

CHAPTER II

REVIEW OF LITERATURE

One of the essential prerequisite of any research study is to get acquainted with latest literature on the subject of research. So an attempt was made to review the relevant theoretical literature and researches on jute and pre-treatments on jute and other cellulosic fibres. The investigator visited and collected the literature from various libraries like J.D Birla library, Kolkatta; Smt. Hansa Mehta library, T.K. Gajjar library and the Clothing and Textile department library of The Maharaja Sayajirao University of Baroda. Another important source of information was the internet.

The review of literature thus collected was catagorized and discussed under the following subsections:

2.1 Theoretical Review

2.1.1 Jute

2.1.2 Bleaches

2.1.3 Natural Dyes

2.1.4 Nano particles

2.2 Related Research Review

2.2.1 Researches on pre-treatments applied on jute

2.2.2 Researches on dyeing of jute with natural dyes

2.2.3 Researches on product diversification of jute

2.1.1 Jute



Figure 2.1 a: Jute Plant and Rope



Figure 2.1 b: Production of Rope

Jute fibre's inherent characteristics of strength, versatility, being eco-friendly, etc can directly cater to technical and industrial requirements through its appropriate functional end uses. The Indian jute industry has been at the forefront of industrialization of the Indian economy. The first jute mill in India was established in the year 1855. Today the Jute industry is one of the major industries in the eastern region, particularly in West Bengal. It supports nearly 40 lakh farm families, provides direct employment to about 2.6 lakh industrial workers besides livelihood to another 1.4 lakh persons in the tertiary sector and allied activities. The production process in the jute industry goes through a variety of activities, which include cultivation of raw jute, processing of jute fibers, spinning, weaving, bleaching, dyeing, finishing and marketing of jute products. The jute industry produces goods worth Rs. 6500 crore p.a. and contributes to export earnings to the tune of nearly Rs. 1200 crores p.a. The jute industry is labour intensive, thus requiring such a large number of people in the value chain. The industry at present faces stiff competition from its cheaper substitutes and is plagued with many problems ranging from obsolete technology, labour unrest, etc. thus detailed study on jute and experimentation with its product diversification is required.

2.1.1. a. Average Chemical Composition Of Jute

- 1) Lignin (12-14%)
- 2) Holocellulose
 - a) Alpha-cellulose (58-63%)
 - i) Glucosan (55-59%)
 - ii) Xylan (1.8-3.0%)
 - iii) Polyuronide (Glucuronic acid)(0.8-1.4%)
 - iv) Other sugar residues
 - (1) Galactose
 - (2) Arabinose
 - (3) Mannose
 - (4) Rhamnose
 - b) Hemicellulose (21-24%)
 - i) Pentosan
 - (1) Xylan (8.0-12.5%)

- (2) Araban (traces)
- (3) Rhamnosan (traces)
- ii) Hexosan (Galactan) (2-4%)
- iii) Polyuronide (Glucuronic acid)(3-4%)
- iv) Acetyl content (3.2-3.8%)
- 3) Minor constituents
 - a) Waxes (0.4-0.8%)
 - b) Pectin (0.2-0.5%)
 - c) Mineral (0.6-1.2%)
 - d) Protein (0.8-1.5%)
 - e) Tannin and pigments (traces)

Table 2.1: Physical Properties of Jute Fibre

Sr. No.	Properties	Range	Average
1.	Ultimate cell length (mm)	0.75-6.0	2.5
2.	Fibre fineness (linear density) Tex	0.90-3.50	2.0
	Denier	8.00-31.0	18.0
3.	Fibre density (g/cm ³)	1.42-1.49	1.48
4.	Tenacity (g/den)	2.7-5.3	3.0
5.	Breaking elongation (%)	0.8-2.0	1.70
6.	Modulus of rigidity (dyne/cm ²) × 10 ⁹	-	4.42
7.	Initial modulus (g/den) (Modulus at 0.1% extension)	130-220	194
8.	Young's modulus (dyne/cm ²) × 10 ¹¹	0.86-1.94	1.45
9.	Moisture regain (at 65% relative humidity and 27 ⁰ C) %	13.0-14.5	13.75
10.	Refractive index (parallel to fibre fibre axis)	-	1.577
11.	Swelling in water: Diametrical (%)	18.0-22.0	20.0
	Area wise (%)	40.0-50.0	45.0
12.	Stiffness index (g/den)	300-400	350

13.	Specific heat (cal/g/ ⁰ C)	-	0.324
14.	Dielectric constant	10 ¹⁴ -10 ¹⁷	-
15.	Insulation resistance (KV/cm)	450-550	500
16.	Heat of combustion (J/g)	16.0-17.0	16.5
17.	Specific internal surface (m ² /g)	10-200	-
18.	Coefficient of friction	0.45-0.54	0.46
19.	Crystallinity (%)	52-60	54

2.1.1. b. Chemical Treatment Of Jute

A. Effect of alkali on Jute:

Jute is sensitive to the action of alkali. The individual cells of jute are cemented with lignin and hemicelluloses. Treatment of jute with alkali, particularly caustic soda, causes dissolution of a part of hemicelluloses and marginal loss in lignin. Caustic soda treatment is known to bring about different types and degrees of modification in both its physical and chemical nature depending mainly on the concentration of alkali, time of treatment and temperature of treatment. Treatment with very dilute solution of sodium carbonate cleans the fibre surface more rather than any damage, making the fibre regular and thus increasing yarn productivity by reducing the end breakage ratio. The most important changes in the characteristics of the jute fibre are brought about when it is treated with strong (10%) sodium hydroxide solution at ambient or lower temperature, when the fibre acquires crimp and extensibility significantly at a range of 5-20% from 1-2% for the untreated fibre.

With the gradual increase in concentration of caustic soda, different physical and chemical changes occur and at the concentration of 15-18%, wool like appearance is observed due to the generation of high degree of crimp- this phenomenon is termed as Chemical Texturisation or Woollenisation of jute. During this treatment longitudinal shrinkage of fibres takes place, along with some partial conversion of cellulose- I to cellulose- II, as a consequence of partial loss of crystallinity due to the lateral swelling effect. Lateral swelling causes softening of the fibre and

develops crimp. Net loss in strength due to this treatment is about 25-40%. The losses in strength and weight in jute due to treatment with caustic soda solution increases with the increase in the concentration of the alkali. The losses are mainly due to removal of about 20% of fibre material consisting of mainly hemicelluloses during the treatment. The purposes and process of woollenisation of jute is entirely different. The mercerization and woollenisation are discussed in the table below:

Table 2.2: Woollenisation Vs. Mercerisation

Woollenisation	Mercerisation
<ul style="list-style-type: none"> • Treatment of jute with caustic soda (15-18%) at room temperature for 30-60 minutes. 	<ul style="list-style-type: none"> • Treatment of cotton yarn/fabric with caustic soda (22-25%) at room temperature for 1-2 minutes.
<ul style="list-style-type: none"> • Stretch is not applied, after immersion in caustic soda and before washing (slack process). 	<ul style="list-style-type: none"> • Yarn/fabric is stretched to original dimensions before washing.
<ul style="list-style-type: none"> • Crimps are introduced in the fibre (chemical texturing). 	<ul style="list-style-type: none"> • Yarn/fabric dimensions are stabilized.
<ul style="list-style-type: none"> • Weight loss of fibre is around 15%. 	<ul style="list-style-type: none"> • Weight loss of yarn/ fabric is around 3%.
<ul style="list-style-type: none"> • Improvement in fibre fineness resulting better spinning performance appearance of fabric. 	<ul style="list-style-type: none"> • Improvement in yarn/fabric lusture and dyeability.
<ul style="list-style-type: none"> • Loss in strength is about 25-40%. 	<ul style="list-style-type: none"> • Improvement in strength of about 10-15%.
<ul style="list-style-type: none"> • Improvement in elongation characteristics (1-2% to 4-6%). 	<ul style="list-style-type: none"> • Slight reduction in elongation at break.
<ul style="list-style-type: none"> • Poor crimp stability- once the fibres are stretched, the crimp imparted is lost. 	<ul style="list-style-type: none"> • The changes such as improved lusture, dyeability, etc., are permanent.
<ul style="list-style-type: none"> • Deterioration in color of fibres. 	<ul style="list-style-type: none"> • No change in color of yarn/fabric.

<ul style="list-style-type: none"> • Batch process. 	<ul style="list-style-type: none"> • Continuous process (fabric mercerization).
<ul style="list-style-type: none"> • Consumption of caustic is more due to higher absorption of alkali by jute. 	<ul style="list-style-type: none"> • Less consumption of caustic as compared to woollenisation.
<ul style="list-style-type: none"> • Difficult to recover the caustic from wash liquor because of higher percentage of impurities. 	<ul style="list-style-type: none"> • Recovery process is efficient. About 95% of caustic soda can be removed from wash liquor.
<ul style="list-style-type: none"> • Though technically important, it is laborious and costly process. 	<ul style="list-style-type: none"> • Technically as well as commercially important process.

Following are the effects of various parameters on Woollenisation

- Concentration of Alkali: Below 6% concentration of caustic soda no crimp is formed at any temperature. The number of crimps increases with increase in concentration of caustic soda solution up to 18% after which the curls take up a stable configuration.
- Reaction time: The reaction of jute materials with alkali is usually accomplished within a short time. But an immersion time of at least 30 minutes is generally recommended for formation of crimps.
- Temperature: At lower temperature crimp formation is better. It has been reported that at -8°C crimp produced with 8% caustic soda solution is almost same to that obtained with 18% caustic soda at room temperature. The optimum temperature for crimp formation is about 2°C and crimp parameter is affected at higher temperature, being zero at 40°C . However the woollenisation of jute is normally done at the ambient temperature.

