result was measurable, which were color fastness, cost-price, production capacities, production sustainability, lead-times of production and processing.
- Achievable; because the production of dyes from the indigo plant leaves was already established as well as formulating a chemical recipe from this dye was achieved from this research work.
- Realistic; being the production and availability of natural dyes are seen all around the world and nowadays application of natural indigo dyes in apparel products are being highly promoted by international fashion houses.
- Time-based; because the whole backward linkage to forward linkage activities such as , production, research, application, results, and evaluation were analyzed within a reasonable time-frame.

Vatting of dye molecules by reduction process using a reducing agent (fermentation): Similar vatting method and recipe was maintained for two different temperatures, which were room temperature [20] 23°C and 30°C. The temperature of the vat dye was controlled using an Incubator, as the containers were all put inside the Incubator during the vatting process. Hence, all the ten experiment was conducted using the same recipe but at different temperature.

In a transparent container, 150 g of the grinded indigo powder was taken and 127 mL of distilled H_2O was added to make a paste. One third of the amount of dye was used for NaOH i.e., 50 g NaOH. Then NaOH and Hydrose were added at a ratio of 1:2 i.e., 50 g NaOH and 100 g Hydrose was added with the paste. A high alkaline pH condition was maintained, which was pH 12 for vatting liquor preparation. Optimum use of hydrose is highly recommended as excess use of hydrose will excessively reduce indigo vat dyes and will cause destruction of dyes [10].

After stirring the solution, the color of paste turned to blue (Figure 2) and a bad odour was coming out, which is an indicator of proper reactive capability of relatively pure hydrose. The bottom of the container got warm too, which indicates the reactivity of the NaOH. Then the container was closed by the lid as a precaution to prevent oxidation (Figure 3).

Every day the gradual change of color change of the vat dyes were checked to identify the end-point through the transparent walls of the container. As the container will be closed to prevent any sort of oxidation during the vatting or fermentation of vat dyes, transparent

Figure 2: Initial blue color of vat at after mixing of recipe chemicals.

containers were used to observe and mark the end point of vatting to produce water soluble leucoindigo dyes from visual color change of dyes. Four different replications is done with each of this two different temperature.

Dyeing recipe preparation to dye the cellulosic substrate: When the water solubilized leucoindigo was prepared, similar dyeing recipe was prepared using the two different samples of the vat dyes obtained from two different tests conducted at 23°C and 30°C. The dyeing recipe and the dyeing conditions were:

- Water soluble leucoindigo dyes: 1 g/L
- Hydrose: 4 g/L
- NaOH: 2 g/L
- Distilled H_2O: 1000 mL
- pH: 12
- Temp: 40°C
- Dyeing time: 2 minutes.

In an open steel bath, 1000 mL distilled H_2O was taken at room temperature and leucoindigo vat dyes (1 g/L) was added. The vat dye was a soft but solid material (Figure 4), which was wrapped in cloth and immersed into water. The cloth was continuously pressed (Figure 5) for 2 minutes while it was immersed into the water. As a result, the whole water color turned into blue color (Figure 6). Then NaOH and Hydrose was added at a ratio of 1:2 (i.e., 2 g/L NaOH and 4 g/L Hydrose) with the dyeing liquor and using a pH meter pH was found 12. After their addition, the liquor inside the dyeing bath was stirred for 1 minute. Then the dyeing bath was put on a hot plate and the temperature was set to 40°C with continued stirring. Within 5 minute the whole liquor color turned to boiling bubbly light green (Figure 7) with no trace of any blue color, which marks the ending point of dyeing liquor preparatory method.

Figure 3: Transparent container.

Figure 4: Fermented vat dyes.

Figure 5: Wrapping the dyes in a white cloth and immersing it inside liquor bath followed by pressing the fermented dyes.

