CHAPTER-II
REVIEW OF LITERATURE

Promotion of natural dyes along with the use of metal mordant is of major concern due to non eco-friendly nature of mordants. It is necessary to develop new techniques of coloration with the help of modern scientific inputs so that these dyes can offer themselves as effective eco-option.

The present study has focused on elimination of the use of non eco-friendly mordant and improvement in colour fastness by the use of eco-friendly mordant.

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2.1 Environment pollution from synthetic dyes

Until the latter half of the 19th century people were using natural dyes (Parkes, 2002) for colouring of textiles. Different parts of the plant were used to obtain various shades.

After invention of synthetic dyes, natural dyes are not used because of the advantage of synthetic dye over natural dye in respect of application, colour range, fastness properties, and availability. But, some synthetic dyes are hazardous, carcinogenic and also release vast amount of pollutant in the environment during their manufacturing (Gulrajani et al. 1999; Nagia and Mohamedy, 2007).

The world is slowly realizing the damaging effects of several chemicals that are synthesized by men in laboratory. Ecology and pollution have therefore become a major concern to all (Nimkar, 2004). Green house effect, ozone layer depreciation, water pollution and improper waste disposal have become important issues (Teli et al., 2002a). So, all developed countries are looking for safe environment. In this context, the textile industry, which uses hundreds of chemicals in production, from raw material to disposal, is generally regarded among the most polluting industry (Nimkar, 2004).

To promote a clean environment and safety to the manufacture and users of textile products Germany has banned certain dyes and the entire European Union (EU) is promoting the concept of eco friendly textiles. This concept is based on the cradle-to-grave approach i.e. it analysis entire life cycle of production distribution and utilization and disposal after use (Subramanian and Phalgunani, 1995). In this context, natural dyes are being promoted but with a word of caution (Chavan, 1995) to keep the revival activities for natural dyes to a limited scale in order to maintain the balance between environment and trade.

Dyes can be of many different structural varieties like acidic, basic, disperse, azo, anthraquinone based and metal complex dyes among others. The textile industry is the largest consumer of dye stuffs. During the coloration process a large percentage of the synthetic dye does not bind and is lost to the waste stream (Weber and Adams, 1995).
Approximately 10-15% dyes are released into the environment during dyeing process making the effluent highly colored and aesthetically unpleasant. The effluent from textile industries thus carries a large number of dyes and other additives which are added during the colouring process (Wang et al., 2002). These are difficult to remove in conventional water treatment procedures and can be transported easily through sewers and rivers especially because they are designed to have high water solubility. They may also undergo degradation to form products that are highly toxic and carcinogenic (Rinde & Troll, 1975).

It is in the textile industry that the largest quantities of aqueous wastes and dye effluents are discharged from the dyeing process, with both strong persistent colour and a high biological oxygen demand (BOD), both of which are aesthetically and environmentally unacceptable (Wang et al., 2007).

Recently, a number of commercial dyers and small textile export houses have started looking at the possibilities of using natural dyes for regular basis dyeing and printing of textiles to overcome environmental pollution caused by the synthetic dyes (Glover and Pierce, 1993).

### 2.2 Natural dyes and mordants

Natural dyes comprise those colourants (dyes and pigments) that are obtained from animal or vegetable matter without chemical processing (Gulrajani & Gupta, 1992).

The word ‘natural dye’ covers all the dyes derived from the natural sources like plants, animal and minerals. Natural dyes 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 colouring matter and the fibre. Transition metal ions usually have strong coordinating power and/or capable of forming week to medium attraction/interaction forces and thus can act as bridging material to create substantivity of natural dyes when a textile material being impregnated with such metallic salt (i.e. mordanted) is subjected to dyeing with different natural dyes, usually having some mordantable groups facilitating fixation of such dye. These metallic mordants after combining with dye in the fibre, forms an insoluble precipitate or lake and thus both the dye
and mordant get fixed to become washing fast to a reasonable level (Samanta and Konar, 2011).

2.2.1 Advantages and disadvantages of natural dyes

In the recent years, there has been a trend to revive the art of natural dyeing. This is mainly because in some aspects natural dyes are advantageous against synthetic dyes. Some of these advantages along with some limitations (disadvantages) are listed below:

Advantages of natural dyes

- The shades produced by natural dyes are usually soft, lustrous and soothing to the human eye.
- Natural dyestuff can produce a wide range of colours by mix and match system. A small variation in the dyeing technique or the use of different mordants with the same dye (polygenetic type natural dye) can shift the colours to a wide range or create totally new colours, which are not easily possible with synthetic dyestuffs.
- Natural dyestuffs produce rare colour ideas and are automatically harmonizing.
- 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.
- In some cases like harda, indigo etc., the waste in the process becomes an ideal fertilizer for use in agricultural fields. Therefore, no disposal problem of this natural waste.
- 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.
- 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.
- Application of natural dyes has potential to earn carbon credit by reducing consumption of fossil fuel (petroleum) based synthetic dyes.
- Some of its constituents are anti-allergens, hence prove safe for skin contact and are mostly non-hazardous to human health.
Some of the natural dyes are enhanced with age, while synthetic dyes fade with time.

