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16. Optimising the Natural Dyeing and Enzymatic Treatment Process: A Sustainable Approach to Rejuvenate the Handloom Sector

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16.1 Introduction:

Nature expresses itself in a wide spectrum of colours all around us. The alchemy of colours started from an early time and the Indians have been forerunners in the art of natural dyeing. The advent of synthetic dyes caused rapid decline in the use of natural dyes, which were completely replaced by the former within a century. Earlier understanding of dyeing techniques and their applications were empirical and were not backed by scientific reasoning. Natural dyeing had developed essentially as a folk art. However, in recent times the dyeing technique is interpreted on sound scientific principles and the interaction between the dye and the dyed material is well understood. The use of natural dyes on textiles has just been one of the consequences of increased environmental awareness. Worldwide the use of natural dyes for the colouration of textiles has mainly been confined to craft dyers and printers. In India, textiles dyed with natural colourants, woven mainly in handloom sectors are exported to USA, Germany and other European countries. The dyed substrates mainly used are cotton and silk. However, recently more interest is being shown in the use of these dyes and a limited number of commercial dyers and small business sectors (Handloom) have started to look at the possibility of using natural dyes for dyeing and printing of textiles **(*(PDF) Application of Natural Dyes in Handloom Sectors*, n.d.).**

Since prehistoric times natural dyes have been used for colouring of food substrate, leather as well as fibres like wool, silk and cotton. The use of non-allergic, non-toxic and eco-friendly natural dyes on textiles have become a matter of significant importance due to the increased environmental awareness in order to avoid some hazardous synthetic dyes **(Verma & Gupta, n.d.).**

In the present day, the handloom sector is known for its heritage and the tradition of excellent craftsmanship. But due to some inherent limitations, our handloom sectors are facing cut throat competition and ever growing challenges imposed by the low cost high end power loom products of various countries including our own especially in this age of globalization. One of the measures to revive our moribund handloom sectors is to produce articles through value addition with eco-friendly natural dyeing.Natural dyes comprises those colourants (dyes and pigments) that are obtained from animal or vegetable matter without chemical processing. They are mainly mordant dyes although some vat, solvent, pigment, and acid types are known.**(Chakrabarti & Vignesh, n.d.)**

A new approach for upgrading the dyeing properties of cotton knits with natural dyes as well as to enhance both the UV-protection and antimicrobial functions of the obtained dyeings was investigated. Factors affecting the dyeing and multifunctional properties of the treated substrates such as fabric structure, type and concentration of mordant, kind and percent of natural dye extract as well as dyeing regime were studied **(Ibrahim et al., 2010).**

Natural colourants and dyestuffs are an important group of non-wood forest products which find use in industries producing confectionery, other food products, textiles, cosmetics, medicines, leather, paper, paint, ink, etc **(Křížová, 2015).**

The textile industry is one of the largest contributors to environmental threats globally, producing 60 billion kilograms of fabric annually and using up to 9 trillion gallons of water. During coloration, large volumes of unfixed dye are released into water bodies, and approximately 10–15% of dye is lost into the environment as wastewater **(Periyasamy & Militky, 2020).**

The major hurdles for using natural dyes are serious gap and lack/non-availability of scientific data base and knowledge base required for their successful application on textiles **(Samanta, 2018).**

Dyes derived from natural materials such as plant leaves, roots, bark, insect secretions, and minerals were the only dyes available to mankind for the colouring of textiles until the discovery of the first synthetic dye in 1856. Rapid research strides in synthetic chemistry supported by the industrialization of textile production not only led to the development of synthetic alternatives to popular natural dyes but also to a number of synthetic dyes in various hues and colours that gradually pushed the natural dyes into oblivion However, environmental issues in the production and application of synthetic dyes once again revived consumer interest in natural dyes during the last decades of the twentieth century **(Saxena & Raja, 2014).**

Two step ultrasonic dyeing of cotton and silk fabrics with natural dyes, Terminalia arjuna, Punica granatum, and Rheum emodi have been developed in which an enzyme is complexed with tannic acid first as a pretreatment **(Vankar et al., 2007).**

However, it is important to impart pre-treatment to cotton to attain whiteness, uniform good absorbency, without chemically damaging cotton. Efforts are being made in recent years to develop a mild and environment friendly process. Thus enzymatic pretreatment has assumed more importance due to the present concern of a clean and eco-friendly environment. It is also a known fact that the crystalline region of cellulose is loosened by swelling agents and thus increasing the absorbency of the fabric towards water and dyes.