The formation of wool like crimp on the individual fibre of jute is believed to be due to non uniform swelling of the fibre. The non cellulosic components and non-crystalline regions are not distributed in an orderly fashion along the length of the individual filament. As a matter of fact, the degree of swelling on treatment with alkali varies from place to place, generating a lot of internal stresses. To get rid of these stresses the filament assumes the characteristic

curly shape. The finer and softer filaments develop more crimp in comparison to coarser and harder filaments.

Characteristic/ Salient Feature on Woollenisation:

- The feel and appearance of jute are improved by Woollenisation which can further be enhanced by subsequent bleaching/dyeing.
- The woollenised jute can be blended to natural wool to produce wool rich textiles.
- The stability of the crimps produced by Woollenisation is very poor.
- The cost of woollenising treatment is a bit high, since to recover caustic soda, from water of woollenising bath, is difficult due to high percentage of impurities.

B. Bleaching of Jute:

A common practice is to omit scouring before bleaching jute due to its alkali sensitivity and it is directly taken for bleaching in spite of the presence of impurities. Bleaching is an important operation in the processing of jute and its blends, to produce a creamy white shade or remove the natural brown tint. But due to photosensitivity, bleached jute material, like other lignocellulosic fibres turns to brownish yellow color when exposed to UV/sunlight. Lignin is responsible for pale brown color of jute. In order to produce different degrees of whiteness ranging from pale cream to milk white, jute fabric is bleached/ oxidized by controlled treatment with selected oxidizing agents like calcium or sodium hypochlorite, hydrogen peroxide in an alkaline pH, potassium permanganate, sodium chlorite under acidic conditions and peracetic acid under neutral or slightly acidic pH in aqueous medium. Oxidizing bleaching agents which are widely used for jute bleaching can be classified as chlorine containing and non-chlorine containing agents as follows:

Table 2.3: Oxidizing bleaching agents

Chlorine Containing Compounds	Non-Chlorine Containing Compounds
Bleaching powder	Hydrogen peroxide
Sodium hypochlorite	Potassium dichromate
Sodium chlorite	Potassium permanganate
	Peracetic acid

Reducing bleaching agents i.e. sulphur dioxide, sodium sulphite, sodium bisulphate, sodium hydrosulphite, sodium boro hydride etc are also used for jute bleaching. But they suffer from major disadvantages of non permanency of whiteness.

Bleaching with Sodium Hypochlorite:

Jute can be successfully bleached with sodium hypochlorite solution having 3-7 g/l available chlorine using sodium carbonate to maintain an alkaline pH in the range of 10-10.5 at room temperature for 1-2 hours. A suitable wetting agent 1-2g/l may also be added for easy wetting of fabrics when directly taken for bleaching. It is then washed and antichlored with 0.2% sodium sulphite for 20 minutes at 50⁰-60⁰C and finally washed and dried.

pH around 7 is dangerous for bleaching with hypochlorite in case of cellulosic material. So care must be taken to control the pH and it should be checked from time to time with pH paper. During the bleaching process the temperature should not go up as the increase in temperature drastically enhances the speed of the reaction and causes degradation. For this purpose, it should be assured that there is no leakage in steam valve in the jigger. Due to the presence of chlorine in hypochlorite, hypochlorite bleaching is not considered eco-friendly.

Bleaching with Sodium chlorite:

Sodium chlorite is a suitable bleaching and delignificating agent for lignocellulosic material like jute. Treatment of jute fabric with acidified 4% sodium chlorite solution at 90⁰C, pH 4.0-4.5 for 90 minutes with M:L- 1:10 appreciably improves the color of the fibre. Lignin portion dissolves while carbohydrate portions remain almost unaffected in this treatment.

Some disadvantages are associated with sodium chlorite bleaching e.g. acidified sodium chlorite solution is very reactive, and corrode commonly used metal of the bleach bath and causes evolution of large amount of chlorine gas which creates environmental pollution.

Bleaching with Hydrogen Peroxide:

Hydrogen peroxide is a most widely used bleaching agent in textiles. It is having a number of advantages over other bleaching agents i.e.

- Reaction products are nontoxic, it decomposes to oxygen and water and therefore reduces the effluent problem of bleaching plant.
- Under optimum conditions of bleaching, cellulose and lignin are not degradable.

However, there are some drawbacks associated with hydrogen peroxide bleaching process like heat is required for bleaching, also catalytic decomposition in presence of metal ions like iron and copper may cause tendering of fabrics.

C. Photo yellowing of jute:

A serious drawback of bleached jute is yellowing on photo exposure. Dyeing may overcome this problem to some extent but the dyed shade also fades after long exposure to sunlight. The reason for yellowing is environmental effects like heat, air, UV radiation of sunlight. Heat and oxygen in the air cause discoloration of bleached jute. Presence of UV radiation in sunlight in the range of 330-370 nm causes yellowing. Radiation in the range 290-320 nm and 380-420 nm also contribute to some degree of yellowing. Within the UV region the most effective region is reported as 350-355 nm. The energy of light absorbed in these regions is higher than that associated with part of the chemical linkages in jute. Therefore absorption of light causes breakdown of some chemical linkages present in jute and this involves scission of the occasional bonds between lignin and cellulose/hemicelluloses chain and methoxy splitting from the lignin constituents which ultimately leads to the formation of orthoquinones and other chromophores which causes yellowing.

A number of approaches have been undertaken to minimize the yellowing problem of jute. Among these Hutex bleaching developed by IJIRA is worth mentioning. The process consists of the following three steps:

1. Chlorination: The treatment of jute fabric with sodium hypochlorite in jigger for 6 ends, pH 6 at room temperature with M:L – 1:10. Under acidic conditions sodium hypochlorite liberates chlorine as per the following reactions:



The nascent chlorine thus liberated converts surface lignin of jute into chloro lignin which is subsequently removed.

2. Extraction of the Chlorinated products: The chlorinated fabric is rinsed in cold water for two ends and then treated with 5% (owf) sodium sulphite solution at 70⁰ -75⁰C in jigger for 45-60 minutes.
3. Bleaching: Bleaching is done with 3% hydrogen peroxide, 2.5% sodium hydrogen phosphate and 10% sodium silicate for 1 hour at 70⁰ -75⁰C pH 10. Extensive damage of fibres, violent evolution of hazardous chlorine gas, high process costs are the major drawbacks of this process.

Bleached or dyed jute fabric treated with copper sulphate- potassium dichromate (0.25% - 0.5%) in the presence of acetic acid (pH 5-5.5) at 70⁰C for 1 hour showed improved photo stability with marginal decrease in color yield in case of dyed samples. But the colour yield was improved after treatment with dye fixing agent. Photo chemical degradation of undyed and dyed jute can be prevented by using UV absorbers. Among a number of UV absorbers tested on dyed and undyed jute, 2, 4 dihydroxybenzophenone was found most effective in preventing photo yellowing of both undyed and dyed jute. In comparison to dyed jute its effect was more pronounced in case of undyed jute.⁷

2.1.2 Bleaches

2.1.2. a. History of Bleaches:

Scouring removes all the impurities other than the coloring matter from the natural cellulosic fibres. Reducing treatments are quite ineffective for bleaching and oxidizing agents are therefore always used. Bleaching as carried out by the Egyptians, the Phoenicians and the Greeks in the olden days but process of producing white linen is unknown. The only information available is some reference to the use of the ashes of plants in Roman writings.

From the termination of the Crusades until the middle of the 18th century the Dutch had the virtual monopoly of bleaching in Europe. Linen woven in Britain was sent to Holland in March to be bleached and would not be returned until the end of October.

The method consisted of steeping jute for several days in liquors made alkaline with extracts from wood ashes. The cloth was then well rinsed till clean and spread out on grass fields where it was allowed to remain exposed for some weeks. These operations were called bucking and crafting respectively. Bucking and crafting were repeated alternately 5 to 6 times after which the cloth was soaked in sour milk for several days, well rinsed and crafted again. The whole cycle of processes would be repeated once or twice more until desired degree of whiteness was obtained. The substitution of sulphuric acid for sour milk in 1756 brought about a great reduction in time because the acid would achieve in 12 to 24 hr, a result which would require steeping for 6 to 8 weeks in sour milk.

In 1785, Berthollet drew attention to the value of chlorine gas as a bleaching agent. This observation was followed up by many practical bleachers who, making their own chlorine, exposed the materials to the gas or treated them with an aqueous solution of chlorine. The process, however, was disagreeable and accompanied by toxic hazards and therefore never made much progress. A complete revolution was brought about in 1799 when Tennant manufactured bleaching powder. He was thus able to supply a solid bleaching agent containing approximately $1/3^{\text{rd}}$ of its weight of available chlorine. This made it possible for the bleachers to deal with the ever-increasing output of cloth which accompanied the industrial revolution.⁶¹

2.1.2. b. Bleaching Of Textiles:

The natural fibres and fabrics even after scouring still contain naturally occurring colouring matter. This yellowish and brown discoloration may be related to flavones pigments of the cotton flower. The object of bleaching is to produce white fabrics by destroying the coloring matter with the help of bleaching agents with minimum degradation of the fibre. The bleaching agents either oxidize or reduce the coloring matter which is washed out and whiteness thus obtained is of permanent nature. Chemical bleaching of textile fibres is further aided by addition of optical brighteners.

The primitive method of cloth bleaching, namely harsh scouring and exposure to the sun was also a chemical process in which light served as an oxidation catalyst. However, the processes are time consumable, labour intensive; highly variable in quality of goods produced and tied up large amount of capital. The first major break

with traditional methods of bleaching came in 1756. During the later stage of 20th century the time required for bleaching dropped steadily from months to days to hours. Now-a-days, manpower required for average plant is declined considerably and the cost of bleached finished product is also reduced. This technical break through will continue in the future also and will reduce the cost of bleaching further.