Natural dyes bleed but do not stain other fabrics, turmeric being an exception.

Natural dyes are usually moth proof and can replace synthetic dyes in kids garments.

Despite these advantages, natural dyes do carry some inherent disadvantages, which are responsible for the decline of this ancient art of dyeing textiles.

**Limitation/ disadvantages of natural dyes**

- It is difficult to reproduce shades by using natural dyes/colourants, as these agro-products vary from one crop season to another crop season, place to place and species to species, maturity period etc.
- It is difficult to standardize a recipe for the use of natural dyes, as the natural dyeing process and its colour development depends not only on colour component but also on materials.
- Natural dyeing requires skilled workmanship and is therefore expensive. Low colour yield of source natural dyes thus necessitates the use of more dyestuffs, larger dyeing time and excess cost for mordants and mordanting.
- Scientific backup of a large part of the science involved in natural dyeing is still need to be explored.
- Lack of availability of precise technical knowledge on extraction and dyeing techniques.
- The dyed textile may change colour when exposed to the sun, sweat and air.
- 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 bath and may pose serious effluent disposal problem.
- With a few exceptions, most of the natural dyes are fugitive even when applied in conjunction with a mordant. Therefore, sometimes their colour
fastness performance ratings are inadequate for modern textile usage. (Samanta and Konar, 2011)

2.2.2 Classification of natural dyes

Natural dyes can be classified (Gulrajani & Gupta, 1992) 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, e.g. on the basis of hue, chemical constitution, application class etc.

A. In “Treatise on Permanent Colours” by Bancroft (1775), natural dyes are classified into two groups: ‘Substantive Dyes’ such as indigo, turmeric etc. which dye the fibers directly and ‘Adjective Dyes’ such as logwood, madder etc. which are mordanted with a metallic salt.

B. Natural dyes are classified according to hue (Predominating colour). Hue of the natural dyes is assigned as with number by Colour Index International started in 1924. The database is jointly maintained by SDC and AATCC. The number of dyes in each hue is given in table-2.1

<table>
<thead>
<tr>
<th>CI Natural</th>
<th>No. of Dyes</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow</td>
<td>28</td>
<td>30.4</td>
</tr>
<tr>
<td>Orange</td>
<td>6</td>
<td>6.5</td>
</tr>
<tr>
<td>Red</td>
<td>32</td>
<td>34.8</td>
</tr>
<tr>
<td>Blue</td>
<td>3</td>
<td>3.3</td>
</tr>
<tr>
<td>Green</td>
<td>5</td>
<td>5.5</td>
</tr>
<tr>
<td>Brown</td>
<td>12</td>
<td>13</td>
</tr>
<tr>
<td>Black</td>
<td>6</td>
<td>6.5</td>
</tr>
</tbody>
</table>

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

- **Red colour 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 colour dyes**: Yellow is the liveliest and perhaps the most abundant of all hues in nature. About 90% of the yellow dyes are flavonoids. Generally, they produce pale shade with quicker fading except turmeric, which produce dull deep shade. Wash fastness rating
of natural yellow dyes ranges from fair to excellent, e.g., tesu, turmeric, kapila.

- **Blue colour dyes**: Indigo and woad are blue colour dye which gives excellent fastness to light and washing.

- **Black colour dyes**: Black shades, generally obtained from tannin rich plant natural dyes and appreciably substantive towards cellulosic and protein fibre, imparts good overall fastness properties. Examples – logwood, harda, custard apple etc.

C. On the basis of origin, natural dyes are broadly classified into three categories: vegetable, mineral and animal origin. There are about 500 vegetable origin dyes, in these the colouring matter is derived from root, leaf, bark, trunk or fruit of plants, details are given in table-2.2

**Table-2.2 Some common natural dyestuffs obtained from different vegetable origin**

<table>
<thead>
<tr>
<th>Part of the Plant</th>
<th>Dyestuffs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Root</td>
<td>Turmeric, Madder (Manjistha), Onions, Beet-root</td>
</tr>
<tr>
<td>Bark/Branches</td>
<td>Purple bark, Sappan wood, Shillicorai, Khair, Red bark, Sandalwood</td>
</tr>
<tr>
<td>Leaf</td>
<td>Indigo, Henna, Eucalyptus, Tea, Cardamon, Coral Jasmine, Lemon Grass</td>
</tr>
<tr>
<td>Flowers (Petals)</td>
<td>Marigold, Dahlia, Tesu, Kusum</td>
</tr>
<tr>
<td>Fruits/Seeds</td>
<td>Latkan, Pomegranate rind, Beetle nut, Myrobolan (Harda)</td>
</tr>
</tbody>
</table>

Mineral origin dyes are derived from specific mineral natural source or so-called mineral colours are produced from purified inorganic compounds. Some of the important mineral dyes 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 insect.