Due to increased environmental awareness the use of natural dyes are much preferred in dyeing of handloom fabrics, thus it has become imperative to revive the art of natural dyeing based on revised technology and scientific methodology. But, the khadi cotton has some major shortcomings like higher maintenance costs for washing, ironing, rough texture, less dyeability and poor colour fastness. Thus, the present research was planned by keeping in view the emerging trend of bio-processing, use of swelling agents and dyeing with natural dyes. The present study was conducted to optimize the pre-treatment process with enzymes and swelling agents on khadi cotton fabric. The dyeing of khadi cotton fabric with two natural dyes using two natural and metallic mordants was carried out. The comparison of colour strength (K/S) and colour fastness properties of untreated dyed sample and enzymatically and swelling agents treated and dyed sample was done. The economic feasibility of the process was also studied.

Experiments were conducted to determine optimum values of four variables for acid and neutral cellulase enzyme treatment, namely, pH, concentration, treatment time and temperature. Concentration, treatment time and temperature were the three variables optimized for the swelling agents. Dyeing variables i.e. concentration of dye material, extraction time, dyeing time, mordant concentration and method of mordanting with natural and metallic mordants were optimized.

The colour strength (K/S) and colour fastness properties against washing, light, rubbing and perspiration of both the untreated and the enzymatically and swelling agents treated and dyed samples were evaluated and compared. Estimation of the cost effectiveness for the adoption of the pre treatments and dyeing was accomplished by conducting cost estimation. The cost of dyeing one metre of untreated and pretreated khadi cotton with cellulases and swelling agents using Tesu and Sandalwood dye without mordant as well as with both natural and metallic mordants were calculated. The cost of the dyeing and pretreatment process was calculated including cost of fabric, dye, mordants, cellulases, swelling agents, labour and electricity charges. Commercial acid cellulase enzyme (Americos Cellscos 450 AP) and neutral cellulase enzyme (Americos Cellucom 110 OM) were selected for enzymatic pre-treatment of khadi cotton.

Sodium hydroxide, Ethylenediamine and Zinc chloride were the three swelling agents used for the treatment of khadi cotton. Two natural dyes namely Tesu (*Butea frondosa*) and Sandalwood (*Pterocarpus santalinus*) were used for the study. The two natural (Babool and Harda) and two metallic mordants (Alum and Copper sulphate) were selected for Tesu dye. In the case of Sandalwood dye, two natural mordants (Babool and Pomegranate) and two metallic mordants (Alum and Tartaric acid) were selected.

In the present study, various statistical tools were used particularly relevant to fulfil the specific objectives of the present study. The data were presented using mean and standard deviation and suitable tables were also made for the classified data as per analysis of different levels of pH, concentration, treatment time and temperature. Weighted mean score was calculated for quantifying the ratings of colour fastness. The fastness to washing was given highest weight 4 since it is most important followed by fastness to light, rubbing and perspiration which were given weight 3, 2 and 1, respectively.

The F-value, as obtained from the one way analysis of variance, was found to be statistically significant at 1% level of significance, which indicated that here was significant different in weight loss, tensile strength loss (warp and weft direction), moisture content, bending length (warp and weft direction), crease recovery angle (warp and weft direction), thickness and water absorption related to different levels of pH, concentration, treatment time and temperature of both acid and neutral cellulase enzyme.

The optimum pH, concentration, treatment time and temperature selected for the acid cellulase enzyme treatment were 5.5, 1.5% (owf), 45 minutes and 50°C, respectively as significant differences in the mean values of all the physical parameters were found upto these levels by comparison of means at 1% level of significance.

In case of neutral cellulase enzyme, the optimum pH, concentration, treatment time and temperature selected were 7.5, 2.0% (owf), 70 minutes and 70°C respectively, as it was proved statistically by comparison of means at 1% level of significance that significant difference in the mean values of all physical parameters occurred upto these levels.