Nine major break throughs in bleaching cellulosics: ⁵⁹

- ❖ 1756 → Sulphuric acid scour
- ❖ 1790 → Chlorine Bleach
- ❖ 1791 → Le Blanc Process for Soda ash
- ❖ 1815 → High Process Kier
- ❖ 1830 → Rope Washer
- ❖ 1900 → Enzyme Desizing
- ❖ 1925 → Peroxide Bleaching
- ❖ 1939 → Continous Peroxide Bleaching
- ❖ 1950 → Flourescent Brighteners

Table: 2.4 Classification of Bleaching agents

Bleaching Agents		
Oxidizing Bleaching Agents		Reducing Bleaching Agents
<p style="text-align: center;">PEROXIDE SYSTEM</p> <ul style="list-style-type: none"> • Examples: 1) Hydrogen Peroxide 2) Peracetic Acid 	<p style="text-align: center;">CHLORINE SYSTEM</p> <ul style="list-style-type: none"> • Examples: 1) Bleaching Powder 2) Sodium Hypochlorite 	<ul style="list-style-type: none"> • Examples: 1) Sulphur dioxide 2) Sodium Hydrosulphite

Oxidizing Bleaching Agents:

Oxidizing bleaching agents are used to a far greater extent than reducing agents. The cheapest and most abundant oxidizing agent is atmospheric oxygen and the medieval method of bleaching was to lay the material out in a field where it was exposed to the sun and the air. This was known as “dew bleaching” and though slow, was the only method available for cotton and linen goods.

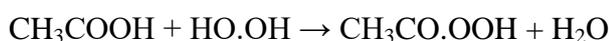
A great change came about in 1799 when Tennant manufactured bleaching powder by the action of chlorine on slaked lime. Bleaching powder contains about 36% of available chlorine. It was replaced by calcium hypochlorite with an available chlorine content of 70-74%. Di or tri- chlorocyanuric acids were used and it contained 91.5% of available chlorine and has bleaching properties comparable with sodium hypochlorite.

Sodium Hypochlorite:

Sodium hypochlorite has virtually replaced bleaching powder which is troublesome to bring into solutions and variable in composition. Sodium hypochlorite is available as a clear solution ready for use, containing 14 to 15% of available chlorine.

Peracetic Acid:

Although the existence of peracetic acid has been known for a long time its use as a bleaching agent is of recent origin. It is, in fact, the acetyl derivative of hydrogen peroxide.



The reaction of acetic acid with hydrogen peroxide is reversible and therefore the more concentrated the acetic acid is the less water will appear on the right-hand side and the greater will be the yield of peracetic acid. The best results, therefore, are obtained by mixing together concentrated acetic anhydride and 90% hydrogen peroxide. Thus, the commercial product, when prepared in this manner is usually peracetic acid diluted with acetic acid and water. A typical composition comprised of 36-40% of peracetic acid, 3-6% of hydrogen peroxide and the remainder acetic acid and water. About 1% of sulphuric acid acts as a catalyst and makes a significant contribution towards increasing the yield of peracetic acid.⁶³

Reducing Bleaching agents:

Many coloured organic compounds are modified structurally so that they become colorless when acted upon by reducing agents. The oldest such substance used for bleaching of which was sulphur dioxide, a reducing agent formed by the burning of native sulphur.

In the past, great quantities of wool and to a lesser extent, silk were bleached with sulphur dioxide. The degree of whiteness was adequate but lacked permanence. On exposure to air, especially in sunlight, the reduced coloring matter tended to reoxidize with the restoration of the original yellowish tint. There was a time when sulphur dioxide was the only bleaching agent available for wool but since hydrogen peroxide became a commercial product it has virtually replaced other methods.⁶³

2.1.3 Natural Dyes

2.1.3. a. Introduction Of Natural Dye:

Ever since man began to create, he has endeavored to add color to the world around him. Initially he used natural material to stain hides, decorate shells and feathers, paint their story on the walls of ancient caves etc. Scientists have traced the black, white, yellow and red pigments used by the primitive man for cave paintings dated over 15,000 B.C. old. With the development of civilization man started settling, cultivating the land for agriculture. He then began to produce and use textiles and wished to add color to them as well.

Dyeing is one of the traditional techniques that have been known to have existed even before 2500 BC. Fragments of dyed cloth with original hues were found to be belonging to Mohanjo-daro and Harappan excavations. The resist dyed fabrics that were used to wrap around the mummies in the pyramids still retain their true color. Egyptians perhaps imported the fabrics from India and learnt the art and science of using various natural materials for dyeing and fixing the colors. Indians have been pioneers of rasayana sastra (chemistry) and were experts in making oxides of metals for use of craftsman to fix color in textiles and paintings. Until the 19th century, the professional dyers all over the world relied on natural dyes for textiles and crafts. The Indian textiles were quite popular in the world market during those times especially for its range of colors and designs. European traders attempted to imitate or duplicate Indian patterns while the chemists in Europe attempted to synthesize popular Indian dyes like Indigo and others.

For the last 150 years, the synthetic dyes and their manufacturing and processing industries have damaged the environment beyond repair. Synthetic dyes cause environmental hazards both in its production and utilization stages. Many

carcinogenic chemicals and solvents are released during manufacturing process. These harmful by-products formed from these processes are discharged into the immediate environments like river, water-ways, in the atmosphere and are dumped into landfills. The chemical dyes effluents are non bio-degradable and create havoc in the bio-diversity of the environment by polluting soil and water. Workers who work in dyeing units and handle the chemicals in the process are affected and become the victims of many skin diseases.

On the other hand, the natural dyes are heading towards another period of renaissance. The raw materials used for natural dyeing are natural and herbal products like leaves, flowers, roots, bark, seeds, stem, etc. with various combinations of these, one can attend many shades such as green, red, yellow, purple, maroon, etc. in various depths and tones.

2.1.3. b. Natural Dye/Colorant:

The word 'natural dye' covers all the dyes derived from the natural sources like plants, animals and minerals. They are mostly non-substantive and must be applied on textiles by the help of mordants, usually a metallic salt having an affinity for both the coloring matter and the fibre. Transition metal ions usually have strong co-ordinating power and /or capable of forming weak to medium attraction/ interaction forces and thus can act as bridging material to create substantivity of natural dyes/ colorants when a textile material being impregnated with such metallic salt (ie mordanted) is subjected to dyeing with different natural dyes, usually having some mordantable groups facilitating fixation of such dye/colorant. These metallic mordants after combining with dye in the fibre, it forms an insoluble precipitate or lake and thus both the dye and the mordant get fixed to become wash fast to a reasonable level.

In recent years, there has been a trend to revive the art of natural dyeing. This is mainly become in some aspects natural colorations are advantageous against synthetic dyes. Some of these advantages and limitations are listed below:

2.1.3. c. Advantages:

1. The shades produced by natural dyes are usually soft, lustrous and soothing to the human eye.

2. Natural dyestuff can produce a wide range of colors by mix and match system. A small variation in the dyeing technique or the use of different mordants with the same dye can shift the colors to a wide range or create totally new colors, which are not easily possible with synthetic dyestuffs.
3. Natural dyestuffs produce rare color ideas and are automatically harmonizing.
4. Unlike non-renewable basic raw materials for synthetic dyes, the natural dyes are usually renewable, being agro-renewable/vegetable based and at the same time biodegradable.
5. In some cases like harda, indigo, etc., the waste in the process becomes as ideal fertilizer for use in agricultural fields. Therefore, no disposal problem of this natural waste.
6. Many plants thrive on wastelands. Thus, wasteland utilization is an added merit of the natural dyes. Dyes like Madder grow as host in tea gardens. So there is no additional cost or effort required to grow it.
7. This is a labour intensive industry, thereby providing job opportunities for all those engaged in cultivation, extraction and application of these dyes on textile/food/leather etc.
8. Application of natural dyes has potential to earn carbon credit by reducing consumption of fossil fuel (petroleum) based synthetic dyes.
9. Some of its constituents are anti-allergens, hence prove safe for skin contact and are mostly non-hazardous to human health.
10. Some of the natural dyes are enhanced with age, while synthetic dyes fade with time.
11. Natural dyes bleed but do not stain other fabrics, turmeric being an exception.

2.1.3. d. Limitations:

1. It is difficult to reproduce shades by using natural dyes, as these agro-products vary from one crop season to another crop season, place to place and species to species, maturity period, etc.

2. It is difficult to standardize a recipe for the use of natural dyes, as the natural dyeing process and its color development depends not only on color component but also on material.
3. Natural dyeing requires skilled workmanship and is therefore expensive. Low color yield of source natural dyes thus necessitates the use of more dyestuffs, larger dyeing time and excess cost for mordants and mordanting.
4. Scientific backup of a large part of the science involved in natural dyeing is still need to be explored.
5. Lack of availability of precise technical knowledge on extraction and dyeing techniques.
6. The dyed textile may change color when exposed to the sun, sweat and air.
7. Nearly all natural dyes with a few exceptions require the use of mordants to fix them on to the textile substrate. While dyeing, a substantial portion of the mordant remains unexhausted in the residual dye both and may pose serious effluent disposal problem.
8. With a few exceptions, most of the natural dyes are fugitive even when applied in conjunction with a mordant. Therefore, sometimes their color fastness performance ratings are inadequate for modern textile usage.

2.1.3. e. Classification of Natural Dyes:

For dyes it is important to know the class so that they could be used according to the substrate. Natural dyes can be classified in a number of ways. The earliest classification was according to alphabetical order or according to the botanical names. Later, it was classified in various ways eg. On the basis of hue, chemical constitution, application class, etc.