D. On the basis of their chemical constitution (Dedhia, 1998).

i. **Indigoid dyes**: Indigo, tyrian purple and woad are the most common examples of this class.

ii. **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. These are generally mordant dyes.


iii. **Alphanaphthoquinones**: Typical examples of this class are lawsone (henna) and juglone, obtained from the shells of unripe walnuts. These dyes are generally dispersing dyes and give shades of orange.

iv. **Flavonoids**, which yield yellow dyes, can be classified under flavones, isoflavones, aurones and chalcones. Flavones are colourless 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 colours on both wool and silk.

v. **Di-hydropyrans**: Closely related in chemical structure to the flavones are substituted di-hydropyrans, viz. haematin and its leuco form, haematoxylin. These are important natural dyes for dark shades on silk, wool and cotton. Logwoods, brazil wood and sappan-wood are the common example.

vi. **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.

vii. **Carotenoids**: The class name carotene is derived from the orange pigment found in carrots. In these, the colour is due to the presence of long conjugated double bonds.

E. On the basis of the method of application (Gulrajani & Gupta, 1992).

i. **Mordant dyes** are dyestuffs which require a mordant in their application as they have no affinity for the fiber being dyed. A mordant dye should have electron donating groups capable of forming a complex with the transition metal salt, e.g., madder, fustic, Persian, berries, kermes, cochineal etc.

ii. **Vat dyes** 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 fibers. The true colour is produced only on oxidation followed by treatment with a hot soap solution, e.g., indigo.

iii. **Direct dyes** are those dyes that have tremendous affinity for the cellulosic fibers. They are dyed from a boiling dye bath. Turmeric, harda, pomegranate rind etc. are the few of the direct natural dyes.
iv. Acid dyes are applied from an acidic medium. The dye molecules have either sulphonic or carboxylic group (s) 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, e.g., saffron.

v. Disperse dye has a relatively low molecular mass, low solubility and no strong solubilizing groups. Disperse dyes can be applied on to 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, e.g., lawsone and many other flavones and anthraquinone dyes.

vi. Basic or cationic dyes on ionization give coloured cations and form an electrovalent bond with the –COOH group of wool and silk. These dyes are applied from neutral to mildly acidic pH. These dyes have poor light fastness, e.g., berberine.

The same dyestuffs can produce many different colours and shades depending on the soil type, cultivation method, environment, weather, season, material to be dyed, and the source of water being used (Chakrabarti & Vignesh, 2011). As a result, it is one of the reasons to explain why the synthetic dyes are adopted in the manufacturing industry instead of natural dyes. The standardization of the natural dyes can enhance the competitiveness in the market.

2.2.3 Mordant and Fixation

The word "mordant" comes from the French word "Mord" or "to bite" and mordants can be described as metallic salts with affinity for both fiber and dyes stuffs and that improves the colour fastness. Even some of the fugitive dyes have been used successfully with the help of mordants. (Vankar, 2007)

A mordant is a substance used to set dyes on fabrics or tissue sections by forming a coordination complex with the dye which then attaches to the fabric or tissue. The mordant is a sort of bridge between the fibre and the dyestuffs that are extracted from the plants or animals (Bohmer, 2002).

However, most of the natural dyestuffs which are known as subjective dyes require some mordants to fix the colour on the fibers and form strong
chemical bonds. The mordant enters deeply into the fibre and combines with dyestuff to form the colour (Brennan, 2004).

Mordants help the fibre receive the dyestuff well and form bonding. Compounds of alum (potassium alum), tannin (tannic acid), and iron (ferrous sulphate) are the safest choices (Brennan, 2004).

Mordant can help the dyestuffs achieve a strong and bright colour on cellulose fibers. They combine with the dyestuff and are then permanently fixed onto the fibre. Intensity of the hue and the fastness of the resultant colour can be improved (Dalby, 1992).

However, mordants have their own colours which may affect the colour of the dyed textile. In addition, the mordants combined with the dyeing molecules lead to a significant influence on the hue produced with a particular dyestuff (Horrocks & Anand, 2000).

### 2.2.4 Mordanting Methods:

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

**A.** In the pre-mordanting method, the textile material is first immersed into the mordant solution for 30 to 60 minutes at the room temperature or higher temperature with a liquor ratio of 1:5 to 1:20. The textile material treated with mordant is then dyed. After dyeing, the dyed material is washed with a non-ionic detergent. It is the most frequently used procedure by natural dyers because large quantities of textile can be treated and stored until dyeing.