The F-values, computed at 1% level of significance from one way analysis of variance confirmed that there was a significant difference in the mean values of all the physical parameters due to different levels of concentration, treatment time and temperature of three swelling agents viz., Sodium hydroxide, Ethylenediamine and Zinc chloride.

The optimum concentration, treatment time and temperature selected for Sodium hydroxide treatment were 20% w/v, 60 minutes and 60°C, respectively. In the case of Ethylenediamine, 80% w/v, 60 minutes and 70°C were selected as optimum concentration, treatment time and temperature, respectively. In case of Zinc chloride treatment, the optimum concentration, treatment time and temperature were selected as 80% w/v, 60 minutes and 70°C, respectively. Significant differences in the mean values of all the physical parameters were found upto these selected level of concentration, treatment time and temperature in all the three swelling agents. Significant differences in the mean values of various physical parameters studied indicated significant improvements in the physical parameters.

It was found that 5 g Tesu dye extracted for 75 minutes gave best results on khadi cotton when dyeing was carried out for 90 minutes whereas 5 g Sandalwood dye extracted for 90 minutes gave best results on khadi cotton when dyeing was carried out for 75 minutes. It was observed that out of various concentrations of mordants used with Tesu dye, best shades of colour were obtained by using 0.04 g of Alum, 0.01 g of Copper sulphate, 5 g each of Babool bark and Harda whereas 0.05 g each of Alum and Tartaric acid, 5 g each of Babool bark and Pomegranate rind gave best shades of colour with Sandalwood dye. On optimizing the method of mordanting, best results were obtained with Tesu dye when samples were simultaneously mordanted and dyed with Alum, Babool bark and Alum. Pre-mordanting was selected for Copper sulphate. In case of Sandalwood's dye, Pre-mordanting was considered as best for both Alum and Tartaric acid. Pomegranate rind gave best shades with Post Mordanting and Simultaneous mordanting and dyeing was considered as best for Babool bark. The blank samples dyed with Tesu dye showed Light yellow colour whereas natural mordants Babool bark and Harda gave Daffodil colour and Golden yellow and Rust colour were obtained with metallic mordant Alum and Copper sulphate, respectively. In case of Sandalwood dye the natural mordant Babool bark and Pomegranate rind gave Bathstone and Pale cream colour, respectively whereas metallic mordant Alum and Tartaric acid produced Honey and Bathstone colours respectively.

It was found that for all the enzyme treated (acid and neutral cellulase) as well as swelling agents treated (Sodium hydroxide, Ethylenediamine and Zinc chloride) samples, the K/S values, and thus the colour strength were increased in comparison to the untreated samples.

Among the three swelling agents, Sodium hydroxide treated sample obtained the highest colour strength (K/S) followed by Ethylenediamine and Zinc chloride treated samples in case of both Tesu and Sandalwood dye.

The K/S values of cellulase treated samples were enhanced in comparison with untreated samples. However, higher depth of dyeing was exhibited by neutral cellulase enzymes than acid cellulase enzyme treated samples in both Tesu and Sandalwood dye.

The swelling agent treatment followed by cellulase enzyme treatment showed higher depth in colour values (K/S) in both Tesu as well as Sandalwood dye. The maximum swelling caused by the Sodium hydroxide followed by cellulase enzyme treatment gave higher K/S value than Ethylenediamine and Zinc chloride treated samples followed by cellulase treatment. The swelling agents treated samples followed by neutral cellulase enzyme treatment showed higher depth of dyeing than acid cellulase enzyme treatment. All the untreated and treated samples dyed without mordant and with natural and metallic mordants were subjected to colour fastness tests to light, washing, crocking and perspiration.

The light fastness grades for Tesu and Sandalwood dye were between poor to fair (2-3) to fairly good (4) for the untreated samples, but improved good (5) due to cellulases and swelling agents treatment and with their combinations.

The washing fastness test showed considerable (2) to slight (4) colour change for the untreated sample, which improved to negligible (5) change in colour when the samples were treated with cellulases and swelling agents and also with their combinations. Staining on wool and cotton was found to be considerable (2) to slight (4) in untreated sample, while it was increased to negligible (5), when the samples were treated with cellulases and swelling agents as well as with their combinations in case of both Tesu and Sandalwood dye.