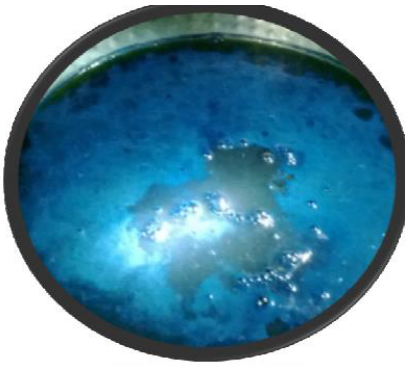

Figure 6: Dye liquor turned blue.

Figure 7: Heating the liquor converts the blue color into completely light green.

Later on, the white cotton fabric and white cotton apparel sample was immersed in the dyeing bath subsequently and separately to dye the cotton substrate. The samples were immersed inside the dye bath for 2 minutes each and were removed thereafter. Hence, the whole dyeing time takes only 2 excluding the 8 minutes required for recipe preparation and time required for oxidation. The dyeing curve is given below (Figure 8).

Re-oxidation of the dye molecules on the substrate surface: After two minutes of immersion inside the open dyeing bath, the fabric samples were brought it in open air and the excel liquor adhering to the sample surface was squeezed out immediately to prevent dye wastages. Then, the samples were dried in open air and the surrounding O_2.

Multiple dipping to create different shades: To produce multiple

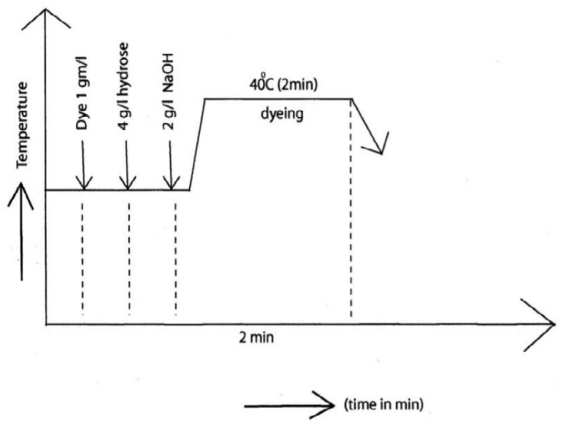

Figure 8: Dyeing curve for the dyeing solution.

Figure 9: Multiple dipping for dark shade.

blue shaded fabric samples, the samples after turning complete blue were again dipped (Figure 9) inside the liquor. We have to relentlessly dip the samples into the liquor and repeat the dipping-oxidation-dipping process until a modest-deep-deeper shade is gained.

After-treatment of the substrate: To remove the loosely adhered dyed particle on the sample, the sample was washed with standard detergent at a concentration of 1 g/L. Thereafter, the sample was dried using a drier.

Dozing to increase chemical strength of the dyeing liquor: With multiple dipping, the dye liquor loses its dyeing strength. For that reason, dozing of chemicals was done. To increase the strength of the liquor which is gradually exhausted or gradually weakened by continuous dipping, dozing was done after the 5th dipping with the same dyeing recipe i.e., 1 g/L dyes, 2 g/L NaOH and 4 g/L Hydrose.

Fastness to washing of the dyed substrate: Standardized method for commercial washing ISO-2 and ISO-3 (Table 1) was used to determine the fastness to washing of the dyed samples.

Fastness to rubbing of the dyed substrate: To determine the fastness to rubbing, a rubbing tester or Crockmeter was used. Sample sizes of (8 × 2.5) inch were used for this test purpose. Both dry and wet samples were rubbed 12 times using the rubbing tester according to ISO standardized testing method and the result outcome was rated by comparing the staining with a gray scale.

Azo test: Azo test is the way to find out whether there is any presence of carcinogenic amine on the dyed substrate that contains harmful azo groups for human skin. The recipe for azo test was 2 g/L Hydrose and 2.1 g/L NaOH added in 1000 mL distilled H_2O. After adding all the chemicals, the chemical liquor was boiled for 30 second. After that, the dyed sample was immersed into the liquor and was cross-checked for any shade variation between the pre-tested and post-tested samples.