- A. In “treatise on permanent colors” by Bancroft, natural dyes are classified into two groups: Substantive Dyes: such as indigo, turmeric, etc. which dye the fibers directly.
Adjective Dyes: such as logwood, madder, etc. which are mordanted with a metallic salts.
- B. Hummel classify the coloring matter as ‘Monogenetic Dyes’, those produce only one color irrespective of the mordant present on the fibre or applied along

with the dye and 'Polygenetic Dyes', those produce different color with different mordants applied, eg. Alizarin.

C. In the color index the natural dyes are classified according to the hue (predominating color). The number of dyes in each hue are as follows in the table:

Table 2.5: Classification of natural dyes according to the hue

CI NATURAL	NO. OF DYES	PERCENT
Yellow	28	30.4
Orange	6	6.5
Red	32	34.5
Blue	3	3.3
Green	5	5.5
Brown	12	13
Black	6	6.5

On the basis of hues, natural dyes can be classified as follows:

- Red color dyes: Most red dyes are hidden in 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 color 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 pale shade with quicker fading except turmeric, which produce dull deep shade but considered to be susceptible to light as they emit fluorescence. Wash fastness rating of natural yellow dyes ranges from fair to excellent, e.g. tesu, turmeric, kapila.
- Blue color dyes are indigo and woad, give excellent fastness to light and washing.
- Black color dyes: black shades, generally obtained from tanni rich plant natural dyes and appreciably substantive towards cellulosic and

protein fiber, impart good overall fastness properties. Example – logwood, harda, custard apple etc.

- D. On the basis of origin, natural dyes are broadly classified into three categories: vegetable, mineral and animal origin. About 500 vegetable origin dyes, coloring matter derived from root, leaf, bark, trunk or fruit of plants, are as follows in table-

Table 2.6: Classification of natural dyes according to the origin

Part of the Plants	Dyestuffs
Root	Turmeric, Madder (Manjistha), Onions, Beet-root
Bark/Branches	Purple bark, Sappan wood, Shillicorai, Khair, Red Sandalwood
Leaf	Indigo, Henna, Eucalyptus, Tea, Cardamon, Coral jasmine, Lemon Grass
Flowers (Petals)	Marigold, Dahlia, Tesu, Kusum
Fruits/Seeds	Latkan, Pomegranate, Beetle nut, Myrobolan (Harda)

Mineral origin colorants are derived from specific mineral natural source or so-called mineral colors are produced from purified inorganic compounds. Some of the important mineral colorants are chrome-yellow, iron-buff, narkin-yellow, Prussian-blue and manganese brown. Animal origin lac, cochineal and kermes have been the principal natural dyes yielding from the insects.

- E. Natural dyes are also be classified on the basis of their chemical constitution.
- Indigoid Dyes: Indigo and Tyrain purple are the most common example of this class. Another blue dye, wood also possesses indigo as the main dyeing component.
 - Anthraquinone Dyes: Almost all the red natural dyes are based on the anthraquinoid structure having both plant and mineral origin. Madder, lacs, kermes, cochineal are some of the dyes possessing this type of structure. These are generally mordant dyes.

- Alphanaphthoquinones: Typical example of this class is lawsone (heena), cultivated mainly in India and Egypt. Another similar dye is juglone, obtained from the shells of unripe walnuts. These dyes are generally disperse dyes and give shades of orange.
 - Flavonoids: Flavonoids are which yield yellow dyes can be classified under flavones, isoflavones, aurones and chalcones. Flavones are colorless organic compounds. Most of the natural yellows are derivatives of hydroxyl and methoxy substituted flavones and isoflavones. Common example is weld (containing luteolin pigment) giving brilliant and fast colors on both wool and silk.
 - Di- hydropyrans: Closely related in chemical structure to the flavones are substituted di-hydropyrans, i.e. haematin and its leuco form, haematoxylin. These are important natural dyes for dark shades on silk, wool and cotton. Logwood, brazil wood and sappan wood are the common examples.
 - Anthocyanidins: The naturally occurring member of this class includes carajurin, a direct orange dye for wool and cotton. It is obtained from the leaves of bignonia chica.
 - Carotenoids: The class name carotene is derived from the orange pigment found in carrots. In these, the color is due to the presence of long conjugated double bonds.
- F. Another method of classifying natural dyes is on the basis of the method of application:
- Mordant dyes: These are dyestuffs which require a mordant in their application as they have no affinity for the fibres being dyed. A mordant dye should have electron donating groups capable of forming a complex with the transition metal salt, eg. Madder, fustic, Persian, berries, kermes, cochineal, etc.
 - Vat dyes: These are water insoluble dyes which are first converted to their water soluble form (reducing with sodium hydrosulphite and then solubilising it with alkali) and then applied to the fibres. The true color is produced only on oxidation followed by treatment with a hot soap solution. Eg: indigo

- Direct dyes: These dyes have tremendous affinity for the cellulosic fibres. They are dyed from a boiling dye bath. Turmeric, harda, pomegranate rind, etc. are the few of the direct natural dyes.
- Acid dyes: These are applied from an acidic medium. The dye molecules have either sulphonic or carboxylic group which can form an electrovalent bond with amino groups of wool and silk. An after treatment with tannic acid known as back tanning improves the fastness of these type of dyes eg: saffron.
- Disperse dyes: These have a relatively low molecular mass, low solubility and no strong solubilizing groups. Disperse dyes can be applied onto hydrophobic synthetic fibre from neutral to mildly acidic pH. They can also be applied to silk and wool. These dyes can be post-mordanted with chromium, copper and tin salts, eg. Lawson and many other flavones and anthroquinone dyes.
- Basic or Cationic dyes: These dyes on ionization give colored cations and form an electrovalent bond with the carboxylic group of wool and silk. These dyes are applied from neutral to mildly acidic pH. These dyes have poor light fastness. Eg. Berberine.

2.1.3. f. Mordants:

Limitation on color yield and poor fastness properties prompted a search for ideal mordants, the chemicals which increase natural dye uptake by textile fibres. Different types of mordants yield different colors even for the same natural dye. Therefore, final color, their brilliance and color fastness properties are not only dependent on the dye itself but are also determined by varying concentration and skillfull manipulation of the mordants. Thus, a mordant is more important than the dye itself.

Moreover, the ideal mordant for bulk use should produce appreciable color yield in practicable dyeing c beyond a conditions at low cost, without seriously affecting physical properties of fibre or fastness properties of the dyes. Also, it should not cause any aoxious effect during processing and the dyed textile material should not have any carcinogenic effect during use. Mordants can be classified into the following categories:

- I. Metallic Mordants: They are generally metal salts of aluminium, chromium, iron, copper and tin. The metallic mordants are of two types.

i. Brightening Mordants:

- Alum: Among all types of alum, potash alum is cheap, easily available and safe to use mordant. It usually produces pale versions of the prevailing dye color in the plant.
- Chrome (Potassium Dichromate): It is also referred to as red chromate. It is relatively more expensive. However, Cr^{+3} or Cr^{+6} is considered to be harmful for human skin as objectionable heavy metal certain limit of its presence. Its use has been limited as per the norms of the eco-standards. The dichromate solution is light sensitive and therefore it changes color under light exposure.
- Tin (Stannous Chloride): it gives brighter color than any other mordant. However, they are oxidized on exposure to air and may impart a stiff hand to the fabric. Stannous chloride also causes higher loss of fabric tenacity (tensile strength) if applied beyond a certain concentrations.

ii. Dulling Mordants:

- Copper (Cupric Sulphate): It is known as blue vitriol, it is readily soluble in water and easy to apply. It gives some special effects in shades, which otherwise cannot be obtained. However, copper beyond a certain limit is also under the eco-standard norms as objectionable heavy metals.
- Iron (Ferrous Sulphate): it is also known as green vitriol and is readily soluble in water. It is used for darkening/ browning and blackening of the colors/shades. It is easily available and one of the oldest mordants known. It is extensively used to get grey to black shades.

II. Non-metallic Mordants: The non-metallic mordants are categorized into two types:

- i) Tannins: The term 'tanning agent' is given initially to those water soluble cellulosic materials that precipitates gelatin from solution. But all gelatin precipitation did not identified as tanning agent. Tannins are polyphenolic compounds having capacity of gelling under certain conditions.
- It may be hydrosable pyrogallol tannins exemplified by 'tannic acid' by Chinese or Turkish gallotannins (galls) and by Sicilain and Stagshorn sumac.

- Hydrolysable ellagitannins that give ellagic acid or similar acids on hydrolysis, exemplified by valonea, chestnut.
 - Condensed or catechol tannins that contain little or no carbohydrates and are converted to acids to insoluble amorphous polymers. Among the tannins, myrobalan and galls/sumach are most important.
- ii) Oils type mordants: Vegetable oils or Turkey red oil (TRO) are such type of mordants. TRO as mordant is mainly used in the dyeing of deep red color from madder. The main function of the TRO as oil mordant is to form a complex with alum when used as a main mordant. Sulphonated oil possesses better binding capacity than the natural oils. Oil mordanted samples exhibit superior fastness and hue.

2.1.3. g. Different Mordanting Methods:

Mordanting can be achieved by pre-mordanting (before dyeing), simultaneously mordanting and dyeing or it may be a post mordanting system (after dyeing).