In case of both dry and wet crocking tests, the untreated samples showed considerable (2) to slight (4) change in colour in both Tesu and Sandalwood dye. The treatment with cellulases and swelling agents and their combinations improved the colour change to negligible (5) in dry and wet crocking in case of both Tesu and Sandalwood dye. Staining on wool and cotton was considerable (2) to slight (4) for the untreated for Tesu and Sandalwood dye in both dry and wet crocking, whereas it improved to negligible (5) in both dry and wet crocking when the samples were treated with cellulase, swelling agents and with their combinations.

During perspiration fastness tests for Tesu dye, it was observed that the untreated sample showed noticeable (3) to slight (4) change in colour in both acidic and alkaline perspiration, which improved to negligible (5) when the sample were treated with cellulases, swelling agents and their combinations. In case of Sandalwood dye, considerable (2) to slight (4) colour change in untreated sample in acidic perspiration and noticeable (3) to slight (4) change in colour was observed in case of alkaline perspiration. Staining on wool and cotton in case of both Tesu and Sandalwood dye was found to be noticeable (3) to slight (4) in both acidic and alkaline perspiration, which was improved to negligible (5) in the samples treated with cellulases, swelling agents and with their combinations.

On the basis of weighted mean score, khadi cotton samples pretreated with cellulases, swelling agents as well as with their combinations and dyed with Tesu and Sandalwood dye without and with both natural and metallic mordants were given rank for their fastness.

In case of khadi cotton dyed with Tesu dye without mordant, samples treated with Neutral cellulase obtained first rank (3.05) whereas samples treated with Zinc chloride obtained seventh rank (2.47). The last rank was occupied by an untreated sample (2.16).

In case of khadi cotton dyed with Tesu dye and mordanted with Babool bark, the first rank (4.00) was secured by samples treated with Acid cellulase, Neutral cellulase, Sodium hydroxide and Sodium hydroxide, Ethylenediamine and Zinc chloride combined with Acid cellulase and Sodium hydroxide, Ethylenediamine and Zinc chloride combined with Neutral cellulase. Sample treated with Zinc chloride occupied fourth rank (3.55). The last fifth rank (2.85) was occupied by an untreated mordanted sample.

In case of khadi cotton dyed with Tesu dye and mordanted with Harda, it was found that the sample treated with Sodium hydroxide plus Neutral cellulase secured the first rank (4.43), whereas Zinc chloride and untreated mordanted sample occupied third rank (3.73). This showed that Zinc chloride treatment had no effect on the improvement of colour fastness property in case of Tesu dye mordanted with Harda.

In case of khadi cotton dyed with Tesu dye and mordanted with Alum, it was observed that the sample treated with Neutral cellulase secured first rank (4.73). Here, it was found that the samples treated with Acid cellulase, Sodium hydroxide, Ethylenediamine and Zinc chloride occupied eighth rank (4.00) whereas the untreated mordanted sample secured seventh rank (4.06). This result showed that the treatment with Acid cellulase, Sodium hydroxide, Ethylenediamine and Zinc chloride had no improvement on the colour fastness property and untreated mordanted sample were more colour fast than these pretreated samples of khadi cotton dyed with Tesu dye.

In case of khadi cotton dyed with Tesu dye and mordanted with Copper sulphate, the first rank (5.00) was occupied by samples treated with Neutral cellulase and Sodium hydroxide, Ethylenediamine and Zinc chloride combined with Acid cellulase. Samples treated with Ethylenediamine and Zinc chloride secured seventh rank (4.16). The last seventh rank (4.00) was occupied by an untreated mordanted sample.

In case of khadi cotton dyed with Sandalwood dye without mordant, it was observed that samples treated with Sodium hydroxide plus Neutral cellulase obtained first rank (3.05). Zinc chloride obtained sixth rank (2.21) whereas the untreated sample the seventh rank (2.20).

In case of khadi cotton dyed with Sandalwood dye and mordanted with Babool bark, samples treated with Sodium hydroxide plus Neutral cellulase secured first rank (4.07). Zinc chloride treated sample occupied eighth rank (3.60). The last rank i.e. ninth (2.83) was secured by an untreated mordanted sample.