**B.** As for the simultaneous mordanting and dyeing, the textile material is immersed in a dyebath solution containing both mordant and dye. Dyeing auxiliaries can be added during the dyeing process. For the optimization of dyeing condition, dyeing process variables can be studied for the specific fibre-mordant-natural dye system in order to improve the colour yield of textiles. After dyeing, the textile material is washed with non-ionic detergent.

**C.** With regard to the post-mordanting method of natural dyeing, the dyeing process is carried out on the bleached textiles in the dyebath without
mordant. The dyed fabric then is treated in another bath called saturator containing the mordanting solution. Treatment condition may vary depending on the type of fibre, dye and mordant system being used. After dyeing, the textile material is washed properly with non-ionic detergent. When using this mordanting method, the colours are usually different and often less strong.

In all these three applications, mordants act as dye setters that will prevent the colour from running or streaking after dyeing (Yee, 2013).

2.2.5 Types of mordants

Limitation on colour yield and poor fastness properties prompted a search for ideal mordants, the chemicals which increase natural dye uptake by textile fibers. Different types of mordants yield different colours even for the same natural dye. Therefore, final colour, their brilliance and colour fastness properties are not only dependant on the dye itself but are also determined by varying concentration and skillful manipulation of the mordants. Thus, a mordant is more important than the dye itself. Moreover, the ideal mordant for bulk use should produce appreciable colour yield in practicable dyeing conditions at low cost, without seriously affecting physical properties of fibre or fastness properties of the dyes. Also, It should not cause any noxious effect during processing and the dyed textile material should not have any carcinogenic effect during use. Mordants can be classified into the following categories:

A. Metallic mordants

They are generally metal salts of aluminum, chromium, iron, copper and tin. The metallic mordants are of two types.

i. Brightening mordants

a) Potash 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 colour in the plant.

Alum or other metallic mordants fix dyes on fibre by chemically combining with the functional groups of the natural dyes to form covalent bonds, hydrogen bonds and other interactional forces as shown in figure 2.1
Figure: 2.1 Bondings between alum and dye (Samanta & Konar, 2011)

Alum occurs in nature but is also found in many plants. Alum reacts chemically with water first, whereby the aluminum forms a mildly basic hydroxide which is no longer soluble in water. Alum attaches itself to the mildly acidic groups of the protein molecules of the wool or silk fibers and heat can accelerate the process. During dyeing, the aluminum then binds the molecules of mildly acidic dyestuff, thereby creating the so-called lac which is insoluble. Hence, the dyed material is colourfast when washed. (Bohmer, 2002).

b) **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 beyond a certain limit of its presence. Its use has been limited as per the norms of the eco-standards. Chrome is known as potassium dichromate and is a kind of brightening mordant. It produces a deep version of the prevailing dye colour, and leaves wool with beautiful softness, while other mordants will harden wool (Dyer, 1976; Salvendy & Ji, 2012).

c) **Tin (stannous chloride):** It gives brighter colours 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**

a) **Copper (cupric sulphate):** Known as blue vitriol available as bright blue crystals. 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 metal. Copper mordant also reacts with water to form a mildly basic hydroxide (Bohmer, 2002). Copper mordant is less frequently used than the other mordants as it is toxic. (Liles, 1990).

b) 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 colours/ shades. It is easily available and one of the oldest mordants known. It is extensively used to get grey to black shades.

B. Tannins

The term ‘tanning agent’ is given initially to those water-soluble cellulosic materials that predicates gelatin from solution. But all gelatin precipitation did not identified as tanning agent. Tannins are polyphenolic compounds having capacity of gelling under certain conditions. Among the tannins, myrobalan (harda) and galls/sumach are most important.

Tannic acid is available in its natural form and can be extracted from number of vegetables. Oak galls, sumach, cutch and some barks are all rich in tannic acid. Dyestuffs that contain tannin such as black oak, pomegranate, cutch, fustic, etc. do not need an additional tannin mordant. Some of these tannic acid rich sources may also contain dyes, and so this may affect the resultant colour after dyeing has taken place, resulting in darker and less brilliant colour. (Bohmer, 2002). Tannic acid extracted from the vegetable sources for natural dyeing is more natural than those metal salts or the chemical tannic acid (Dalby, 1992). During dyeing, the tannin combines with the cellulose on one side and then binds with another mordant such as alum or iron mordant. The chemical processes involved in the use of tannic mordant are not entirely clear.

C. Oil 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 colour from madder. The main function of TRO as oil mordant is to form a complex with alum when used as a main mordant. Sulphonated oil posses better binding-capacity than the natural oils. Oil mordanted samples exhibit superior fastness and hue.

2.3 Studies on natural dyes
In the last fifteen to twenty years many scientific research studies on natural dyes have been carried out very systematically. These studies mainly deal with identification of dye, extraction procedure standardization, application method and colour fastness test. Some important ones are grouped and summarised below.