- Pre-mordanting: In this the textile substrate is first treated in aqueous solution of mordant for optimized time and temperature with a M:L ratio of 1:5 to 1:20 and then dried with or without washing. The mordanted textile material is then dyed following optimized dyeing conditions may be required as salt, soda ash or acid depending on the type of textile material and type of natural dyes. After dyeing, the textile material is washed properly and soaping is carried out by 2g/l industrial soap solution as described in standard method of AATCC or ISO method.
- Simultaneous Mordanting: In this process, the textile substrate is immersed in a dye bath solution containing both mordant and dye in a definite quantity and dyeing may be started at the pre-determined optimum condition. Dyeing auxiliaries may be added as required for the standard dyeing process. However, for optimization of dyeing condition, dyeing process variables can be studied for specific fibre-mordant-natural dye system in order to maximize color yield on textiles. After dyeing the textile material is washed properly and soaping is carried out by 2g/l industrial soap solution.
- Post Mordanting: In case of post mordanting method of natural dyeing, the dyeing process is carried out for bleached textiles in the absence of mordant at

pre-determined dyeing condition and the dyed fabric is treated in a separate bath called saturator containing suitable mordanting solution. Treatment condition may vary depending on type of fibre, dye and mordant system. After dyeing, the textile material is washed properly and soaping is carried out by 2g/l industrial soap solution.⁴⁹

2.1.4 Review of Natural Dye

Four natural dyes namely madder, turmeric, eucalyptus leaves and Indian almond leaves were selected for the research. Review of these dyes were studied.

2.1.4. a. Madder:

Binomial Name: *Rubia Cordifolia*

Class of Dye: Quinones

Part of Dye Used: Roots

Madder roots have been used as a dye for over 5,000 years. Archaeologists have found traces of madder in linen in Tutankhamen's tomb (1350 BC), and in wool discovered in Norse burial grounds. Very recently (August 2009), Marco Leona of the Metropolitan Museum of Art, New York, showed that the 4,000-year-old dye found on leather from an ancient Egyptian quiver was madder red dye (madder lake). Leona used a refined version of a technique called Raman spectroscopy and dated the madder-dyed leather to the Middle Kingdom era. Druids are said to have used garments dyed with madder red dye in girls' coming of age ceremonies. Madder root was fed to white horses to colour hooves and teeth, and to hawks to colour beak and talons. There is even a mention of feeding madder plants to sheep to dye their wool. Madder roots produce a variety of reds including orange reds, brick red, blood red and fiery reds. The colour depends on the soil the roots where grown, their age, the mineral content of the water used for dyeing, the temperature of the dye pot, and how much madder you use in relation to the fibre.



Figure 2.2 a: Madder
Plant



Figure 2.2 b: Madder Roots



Figure 2.2 c: Madder Dye
Powder

(Source: <https://www.google.co.in/search?q=madder&rlz=1C1CHBF>)

2.1.4. b. Turmeric:

Binomial Name: *Curcuma longa*

Class of Dye: Curcuminoids

Part of Dye Used: Roots

Turmeric has been used in Asia for thousands of years and is a major part of Siddha medicine. It was first used as a dye, and then later for its medicinal properties. The origin of the name is uncertain, possibly deriving from Middle English/early modern English as turmeryte or tarmaret. Speculation exists that it may be of Latin origin, terra merita (merited earth). The name of the genus, *Curcuma*, is from an Arabic name of both saffron and turmeric. Turmeric has played an important role in Hindu spiritualism. The robes of the Hindu monks traditionally were colored with a yellow dye made of turmeric. Because of its yellow-orange coloring, turmeric was associated with the sun. Turmeric makes a poor fabric dye, as it is not very light fast, but is commonly used in Indian and Bangladeshi clothing, such as saris and Buddhist monks's robes. Turmeric (coded as E100, when used as a food additive), is used to protect food products from sunlight. The oleoresin is used for oil-containing products. A curcumin and polysorbate solution or curcumin powder dissolved in alcohol is used for water-containing products.



Figure 2.3 a: Turmeric Plant



Figure 2.3 b: Turmeric dye powder

(Source: <https://www.google.co.in/search?q=turmeric&rlz=1C1CHBF>)

2.1.4.c. Eucalyptus Leaves:

Binomial Name: *Eucalyptus globules*

Class of Dye: Flavonoids

Part of Dye Used: Leaves

Eucalyptus is a diverse genus of flowering trees and shrubs (including a distinct group with a multiple-stem mallee growth habit) in the myrtle family, Myrtaceae. Members of the genus dominate the tree flora of Australia, and include *Eucalyptus regnans*, the tallest known flowering plant on Earth. There are more than 700 species of eucalyptus and most are native to Australia; a very small number are found in adjacent areas of New Guinea and Indonesia. One species, *Eucalyptus deglupta*, ranges as far north as the Philippines. Some eucalyptus species have attracted attention from horticulturists, global development researchers, and environmentalists because of desirable traits such as being fast-growing sources of wood, producing oil that can be used for cleaning and as a natural insecticide, or an ability to be used to drain swamps and thereby reduce the risk of malaria. All parts of Eucalyptus may be used to make dyes that are substantive on protein fibres (such as silk and wool), simply by processing the plant part with water. Colours achieved range from yellow and orange through green, tan, chocolate and deep rust red.



Figure 2.4 a: Eucalyptus Tree

Figure 2.4 b: Eucalyptus Leaves

(Source: <https://www.google.co.in/search?q=eucalyptus+leaves&rlz=1C1CHBF>)

2.1.4.d. Indian Almond Leaves:

Binomial Name: *Terminalia catappa*

Class of Dye: Flavonoids

Part of Dye Used: Leaves

Terminalia catappa is a large tropical tree in the leadwood tree family, Combretaceae, that grows mainly in the tropical regions of Asia, Africa, and Australia. It is known by the English common names country-almond, Indian-almond, Malabar-almond, sea-almond, tropical-almond and false kamani. It is widely grown in tropical regions of the world as an ornamental tree, grown for the deep shade its large leaves provide. The fruit is edible, tasting slightly acidic.

The tree grows to 35 m (115 ft) tall, with an upright, symmetrical crown and horizontal branches. It has corky, light fruit that are dispersed by water. The seed within the fruit is edible when fully ripe, tasting almost like almond. As the tree gets older, its crown becomes more flattened to form a spreading, vase shape. Its branches are distinctively arranged in tiers. The leaves are large, 15–25 cm (5.9–9.8 in) long

and 10–14 cm (3.9–5.5 in) broad, ovoid, glossy dark green, and leathery. They are dry-season deciduous; before falling, they turn pinkish-reddish or yellow-brown, due to pigments such as violaxanthin, lutein, and zeaxanthin.

The leaves contain several flavonoids, several tannins, saponines and phytosterols. Due to this chemical richness, the leaves (and the bark) are used in different herbal medicines for various purposes. For instance in Taiwan, fallen leaves are used as an herb to treat liver diseases. In Suriname, an herbal tea made from the leaves is prescribed against dysentery and diarrhea. The leaves may contain agents for prevention of cancers (although they have no demonstrated anticarcinogenic properties) and antioxidants, as well as anticlastogenic characteristics.



Figure 2.5 a: Indian Almond Tree



Figure 2.5 b: Indian Almond Leaves

(Source: <https://www.google.co.in/search?q=indian+almond+leaves>)

2.1.5 Nano particles

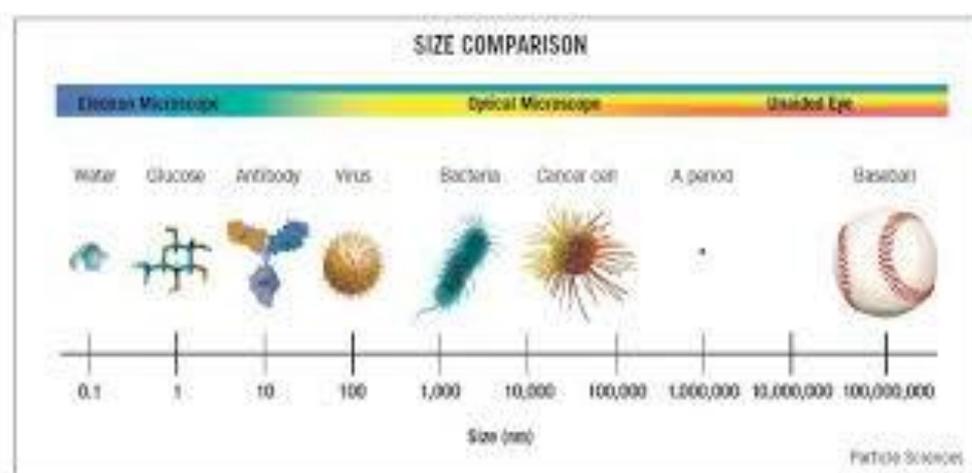
Nanotechnology is widely perceived as one of the key technologies of the 21st century. This new science of the small presents greater challenges and opportunities. It has virtually unlimited future potential to produce and improve new and existing products.²⁴

The emerging fields of nanoscale science, engineering and technology is the ability to work at the molecular level, atom by atom, to create large structures with fundamentally new properties. “The Science of the small” is truly an interdisciplinary

science, in which material scientists, mechanical and electronic engineers, biologists, chemists and physicist share knowledge to extend the nanoscale boundaries.²⁴

Nano technology is the application of scientific knowledge to control and utilise matter at the nanoscale, where size related properties and phenomenon can emerge. The term 'nanotechnology' comes from nanometer a unit of measure of one billionth of a meter of length. For comparison purpose, a human hair is 50,000 nanometer thick. Nanotechnology size comparison is given in the figure 2.6