In case of khadi cotton dyed with Sandalwood dye and mordanted with Pomegranate rind, it was found that the sample treated with Sodium hydroxide plus Neutral cellulase secured first rank (4.23). Sample treated with Zinc chloride secured seventh rank (3.48). Untreated mordanted sample obtained the last rank i.e. eighth rank (2.83).

In case of khadi cotton dyed with Sandalwood dye and mordanted with Alum, the sample treated with Sodium hydroxide plus Neutral cellulase obtained first rank (4.72) whereas Zinc chloride treated sample secured the eighth rank (4.02). The untreated mordanted sample obtained the last ninth rank (3.67).

In case of khadi cotton dyed with Sandalwood dye and mordanted with Tartaric acid, it was observed that the first rank (5.00) was occupied by samples treated with Sodium hydroxide and Ethylenediamine combined with Acid cellulase and Sodium hydroxide, Ethylenediamine and Zinc chloride combined with Neutral cellulase as these samples got same score. Zinc chloride treated sample obtained sixth rank (4.48) whereas eighth rank (3.81) was occupied by untreated mordanted sample. The cost of dyeing one metre of untreated and treated khadi cotton with cellulases and swelling agents using Tesu and Sandalwood dye without mordant as well as with both natural and metallic mordants were calculated. When the dyeing costs of Tesu and Sandalwood dye without pretreatment was compared with the cost of dyed pretreated cotton with cellulases and swelling agent, it was observed that the cost of the pretreatment process and dyeing was increased in both the cases i.e. without mordant as well as using natural and metallic mordants.

The conclusion can be drawn from the study on the basis of physical properties, colour strength (K/S), colour fastness as well as economic analysis that Neutral cellulase when used alone as well as its combination with Sodium hydroxide swelling agent gave best results on khadi cotton fabric. The combination of other two swelling agents i.e. Ethylenediamine and Zinc chloride also gave good results but not as good as the combination of Neutral cellulase with Sodium hydroxide swelling agent. Similarly, good results in terms of physical properties, colour strength (K/S), colour fastness and economic analysis was also obtained with Acid cellulase and combination of Acid cellulase with three swelling agents i.e. Sodium hydroxide, Ethylenediamine and Zinc chloride. In case of Acid cellulase also, the best result was observed with Sodium hydroxide followed by Ethylenediamine and Zinc chloride swelling agent. Although the results obtained with Acid cellulase and its combination with swelling agents in relation to physical properties, colour strength (K/S) and colour fastness were not better than those of Neutral cellulase and its combination with swelling agents, but it was also revealed by economic analysis that the dyeing costs of treatment with Acid cellulase and its combination with swelling agents were less than those obtained with Neutral cellulase and its combination with swelling agents. The swelling agents when used alone also showed improvement in physical properties, colour strength (K/S) and colour fastness, but not as good as cellulases and their combination with swelling agents. The cost calculated for treatment with Ethylenediamine and Zinc chloride were higher than the cellulases.

The weighted mean score of colour fastness has also revealed that in most of the cases samples treated with Neutral cellulase and its combination with swelling agents followed by Acid cellulase and its combination with swelling agents had secured higher ranks whereas samples treated with Ethylenediamine and Zinc chloride occupied lower ranks. The untreated samples have obtained the last rank. The enzymatic pretreatment of the textiles are not aggressive to fibres and the environment. The 'clean chemistry' approach is an advantage in comparison to the powerful alkalies, acids, oxidizers and reducers needed in traditional processes tending to attack the textile material as well as causing considerable contamination in the environment. The residues of enzymes are present only in the form of primary structure and there are no chemical residues likely to affect the skin. Besides, they do not leave chemical residues on the processed materials and the colour change of the dyed is minimal. Although the dyeing costs increased with the pretreatment with cellulases, swelling agents as well as with their combinations, nowadays the use of cellulases in the pretreatment process has found much broader acceptance as the effect of the treatment is long lasting and eco-friendly in nature. The pretreatment with swelling agents with optimized conditions enhances the physical properties as well as colour strength and colour fastness properties. Thus, some of the shortcomings of khadi cotton like rough texture, less dyeability and poor colour fastness can be minimised by chemical processing by an eco-friendly approach as well as using swelling agents in optimum conditions and can be recommended for handloom sectors as these sectors supports and strengthen the rural economy of our country.

16.2 References:

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