2.3.1 Natural dyes for cellulosic fibre

Most of the studies reported on dyeing of cotton with natural dyes are mainly on use of different mordants, pre, post and simultaneous mordanting techniques, standardization of dyeing condition, influence of pH on colour, mordant mixing along with use of sonicator for optimum extraction technique. Some important and recent ones are given below.

Deo and Desai (1999) dyed cotton and jute fabrics with an aqueous extract of tea, containing tannins as the main colorant species. The dyeing was carried out with and without metal salts as mordants, using three different dyeing methods: pre-mordanting, meta-mordanting and post-mordanting. The resulting wash and light fastnesses of the dyed fabrics were good to excellent. The colour of the fabrics was investigated on computer colour matching system in terms of K/S, and CIELAB colour-difference values. Deep shades (K/S = 3.9) were obtained for jute in acidic media, while cotton fabrics got dyed in medium depths (K/S = 2.0) under identical conditions of dyeing.

Gulrajani (2001) evaluated cotton dyeing by using various natural dyes alone and in combination to yield six basic shades: blue, yellow, red, black, green and fawn. These dyed fibers were then blended in various proportions along with undyed cotton fibers and spun on a rotor-spinning machine to produce 204 coloured yarns. The fastness properties of the six basic shades were determined. The L*a*b* and L*C*h values of the yarns having 50% dyed fibre and 50% undyed cotton fibre was also determined. The values were plotted to obtain the colour gamut of natural dyes on cotton yarns.

Teli et al. (2002) used water borne extracts of madder and tea to dye cotton fabric using conventional single dip dyeing method with different mordanting methods. The results were compared with a new method that uses ferrous sulphate and tannic acid as mordants in a multiple dip process. Results show that the multiple dip method was capable of producing deeper shades,
uses less dye and indicates a potential for industrial use. Ferrous sulphate mordant produced the deepest shades.

In a study by Samanta et al. (2003) cotton fabric was dyed with four different natural dyes (turmeric, myrobolan, madder, red sandalwood) using pre, post and simultaneous-mordanting techniques. Aluminium sulphate was used as a mordant. Some samples were also dyed with a combination of turmeric with madder or red-sandalwood and a combination of myrobolan with madder or red sandalwood in different proportions. Selected mordanted and dyed samples were after-treated with a cationic dye fixing agent. Turmeric being a direct dye type, gave maximum colour strength when applied by the simultaneous-mordanting method, either singly or in combination with other dyes. Turmeric also showed poor wash fastness, which was improved to some extent by after-treatment with a cationic dye fixing agent and on combination of turmeric with other dyes of better fastness. Combined dye application of turmeric with the other dyes by the simultaneous-mordanting method resulted in a better shade development as the observed colour strength values were always higher than the calculated or the expected values. However, myrobolan on combination with other dyes gave higher colour strength when applied by the post-mordanting method. In the case of the simultaneous-mordanting method, myrobolan did not show a synergistic effect in terms of the observed and calculated K/S values.

Garima et al. (2004) efficiently dyed cotton yarns with a plant dye, Ornamental Mustard (Brassica juncea) using certain optimum variables. Medium of dye extraction, wave length, extraction time, dye material concentration, dyeing temperature, dyeing time, and dyeing pH were standardized. Ornamental mustard leaves were extracted in aqueous, alkaline, and alcoholic mediums, and the best color was obtained in the alkaline medium. The results showed that the optical density increased with increased extraction time up to 30 minutes, and further decreased with increase in extraction time. The maximum dye absorption was observed at 7% dye material concentration, and increased with increase in dyeing temperature. The dye absorption also increased with increasing pH, and thus the optimum pH selected for dyeing was 10. Thus, dye extraction in an alkaline medium with optimum wave length of 360nm, extraction time 30 minutes, dye material
concentration 7%, dyeing temperature 100°C, dyeing time 45 minutes, and dyeing pH 10, gave excellent results for dyeing cotton yarns.

Study on cotton fabric using Eclipta as natural dye in both conventional and sonicator methods has been reported by Vankar et al. (2007). The effects of dyeing showed higher color strength values obtained by the latter. Dyeing kinetics of cotton fabrics were compared for both the methods. The time/dye uptake reveals the enhanced dye uptake showing sonicator efficiency. The results of fastness properties of the dyed fabrics were fair to good. CIELAB values have also been evaluated.

Teli and Paul (2006) have highlighted the creative potential, non-pollutant nature, and soft lustrous colors of coffee seed coat as a natural dye enabling it to be used in eco-friendly dyeing of textiles. For the study natural dye from coffee-seed coat was extracted for its application in dyeing cotton. Dye extract and filtered after boiling coffee-seed coat in 5 liter water for 4 hours and kept overnight. Dyeing was carried out by pre-mordanting, metemordanting and post-mordanting, using several mordants including myrobolan and ferrous sulphate. The fastness properties of dyeing were satisfactory give different tones and higher depth of dyeing. The result indicated that coffee-seed extract develops a range of shades with good fastness properties on cotton.