Figure 2.6: Nanotechnology Size Comparison

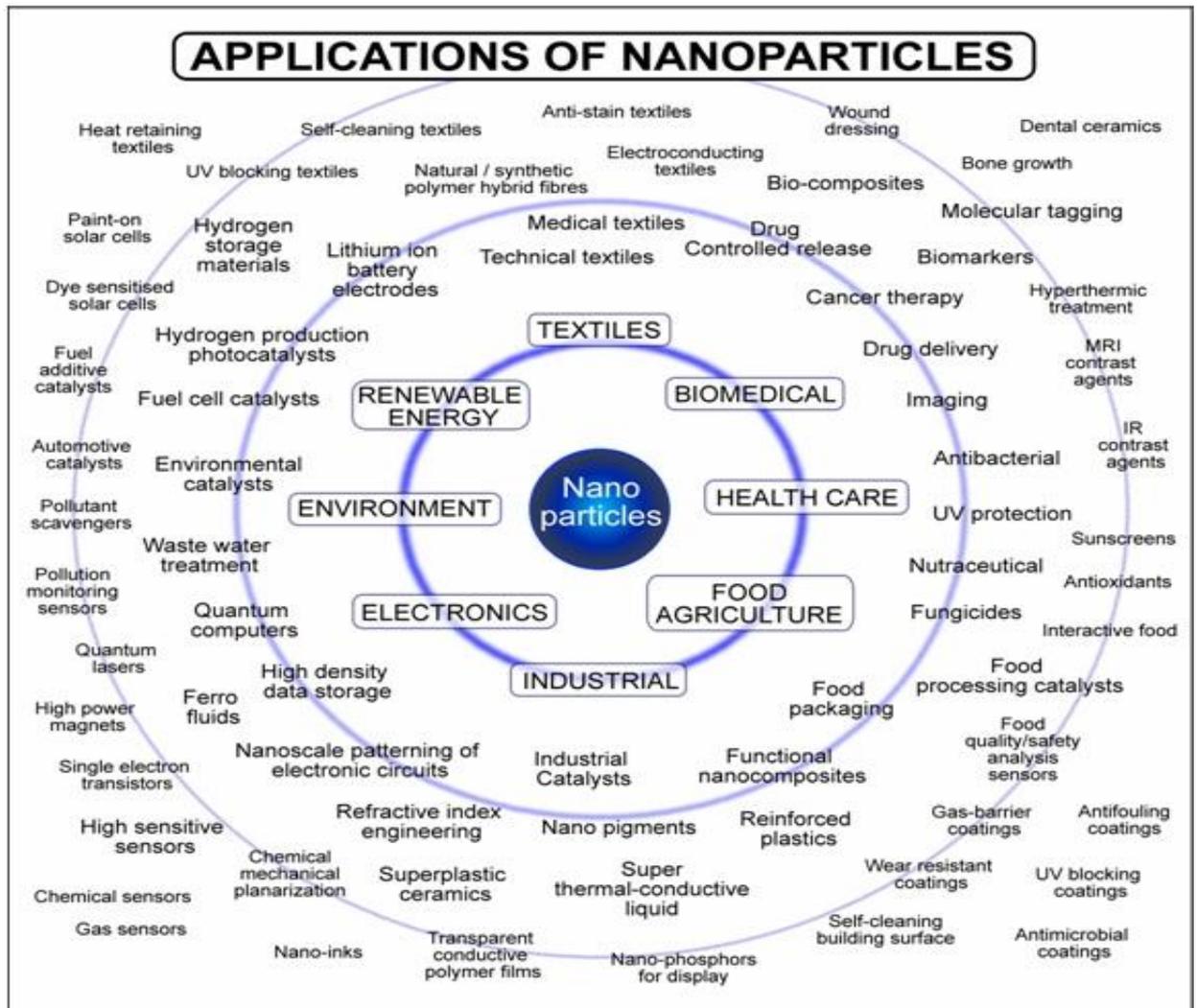


(https://investorshub.advfn.com/boards/read_msg.aspx?message_id=113995461)

The textile industry has already been impacted by nanotechnology. Research involving nanotechnologies to improve performances or to create unprecedented functions of textile materials are flourishing. These research endeavours mainly focused on using nanosize substances and generating nanostructures during manufacturing and finishing processes. (NID Booklet) Nanotechnology research in textiles has three main objectives:

- Upgrading of both present function and performance of textile materials
- Introduction of innovative functionalities like antibacterial, self-cleaning, UV-blocking, conductivity, etc
- Development of smart/intelligent textiles.

Figure 2.7: Applications of nanoparticles



(<https://champagnewhisky.com/2013/02/11/smaller-still-nanoparticles-in-food/nanoparticle-uses-illustration/>)

2.2 Related Research Reviw

2.2.1. Researches on pretreatments applied on jute

1) Researches on bleaching of jute

Wang W, and et al (2010) researched on Study on Chemical Modification and Dyeing Properties of Jute Fiber. In this Glytac (Glycidyl trimethyl ammonium chloride) was used as modifier for surface modification of jute fiber. The researcher in this paper tried to study the application of Glytac on jute fiber cationic modification to improve its dyeability and hence the characteristic surface charge of raw jute and modified jute has been investigated through a zeta potential measurement. After modification, the

dyeing properties like dyeing rate curve, exhaustion, fixation, total fixation and fastness were analyzed. Also the effects of salt and alkali on the K/S values of the modified jute fiber were discussed. The optimization of the modifying effect factor was as follows: Glytac concentration 60g/lit, sodium hydroxide concentration 20g/lit, temperature 60⁰C and time 60 minutes. The results revealed that the modified jute fibers exhibited a small +ve charge on the surface when the pH value was below 4.6 and the zeta potential values were higher than the unmodified jute fibers over the pH range of 3.5-9.5. The modified jute fibers showed higher exhaustion, fixation, total fixation than those of the untreated jute fibers and exhibited good washing and dry rub fastness. In addition, the treated jute fiber could be dyed with reactive dyes using a small amount of salt and alkali resulting higher K/S value of the modified jute fiber than the untreated ones.

Samanta A.K., and et al (2007) studied on Hydrogen peroxide and potassium per-oxo-disulphate combined room temperature bleaching of jute, cotton and jute-cotton union fabrics—An energy- efficient ecofriendly process. In this study a method for room temperature bleaching of jute, cotton and jute-cotton union fabrics using a combination of H₂O₂ and K₂S₂O₈ has been optimized. The measurement of physical properties, such as breaking tenacity, weight loss and surface appearance, including SEM study indicates that the proposed room temperature bleaching process is less damaging to the three types of fabrics studied as compared to conventional hot (85⁰C) H₂O₂ bleaching. The whiteness index is within the acceptable range. The suggested reaction mechanism indicates that K₂S₂O₈ acts as a peroxide booster showing a synergistic action. This room temperature bleaching process is energy efficient, eco friendly and economical, which can be easily adopted by both small scale and large scale sectors.

Chattopadhyay D.P., Sharma J.K., & Chavan R.B. (2003) studied bleaching of jute with peracetic acid formed in-situ in bleach bath. It was observed that in an unbuffered system, the bleach bath pH drops from its initial set value. Excellent bleaching of jute with relatively higher loss in peroxide of in-situ peracetic acid bleach bath. A high degree of whiteness in jute with lesser damage was seen at low temperature.

Ghosh S.B., Bajaj P & Kothari V.K. (2003) studied the effect of different dyes and finishes on UV protection property of jute/cotton union fabrics. It was observed that bleaching with H₂O₂ makes the fabrics more permeable to UV rays and then the fabrics were dyed with reactive dyes. It is observed from spectral analysis that the monochlorotriazinyl reactive dye with cyanuric chloride nucleus, such as Cibacron Red FAL, is quite effective in UV protection. From the UV- visible spectral analysis, Cibatex UPF is found to be a suitable finishing agent for rendering sufficient UV protection to the jute/cotton fabric. Simultaneous dyeing and finishing with Cibacron Red FAL and Cibatex UPF provides higher UV protection. The treatment of jute/cotton fabric with titanium dioxide also provides satisfactory protection against UV rays.

Mondal I (2002) conducted a research on effect of hydrogen peroxide bleaching on sulphonated jute-cotton blended fabrics. Raw sulphonated jute, raw sulphonated jute-cotton and cotton fabrics were bleached under different conditions by varying pH, treatment time, temperature, hydrogen peroxide concentration and fabric-liquor ratio. It was observed that bleaching affected the brightness and breaking strength. The optimum brightness (76.9%) and breaking strength (13.6 kg/l) for blended fabric were obtained with 6.5% hydrogen peroxide at pH 11, temperature 90⁰C, treatment time 100 min and fabric-liquor ratio 1:30. Brightness increased with the increase in bleaching variables upto certain value and then decreased. On the other hand the breaking strength decreased with the increase in the value of bleaching parameters. Also it was observed that the pH is the important factor which critically affects both breaking strength as well as the brightness. The thermal degradation of bleached sulphonated jute-cotton fabric was characterized by TG analysis and compared with the bleached cotton and bleached sulphonated jute fabrics. It had been observed that the thermal stability as well as brightness and breaking strength of the blended fabrics largely depend on the amount of lignin and hemi-cellulose present in the fabric sample.

Mwaikambo L., & Ansel M., (2002) aimed to properly assess changes at the fiber surface and fine structure due to chemical treatment by alkalization in their work on Chemical Modification of Hemp, Sisal, Jute and Kapok Fibers by Alkalization. In this study, four characterization methods were employed namely wide-angle X-ray

analysis (WAXS), differential scanning calorimetry (DSC), Fourier Transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). These were used to analyze the effect of alkalization on the crystallinity and thermal characteristics of all the four natural fibers. These fibers were soaked in various concentration of caustic soda for 48 hrs. The fibers were then neutralized with 1% acetic acid and then thoroughly rinsed. The results revealed that there was sharp decrease in the decomposition and 8% NaOH concentration indicated increase in amorphous cellulose and decrease cellulose crystallite length with poor thermal resistance. Hemp fiber was more crystalline than the other fibers and was found to be more stable to thermal degradation. WAXS results indicated that the crystallinity index initially increases but then declines at high alkali concentration with damage in cell-wall. FTIR provided additional information on the reactivity of fibers following treatment by alkali. Fibers with high crystallinity index, showed least reactivity. SEM results indicated that after the treatment at low concentration except Kapok, possess rougher surfaces which will enhance mechanical inter-locking with resins. Hence in this study, hemp appeared to have the highest crystallinity index and thermal stability followed by Kapok fiber having the highest reaction affinity to chemicals followed by jute and sisal.