Results and Discussion

Results

Formation of water-soluble natural indigo dye molecules after the vatting process: Whenever the color of the vat was turned from blue to yellowish-green (Figures 10-12), it indicated the end-point of vatting, which means vatting procedure of dyes was completed and it was ready to be used in the dyeing recipe of cellulosic cotton fiber. It can be identified by the transparent walls of the container. Time taken to reach the end of vatting point for 23°C and 30°C is given below (Table 2).

Test	Temperature (°C)	Time (minutes)	Steel balls	Chemical solution parameters
ISO-2	50	45	0	5 g/L soap
ISO-3	60	30	0	5 g/L soap +2 g/L Na_2CO_3 (sodium carbonate)

Table 1: Washing testing parameters.

Figure 10: Visible green color of the vat dye after vatting.

Figure 11: Yellowish-green color of the vat dyes after 188 hours.

Figure 12: Yellowish-green color of the vat dyes after 72 hours.

Successful dyeing of the cellulosic substrate after chemical dyeing and oxidation by O_2: When the samples were brought out from the green liquor dyeing bath (Figure 13), the sample color was green (Figure 14). However, within less than 3 minutes the sample color turned completely blue (Figure 15). The reason behind it is the oxidation of the dye particles by the surrounding atmospheric O_2 and hydrose being a such reducing agent that gets easily oxidized in atmospheric O_2 providing a fast completion of dyeing method [10]. Hence the whole dyeing time takes 5 minutes in total (2 minute inside the liquor and 3 minutes to oxidize the dye molecules for permanent fixation) for both the woven fabric samples and the knit apparel.

Different shades of the dyed substrate by multiple dipping: Three individual woven samples were dipped inside the liquor for individual 3, 5, 7 times or in short 3 dipping, 5 dipping, 7 dipping were done to produce three different shaded cotton woven samples (Figure 16). The white pretreated knit garments (Figure 17) were dipped 10 times for different fabric shade.

Vatting time for experiments at 23°C				
Sl	**Trial no**	**Vatting time (hours)**	**Mean Value**	**S.D. (σ)**
A	01	192	191.5	0.58
B	02	191		
C	03	191.5		
D	04	192		
Vatting time for experiments at 30°C				
Sl	**Trial no**	**Vatting time (hours)**	**Mean Value**	**S.D. (σ)**
A	01	92	92.13	0.63
B	02	92		
C	03	91.5		
D	04	93		

Table 2: Vatting time for the two different experiments conducted at 23°C and 30°C.

Figure 13: Open dyeing bath of green colored dyeing liquor.

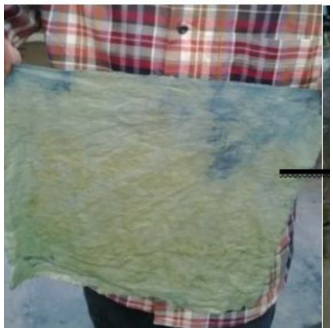

Figure 14: White sample turned green after immersing.

Figure 15: Green color turned blue within less than 3 minutes.

Figure 16: Three different shades of different woven samples.

Figure 17: Indigo dyed knit apparels.

Figure 18: ISO-2 washing results.

Washing fastness results: The pictures after the treatment of the samples are provided below (Figures 18 and 19): The results are furnished in the following table (Table 3).

Rubbing fastness results: The results are furnished in Table 4. No substantial visual change was observed (Figures 20 and 21) which supports the fact that, there was no carcinogenic amine present which contains azo group.

Discussion

From the data table, if vatting time is considered a dependent variable against vatting temperature as an independent variable, a predictive regression equation can be derived to form a predictive model. If vatting time is designated as (Y) and vatting temperature as

Figure 19: ISO-3 washing results.