Lee (2007) extracted natural colorant from *Coffea arabica L.*, using water as extradant at 90°C for 90 min. Studies have been made on the dyeing, color fastness, and deodorization properties of cotton fabric dyed with *Coffea arabica L.* extract solutions, The best mordants were found to be FeSO₄, CuSO₄, and SnSO₄ for improving the color strength (K/S) of cotton fabric. Perspiration fastness for mordants MnSO₄, ZnSO₄, and NiSO₄ for cotton was rated 3. It was found that cotton fabric dyed with the *Coffea arabica L.* extract showed good deodorization performance.

Natural dye was extracted by Shanker and Vankar (2007) from *Hibiscus mutabilis* (Gulzuba)/Cotton rose/ belonging to family Malvaceae for dyeing cotton. Pretreatment with 2-4 % metal mordants and keeping M:L ratio as 1:40 for the weight of the fabric to plant extract is optimum showing very good fastness properties for cotton. Aqueous extract of Gulzuba flowers yield
shades with good fastness properties. It was concluded that the dye had good scope in the commercial dyeing of cotton for garment industry.

Dayal et al. (2008) isolated natural dye from *parthenium hysterophorus* weed and applied on cotton. The dye was extracted by boiling 1 kg weed with 10 liter water for 60 min at 95-98°C. The study indicates that its aerial part may be used for the isolation of dye in solid form (13%). The dyebath was set with 4 gram per liter of dye with M:L ratio 1:100 at 95-98°C for 60 minute. Post mordanting method was used with common mordants like CuSO₄, alum and SnCl₂. The dyed cotton fabric was immersed in mordant bath (0.5%) by keeping M:L ratio 1:100 at 95-98°C for 45 minute which imparts a number of shades on cotton with good fastness properties.

Indi & Chinta (2008) have studied application and properties of natural dye *phyllanthus reticulatus* on cotton. Dye was extracted from the fruit of *phyllanthus reticulatus*. Cotton fabric (M:L ratio 1:20) was premordanted with alum (8%) and tannic acid (4%) at 80°C for 1 hr. Same conditions was applied for post mordanting. Dyeing was carried out for 10% shade at 80°C for 45 minute at pH range from 3 to 7 followed by post treatment with soap 0.5 gpl for 20 minute at 60°C. It was concluded that colour obtained totally depends on the type of mordant and method of mordanting used and pH conditions. Light fastness was poor for all application methods used in this experiment but slight improvement was observed in post mordanting methods. Overall wash fastness for all application methods of dyeing remained same. Rubbing fastness was very good for all the application methods.

Saha & Dutta (2008) have studied the use of marigold flower as floral dye because huge amount of unsold flowers are wasted everyday. These unsold flowers create a big problem for disposal as well as these can create environment pollution also. These unsold flowers can be used for dyeing purpose for cotton fibre and residuals after dyeing can be used as bio-fertilizers. In the study cotton was mordanted before dyeing. For mordanting, low concentration of eco-friendly mordanting agents: Alum, Copper Sulphate, Ferrous Sulphate, Stannous Chloride were used. The mordanted samples were immersed in dye bath for 2 hour at a temperature range of 80°C. After dyeing, soaping was done with 2g/l non-ionic soap at room temperature for 10 minute, and then dried in shade. Various shades of yellow, brown, grey and grey black were obtained using
different mordants. Good wash fastness properties were noted and so the flowers were recommended for use in industry. This floral dye has no side effects on skin and it has no harmful effect on environment also. 

Vankar & Shanker (2008) studied ultrasonic dyeing of cotton with *Nerium oleander* flower. The scoured fabric was soaked in clean water for 30 minute prior to dyeing and mordanting. Mordanting with metal salts such as FeSO$_4$, SnCl$_2$, CuSO$_4$, SnCl$_4$, K$_2$Cr$_2$O$_7$, and alum was carried out at 60ºC for 30 minute. Cotton was then dyed with dye extract, keeping M:L ratio as 1:30 and pH was maintained at 4 by adding buffer solution. It was concluded that aqueous extract of nerium flowers yield cream to green to purple shades on cotton fabrics with good fastness properties the colour strength (K/S value) were good particularly for cotton mordanted by stannic chloride. The dye showed good scope in commercial dyeing of cotton fabric for garment industry.

An attempt was made by Gahlot and others (2008) to optimize various dyeing variables such as extraction medium, extraction time, dyeing time, mordants concentration and methods of mordanting for dyeing of cotton with jatropha flower dye. Four metallic mordants: alum, chrome, copper sulphate and ferrous sulphate were taken in various concentrations. Dyeing was carried out at optimized dyeing time (60 minute) and 4-6 pH. Various tones of peach, brown and grey were obtained. The dyed materials had good colour fastness properties also. The processing of dye materials was found to be easy as well as safe from the point of environment.