Chattopadhyay D. & Sharma J. (1999) conducted a research on sequential bleaching of jute with eco-friendly peracetic acid and hydrogen peroxide. In this study, the researcher attempted to investigate two- stage eco-friendly bleaching of jute with peracetic acid-hydrogen peroxide as a substitute for the conventional sodium hypochlorite-hydrogen peroxide bleaching. A non-silicate organic stabilizer has been used in place of conventional sodium silicate in hydrogen peroxide bleaching. It is observed that peracetic acid-hydrogen peroxide bleaching gives higher whiteness, lower loss in strength and abrasion resistance, and improved softness compared to the conventional process. However, the problem of photoyellowing of the fabric on photoexposure for long duration still persists.

Pandey, S., Chattopadhyay, S. & Pan, N. (1993) studied on recent developments in bleaching of jute and allied fibres. The paper critically reviews the merits and demerits of different bleaching agents used for bleaching jute and allied fibres to obtain maximum whiteness retention with minimum strength and weight loss. The

results reveal that generally three bleaching processes for jute are known and practiced in the industry. They are hypochlorite bleaching at pH 10-10.5, Sodium chlorite bleaching at pH 4.0-4.5 and Hydrogen peroxide bleaching at pH 10-11. Jute and allied fibres belong to a heterogenous system eg, cellulose, hemicelluloses and lignin. Lignin is an organic aromatic polymer which strongly absorbs UV radiation present in the sunlight. So, it is difficult to get an uniform and expected results. So, the study also throws light on recent developments in bleaching and the future direction of research.

2) Research on pretreatments influencing dyeability property

BH Patel and et al (2014) studied the changes in cotton treated with choline chloride. The main purpose of this study is to improve the dyeability of the cationised cotton towards anionic dyes particularly reactive and direct dyes. In this study, choline chloride- a quaternary ammonium salt was linked to the cotton fabric on a process that can improve dyeability. Effect of this treatment on mechanical properties of cotton was measured in terms of tensile strength and % elongation of the cationised cotton compared to the untreated cotton sample. Different dyeing conditions were tested with acid dyes and direct dyes, with and without salt, at different pH levels. Results revealed that cotton treated with a choline chloride can be dyed without electrolytes with improved color strength values with a variety of direct dyes with minor loss in tensile strength. Both the wash and light fastness of direct dyed cotton were also upgraded due to the pretreatment. Cotton treated with a choline chloride that provides cationic dye sites can be dyed with acids dyes. However, their fastness to wash and light was found to be poor.

Kantouch A and et al. (2012) conducted a research on effect of pre-treatment of wool fabric with keratin on its dyeability with acid and reactive dyes. Keratin has been extracted from wool using ammonium thioglycolate under nitrogen atmosphere and then used for treating wool fabric in the presence of epichlorohydrin as a cross-linking agent. The treated fabrics are then dyed with acid and reactive dyes at various temperatures. Complete exhaustion of these dyes on the treated fibres takes place at room temperature within 20 min. Higher dyeing temperatures result in complete exhaustion of the dyebath within a short time. The dyeing kinetics of the treated fibers were also evaluated. The half dyeing time of the treated samples decreases to <12 s

against the 300 s for the untreated ones. The wash and rub fastness of the dyed fabrics have also been assessed. It is found that urea-bisulphite solubility values assure that epichlorohydrin is able to form permanent crosslinks between keratin and wool. Scanning electron micrographs of the treated fabrics reveal formation of very thin keratin layer onto wool surface.

Chattopadhyay D.P., Samanta A.K., and et al. (1999) studied about the effect of caustic pretreatment at varying tension level on dyeing behaviour of jute, flax and ramie yarns has been studied using direct, reactive (cold and highly exhaustive brands) and basic dyes. For the study, 100% jute, 100% flax and 100% ramie were used. The initial weights of the respected yarn samples were noted. The yarns were then treated with three different concentration of caustic soda (6, 12 & 18%) at three different tension levels (of equivalent extensions 0, 0.5 & 1%) for 20 minutes at room temperature. It was observed that the higher the hemicelluloses content of the lignocellulosic fibre, the higher is the weight loss on caustic soda treatment. Weight loss increases for all the fibres with the increase concentration of caustic soda or decrease in tension level during the treatment. Results revealed that the maximum weight loss was observed in case of jute and minimum for ramie. Decrease in basic dye uptake and increase in direct and reactive dye uptake are observed with the increase in caustic soda concentration during the pretreatment for all the fibres. Dye uptake of reactive dyes increased for ramie and flax with the increase of caustic soda but in case of jute, dye uptake showed a drop. With the increase in tension level during treatment, the dye uptake decreases to some extent, irrespective of the fibre type or caustic soda concentration.

Sharma I.C., Chattopadhyay D.P, Mukhopadhyay A., Boruah R.K., & Vishwanath (1999) studied the effect of degumming followed by sequential oxidative and reductive bleaching on physical properties such as tenacity, thickness, fabric weight, bending length, crease recovery, flexural rigidity and air permeability of mulberry and tussar silk fabrics. It was observed that tenacity, thickness, fabric weight, bending length, crease recovery, flexural rigidity decreases whereas air permeability increases after degumming and bleaching.

3) Research on various properties influenced by pretreatments

Wang W and et al., (2008) conducted a study on study on the chemical modification process of jute fiber. Degumming of pre-chlorite treated jute fiber was studied in this paper. The effects of sodium hydroxide concentration, treatment time, temperature, sodium silicate concentration, fiber-to-liquor ratio, penetrating agent TF-107B concentration and degumming agent TF-125A concentration were examined. With respect to gum decomposition, fineness and mechanical properties, sodium hydroxide concentration, sodium silicate concentration and treatment time were found to be the most important parameters. An orthogonal $L_9(3^4)$ experiment designed to optimize the conditions for degumming resulted in the selection of the following procedure: sodium hydroxide of 12g/L, sodium silicate of 3g/L, TF-107B of 2g/L, TF-125A of 2g/L, treatment time of 105 min, temperature of 100⁰C and fibre to liquor ratio 1:20. The effect of the above degumming process on the removal of impurities was also examined and the results showed that degumming was an effective method for removing impurities, especially hemicelluloses.

Sinha E & Rout S.K. (2008) in their study used jute fibres which were degummed and then were chemically modified by treatment with 1.26 M (5 wt%) solution of NaOH solution at room temperature for 2,4 and 8 hrs. The above samples were characterized by small angle X-ray scattering (SAXS) technique and XRD for macromolecular and microstructural parameters of the fibres before and after alkali treatment where as FTIR and SEM was used for fine structural details and morphological studies of the fibres. Differential scanning calorimetry (DSC) and instron 1185 analyzed thermal and mechanical behavior of the fibres. Comparison analysis of results confirmed some changes in the macromolecular structure and microstructure of the fibres after chemical treatment due to swelling of macromolecules and removal of some non-crystalline constituents of the fibres. The findings conclude that change in crystallinity developed after alkali treatment resulting improvement in mechanical strength of the fibres. However, the removal of structural constituents after alkali treatment leads the thermal decomposition temperature of the cellulose went down to 360.62⁰C after 8 hrs alkali treatment from 365.26⁰C for raw jute fibre.

Sayed U., & Joshi K., (2002) studied on jute and jute blends. In this study, the main focus is to study the fibre structure and chemical composition of jute and how it can

be modified to overcome the deficits. The chemical composition of jute constitutes three chemical constituents namely α -cellulose (58-63%), hemicelluloses (21-24%) and lignin (12-14%) and three minor constituents such as fats and waxes (0.4-0.8%) and traces of pigments. Jute fibre can be modified chemically by alkali-treatment, cyanoethylation, acetylation, benzylation. It is been observed that moisture-regain, tension modulus and resistance towards chemical reagents is increased by chemical modification. Jute can be made to react with acrylonitrile in the presence of alkali under conditions that do not reduce tensile strength of the fibres to any important extent. Jute fibre when treated with strong alkali, profound changes occurred in physical structure resulting in high degree of crimpness or waveness and fibres were softened to touch. Enzymes were used to improve softness and smoothness of jute fibre. It was observed that γ -irradiation of jute yarn resulted in formation of reducing groups and carboxyl groups increased solubility. Also it was observed that to minimize the disadvantages of jute fibre, it could be blended with other fibres such as viscose, polyester, polypropylene to achieve the desired properties.

Pan, N. and et al. (1999) studied infrared spectra of bleached jute. The Infrared spectra of jute fibre in raw, dewaxed and bleached condition have been observed over the frequency range of $500-4000\text{cm}^{-1}$ using KBr Pellet technique. The raw jute was bleached with sodium hypochlorite, sodium chlorite and hydrogen peroxide. Raw jute was dewaxed with ethyl alcohol benzene mixture (1:2 v/v) for 6 hrs. in a Soxhlet apparatus. The raw jute, dewaxed jute and bleached jute were evaluated in Fourier Transform Infrared (FTIR) spectrophotometer. The results revealed that there was no change observed in case of dewaxed jute when compared to raw jute. Sharp reduction in the intensity of the bands at 1764cm^{-1} , 1725cm^{-1} and 1709cm^{-1} in the spectra of sodium hypochlorite and hydrogen peroxide bleached jute fibre. In sodium chlorite bleaching, the band intensity has been found to be same as raw jute.