Sl	Criteria	After ISO-2	After ISO-3
1	Shade change of sample	Rating grade - 4	Rating grade - 4
2	Staining of multi-fibre	Acetate rating grade - 4/5	Acetate rating grade - 3/4
		Cotton rating grade - 5	Cotton rating grade - 4/5
		Nylon rating grade - 4	Nylon rating grade - 3/4
		Polyester rating grade - 5	Polyester rating grade - 4/5
		Acrylic rating grade - 5	Acrylic rating grade - 5
		Wool rating grade - 5	Wool rating grade - 5

Table 3: Washing fastness results.

Rating after dry rubbing test		Rating after dry rubbing test	
Test	Gray scale rating	Test	Gray scale rating
Color change	Grade 3/4	Color change	Grade 3/4
Color staining	Grade 4	Color staining	Grade 3

Table 4: Rubbing fastness results.

Figure 20: Color of dyed sample before azo test.

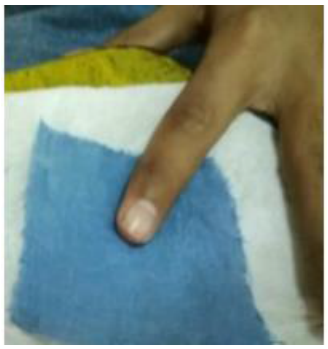

Figure 21: Color of dyed sample after azo test.

(X), then a simple linear regression equation was formed using the data from the data table:

$$Y=-13.214X+518.55 \quad (1)$$

Hence a negative or inverse linear relationship exists which predicts the decrease of vatting time with the increase of vatting temperature. Value of R2 is 0.999, which indicates more than 99% of the variability can be explained with this equation. At 95% confidence interval, the probability value of this statistics is also less than α (0.05), which supports the predicted statement.

There were some major, controlling points, which were observed for optimum dyeing procedure, such as:

(a) Optimum vatting temperature: It has to be within 26-30°C. Otherwise it will take more time for vat preparation, which will result in a prolonged dye liquor preparation. If the vatting time is reduced the overall dye liquor preparation time will be reduced. The observed optimum vatting temperature was 26-30°C.

(b) Dyeing temperature: The dyeing temperature for optimum dyeing time (2 min) was 40°C. Dyeing temperature below 40°C will increase the dyeing time as it will take longer time to get greenish dye liquor with bubbly appearance that marks the maturity point of dyeing liquor.

(c) Application of NaOH: If the bottom of container is not felt warm after adding NaOH, it can be assumed that, the NaOH has improper reactivity power, which needs to be changed immediately.

(d) Application of Hydrose: If bad smell of Hydrose is not felt, it means the HYDROSE has improper reactivity power, which needs to be changed immediately.

(e) Checking the color of Vat: It has to be yellowish-green when the vat is prepared or reached the optimum solubilized form.

(f) Preventing oxidation: The bucket top needs to be with covered tightly by its lid as an increased precaution to prevent oxidation, which will spoil the over-all mechanism.

Conclusion

Brands like LEVI's has recently introduced their natural indigo dyed denim and other apparel, for the growing consumer demand of natural dyed products. Denim being a cellulosic can also be dyed with natural indigo dyes by the chemical recipe stated in this paper. Padding technology can be easily applied for industrial or continuous dyeing using this chemical recipe formulation for natural indigo dyeing besides manual dipping. Because, padding technology being a cheaper and faster way of dyeing also accommodates both multiple dipping and squeezing arrangements with a large dyeing bath which can be used by the local artisans for mass dyeing. With a regulated temperature control panel, achieving 40°C is commercially achievable as well as competitive for the artisans, SMEs, and industries because it requires very less dye to dye mass volume of substrates. Future work will be done, which will concentrate to introduce a mechanism that will reduce the vatting time. With the alarming global climate change and concerns of consumers for getting natural eco-friendly dyed apparels, this chemical recipe can benefit any entity who wants to dye cellulosic cotton substrate with natural indigo dyes at a faster rate, as this mechanism needs very less time to produce export quality blue indigo dyed cellulosic substrate, which can be made available commercially.

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