An attempt was made to dye cotton with areca nut extract by Mhale (2008). Mordanting was done by mixing two mordants in different proportions. Alum + potassium dichromate, alum+ copper sulphate, alum+ ferrous sulphate, potassium dichromate + copper sulphate, potassium dichromate + ferrous sulphate were used in 1:1,1:3 and 3:1 ratio. Mordant combination was done in such a way that amount of mixed mordant did not exceed 5grams per 100grams of cotton fabric. Shades obtained were light, medium and dark rust, sand brown, brown, olive green and leaf green. It was concluded that samples post mordanted with potash alum: potassium dichromate 1:1 and 1:3 combinations had better fastness to sunlight, washing, rubbing and perspiration in alkaline media. Simultaneously mordanted sample with potash alum : copper sulphate 1:1 and potash alum: ferrous sulphate 3:1
combinations exhibited better fastness. Pre mordanted samples with potassium dichromate copper sulphate 1:3 and copper sulphate: ferrous sulphate 1:3, 1:1 and 3:1 combination showed better fastness to sunlight, washing, rubbing and perspiration. Areca nut dyed cotton post mordanted with potassium dichromate: ferrous sulphate 1:1 combination gave excellent results to colour fastness.

Prusti, et. al. (2009), have studied *Terminalia catappa* as a suitable natural dye for cotton yarn. Process development for the extraction of natural dye in pure form, from the waste leaves of Indian almond (*Terminalia catappa*) and its application on different yarns have been carried out successfully. Cotton yarn was dipped in mordant such as alum + turmeric, ferrous sulphate, stannous chloride, copper sulphate, potassium dichromate. The mordanted cotton yarn was dyed at 80ºC-90ºC. Golden yellow, slate gray, pale yellow and brown colours were obtained. It was concluded from the study that it was possible to obtain various intensities of colour shades for cotton yarn by using a known quantity of isolated dye materials, which is not possible in case of the traditional method.

Mukherjee et. al. (2009) studied modification of natural yellow dyes for improvement of washing and light fastness. Cotton fabric was premordanted with aluminium sulphate, zinc sulphate, copper sulphate, magnesium sulphate, copper sulphate and sodium dichromate. Dyeing was carried out at 90ºC for 45 minute with M:L ratio 1:20. Modifications of dyes were performed using poly carboxylic acid (oxalic acid, tartaric acid citric acid) and cyanuric chloride in liquid dye. Most of the natural dyes namely Turmeric (*Curcuma longa*), Palas (*Butca mnноперма*), Ganda (*Tagetes Erects*) and shruh (*Nyctanethes Arbortristis*) are having poor to moderate washing fastness and very poor light fastness owing to their inbuilt dye structure. They contain -OH groups along with -OCH3 which intensify the depth of shade according to their increased numbers in one dye molecule. These -OH groups are prone to metallic mordants to produce shades of different tones. On the other hand, these groups are the common path way to UV rays of sunlight and therefore, colour fades quickly due to a photo chemical reaction. In this research work, attempts were made to block the -OH groups of the dye with poly carboxylic acid for improvement of light fastness.
along with improvement in intensity of color and washing fastness. It was concluded that all yellow dyes having -OH group in their structure can be improved for their washing and light fastness through modification of the dye with Cyanuric Chloride. For controlling of tone of yellow, prior introduction of -COOH group may be helpful. Further investigation in this regard is necessary so that fast natural yellow with brighter hue and purity of tone can be achieved.

Patel (2009) successfully dyed cotton in presence and in absence of mordants in different hues and tones at various concentration levels of babool. SnCl₂, FeSO₄, CuSO₄ and mix of FeSO₄, + CuSO₄ were selected for pre mordanting. The sample were treated in mordant solution at boil for 1 hour and then entered in the dyebath; in meta mordanting process mordanting and dyeing was carried out simultaneously. The increase in the colour strength value of cotton dyed with babool was possible with selection of metallic mordants and varieties of shades were produced on cotton. Shade ranging from cream to medium brown to dark brown can be readily produced on cotton without mordants. Mixed mordant system (i.e. FeSO₄, + CuSO₄) was found to be the best in pre mordanting method as far as the colour strength was concerned while copper sulphate was found to be the best in case of metamordanting technique. Thus selection of mordanting technique was found to be equally important. Pre mordanting technique was found superior than metamordanting technique. The all round fastness properties of various samples dyed using exhaust dyeing method were adequate and quite comparable with control dyed samples.