George, E.(1994) studied the light and wash fastness characteristics of chemically pretreated jute based fabrics with reactive dyes, where in the measure of degree of fixation of the dichlorotriazinyl (cold brand), monochlorotriazinyl (hot brand) and vinyl sulphone based reactive dyes was a major objective. The results indicated that 100% jute fabrics has superior dye pick up and dye fixation property. Amongst the dyes procion yellow M-Gr had greatest affinity for the substrates and procion bril blue

M-R had least affinity for the substrate. Jute yarns in weft were seen to have higher dye fixation than cotton warps.

Kundu, A and et al. (1993) conducted a study on enhanced bleaching and softening of jute pretreated with polysaccharide degrading enzymes. The results of the study revealed that treating jute enzymes effects an increase in pore volume (46.2%), which leads to an increased capacity to retain peroxide (25.5%) and a larger surface area of lignin accessible to the oxidant (~30%). Improved bleaching is therefore achieved. Enzyme treatment increases transverse swelling (14%) and reduces bulk torsional rigidity (12.5%), making the fibres more flexible and therefore softer. The removal of cementing materials such as hemicelluloses and lignin by bleaching is enhanced by enzyme pretreatment, resulting in better filamentation and fineness. Experiments with purified enzyme preparations have shown that xylanase pretreatment predominates in facilitating bleaching, and cellulose in the swelling or softening. An appropriate combination of the two is required to obtain optimal effects.

Gupta, R. (1992) conducted a study on the physico- chemical characteristics of chemically modified and resin finished jute and jute multi fibres fabrics. It was concluded that the test conducted on different fibres after pretreatment and on the pretreated samples subjected to ageing, accelerated heat and resin finishing showed improvement in particular wear characteristic such as abrasion resistance, strength retention, crease recovery angle and resistance to heat treatment indicating less damage on the fabric.

Madhuban G and et al (1985) studied on acetylation of jute and infrared spectra of acetylated jute. In this study a simple and quick method for partial acetylation of jute is reported. Infrared spectrum of acetylated a shift of the carbonyl absorption band to higher a wave number. Differential IR spectra of jute and acetylated jute showed absorption for acetate of phenolic hydroxyl groups, indicating acetylation of the lignin component with unprotected hydroxyl groups in the fibre. The acetylated fibre, though it lost its strength to some extent, showed reduced hygroscopicity and dye uptake and increased resistance to microbial damage.

2.2.2 Research on dyeing of jute with natural dyes

Kashyap R., (2012) studied on product diversification on jute fabric through Dabu printing. In this study, attempt had been made to print the jute fabric with traditional Dabu art and to explore the possibilities of maintaining the traditional art of block printing on the eco-friendly fabric, easily available in India. The study aimed to find out the acceptability of the products created for the export-market. A range of product like dining mats, lunch box, floor cover and tea coasters were developed in jute fabric to the growing demand of ecofriendly products. The developed products were evaluated by a panel of 30 judges. The fabric gave good response to dabu printing and the products were highly appreciated.

Samanta A.K., Konar A. & Datta S. (2012) conducted a research on Dyeing of jute fabric with tesu extract: Part II – Thermodynamic parameters and kinetics of dyeing. Thermodynamic parameters and dyeing kinetics for colouration of bleached and selectively double pre-mordanted jute fabric dyed with purified natural dye powder obtained from aqueous extract of tesu under optimized dyeing conditions have been studied to understand the physic-chemical interaction amongst dye, fibre and mordant. It is observed that this dyeing process is endothermic. Dye absorption isotherm of this particular fibre-mordant-dye system is found to be linear, following Nernst absorption isotherm. FTIR spectra of bleached, mordanted and purified natural dyed (tesu dyed) jute fabrics have also been compared. It is revealed that dyeing of selectively pre-mordanted bleached jute fabric mostly occurs through H-bond formation along with minor possibility of co-ordinated complex formation for fixation of tesu colourant on the selectively double pre-mordanted jute fibre.

Patel F., (2010) conducted a research on dyeing of minor fibres with natural dyes. Two cellulosic minor fibres namely sisal and jute and two protein minor fibres namely eri silk and kutch goat hair was taken for the study. Madder, ratanjot, marigold, heena, catechu and falme of forest were the six dyes selected and three dye mixtures of two dyes were derived for the study. The variables of the study were variation of pH during dye application, use of natural mordants tea and pomegranate rind and composite dyeing. A total of 180 shades were produced. Products designed and exhibited were highly appreciated and showed a good applicability of the dyes used.

Samanta A.K., Agarwal P. & Datta S. (2008) studied on Physico-chemical studies on dyeing of jute and cotton fabrics using jackfruit wood extract: Part II- Dyeing Kinetics and Thermodynamic studies. Bleached cotton and jute fabrics were double pre-mordanted applying 20% myrobolan (harda) as 1st mordant and 20% alum or 20% ferrous sulphate as 2nd mordant and subsequently dyed with aqueous extract of jackfruit wood under optimized conditions of dyeing. The physic-chemical parameters of dyeing, such as dyeing affinity, rate of dyeing, absorption isotherms and associated thermodynamic parameters like heat of dyeing (ΔH), entropy of dyeing (ΔS) and Gibb's free energy (ΔG), have been assessed to explain the interaction among different fibre-mordant-dye systems. From the observations, it was found that all the dyeing processes are endothermic, ΔH values being positive. However, the negative ΔG values of all the systems studied indicate that the potentiality of chemical interaction of these fibre-mordant-dye systems in some otherwise favorable conditions of dyeing need to be further studied.

Samanta A.K., Agarwal P. & Datta S. (2008) conducted a research on Dyeing of jute with binary mixtures of jackfruit wood and other natural dyes- Study on colour performance and dye compatibility.

Pan N.C., Chattopadhyay S.N. & Day A. (2003) conducted a study on dyeing of jute with vegetable dyes. Raw jute fabric was bleached and mordanted with different concentration with potash alum. Then the mordanted bleached jute fabrics were dyed with jackfruit leaf and marigold flower petals separately. The results revealed that the vegetable color dyed jute fabrics premordanted with 10% potash alum showed better dye uptake and wash fastness properties. Brightness index value of these samples premordanted with potash alum was lower as compared to without mordanted jute fabrics with the same dyes.

Teli M.D., Adivarekar R.V., Bhagat M., & Manjrekar S.G., (2002) conducted a study on response of jute of the dyes of synthetic and natural origin. 100% jute fabric was used for the experiment, variuos classes of synthetic dyes were used for the study like basic, reactive, vat, metal complex, acid dyes. Among the natural dyes, tea turmeric, manjistha, tamarind, red sandalwood, ratanjot and catechu were used. The results revealed that the wash fastness properties were satisfactory with both the groups of

dyes. It was concluded that jute fabric could be dyed in attractive colors using both synthetic and natural dyes.

Verma C., & Venkatachalam V., (2002) studied the effect of mordants on mango (bark) dye for dyeing of jute/cotton union fabric. The mordants used for the study were alum, ferrous sulphate, tartaric acid and myrobalan. The results revealed that the mango (bark) dye yielded yellow shade on the jute/cotton union fabrics with moderate color fastness. The samples dyed with optimized parameters showed good results regarding all the properties such as general appearance, evenness in dyeing, depth of shades, brightness of color and lustre. It was found that the addition of tartaric acid to alum and ferrous sulphate enhanced the brightness and lustre of the samples but reduced the depth of shade.

Bhattacharya N., Doshi B.A., and Sahasrabudhe A.S. (1998) took the study on dyeing jute fibres with natural dyes where the dyes used were Acacia Catechu, Ormosia Echioides, Indigofera Tinctoria, Artocarpus Integrifolia, Adenantha pavonina, Rubia Cardiofolia, Terminalia Chebula etc. The dyeing procedure was standardized without using any mordant except in the case of Rubia Cardiofolia, where aluminium sulphate was used and in the case of artocarpus integrifolia where the copper sulphate and potassium dichromate were used in small amount, (<0.1 %). Studies were also carried out to investigate the efficacy of dyeing from used dyebaths. All the samples showed good dye uptake. The fastness properties i.e. light, water and perspiration (both acidic and alkaline) were found to be good. Slight tonal variations were observed where mordants were used.

Chattopadhyay D.P. and et al. (1997) studied the effect of mordants and mordanting techniques on the dyeing of jute and cotton with the natural dye adula. Different concentrations of mordant and salt are used and are applied through different techniques in pre mordanting, simultaneous mordanting and post mordanting. With jute, simultaneous mordanting was found better at low concentration of mordants as compared to other two techniques. In case of cotton, the depth of shades found was too light and among the three techniques of mordanting, pre and post gave comparatively better results. With both jute and cotton, the color depth found was higher with FeSO_4 than to the alum.

2.2.3. Research on product diversification of jute

Malhan S. (1999) has done a study on value addition and product diversification of minor fibre fabric (Jute & Banana) using Hand Block Printing. Motifs of Sangneri printing of Rajasthan with contemporary colors using pigments were used for printing. Various household articles were constructed like cushion covers, lamp shades, table mats, tray and tray covers, wall hanging, partition panel, bed spreads. Then these were evaluated for market acceptability and the results revealed that the majority of the respondents accepted the product for household use.

Raval, P. (1999) printed the cotton banana union fabric and cotton jute fabric using various colored pigments. When tested for wash, light and crock fastness it was observed that out of the three pigments used i.e. pigment red, pigment yellow and pigment blue, pigment red and yellow gave moderate to good wash fastness on both the fabrics. It was also seen that the cotton banana union fabric was quite resistant to light fading in case of all pigments but the crocking fastness of these dyes came out to be poor on both the fabrics.

Sharma, B. (1993) worked on construction of different types of skirts from jute and jute multi fibre fabrics and the evaluation results revealed that the majority of respondents (98 percent) appreciated the garments and were ready to add them to their wardrobe. When asked about the suitability, higher number preferred jute cotton fabrics best for skirt constructions followed by jute viscose fabrics.