Process development for the extraction of natural dyes from the waste leaves of jack fruit plant (*Artocarphs heterophyllus*) and their application on cotton yarn have been carried out successfully by Purohit, et al (2009). Cotton yarn was treated in the prepared mordant solution (alum + turmeric powder) for 30-45 minute at 50-60°C. Then mordanted yarn was air dried for 15 min. The mordanted cotton yarn was then treated in the dye bath for 45-60 minute at 90-95°C. The dyed yarn was left for 30 minutes for air oxidation. The various fastness studies such as washing, rubbing, perspiration and light fastness were undertaken. It was observed that the traditional way of dyeing is a time consuming and laborious method, whereas the isolated
dye obtained from the waste leaves of *Artocarphs heterophyllus* and its applications on textiles is economical, time saving and easy to handle. It is possible to obtain various intensities of colours shades such as golden yellow, maroon for cotton yarns, which are not possible in case of the traditional method. Different shades in cotton yarn were obtained using the isolated colouring materials. Further the present investigation deals with the waste utilization of the natural resources.

Mahangade et al. (2009) extracted natural dye from the leaves of plant namely (*Maba angustifolia*) known as Kalindrin in Malvanj. It was utilized for coloration of cotton fabric. Two mordanting techniques were explored to study their effect on the colour strength and fastness properties of the dyed samples.

(a) The conventional mordanting technique consisted of a sequential treatment with tannic acid followed by alum solution. In the above sequence normal tap water as well as water modified with specific salts was employed at both acidic pH(3.7) and alkaline conditions pH(11.6). Fabric was treated with hot tannic acid (20% owf) for 1 h. followed by treatment in alum solution (60% owf) for 30 min. at room temperature. The treated fabric was washed with respective water employed for preparing the solutions and dried at room temperature.

(b) In the modified technique the sequence adopted was alum, tannic acid and the used alum solution. In the modified technique also normal tap water as well as water modified with specific salts was employed at both acidic pH (3.7) and alkaline pH (11.6) conditions. Fabric was treated with alum (60% owf) solution for 30 minutes at room temperature, hot tannic acid (20% owf) treatment for 1 hour, followed by treatment with used alum from the earlier step for 30 min. Fabric sample was washed with respective water employed for preparing the solutions and dried at room temperature.

Dyeing was carried out under acidic and alkaline conditions at different temperatures. Colour strength and fastness properties were found to be superior in the modified mordanting technique as compared to the conventional mordanting technique.

Goel et. al. (2010)extracted dye from onion peels in acidic medium for dyeing cotton. Metallic mordants(alum, ferrous sulphate and stannous
chloride) were used to enhance the colourfastness of the dyed cotton yarns. Brown, rust green, dark green and golden yellow shades were obtained. Colourfastness was evaluated against washing, rubbing, perspiration and light according to ISO standards. It was concluded that for all the dyed yarns, mordants improved the colourfastness properties.

Kulkarni et. al. (2011) studied dyeing of cotton with natural dye extracted from Pomegranate (*Punica granatum*) peel. Accurately weighed cotton cloth was treated with different metal salts cupric sulphate (2%) and ferrous sulphate(2%). Three processes of mordanting were used: pre mordanting, simultaneous mordanting and post mordanting. Dye concentration was 4% and M:L ratio 1:40 at 80°C for 60 minutes. After dyeing, the dyed material was washed with cold water and dried at room temperature. The fabric dyed with pomegranate peel gave different shades of yellow, brown and black. The obtained results have shown the dyeing potential of pomegranate peel as source for cotton dyeing. Good fastness was exhibited by the dyed cloth mainly because of the mordants used. It was concluded that there is a lot of scope to use pomegranate peel as dye for obtaining various color shades using safe mordants under eco-friendly textile dyeing. The process of production of pomegranate peel dye was found to be cost-effective as compared to the cost of dyes in local market.

Srivastava et. al. (2012) found that the required scientific studies and systematic reports on dyeing of textiles with natural dyes are still insufficient. There are numerous natural products still unexplored and untouched. As a result, more such studies need to be conducted. In this study, litchi peels were utilized for imparting color on selected cellulosic fabrics. Dyeing was done on the chosen fabrics with multiple trials, and by treating it like other vegetable dyes to achieve satisfying results. A series of experiments were conducted to determine the dyeing variables, such as extraction medium, optimum concentration of dye material, extraction time, and concentration of mordants and methods of mordanting. After the tests following recipe was finalized:

- **Dye materials:** 5 gm
- **Water:** 100 ml
- **Temperature:** 60°C (as per the experiment conducted)
- **Time:** 60 min. (as per the experiment conducted)
- **Mordants:** FeSO₄, alum and tannic acid, post mordanting 45 min. at 90°C
During the study, a wide range of colors were obtained on jute selected for the study. Mordants were capable of improving the shades and the fastness in many cases. Litchi dye gave best fastness towards perspiration, crocking and then towards washing, while just satisfactory results for light fastness were achieved. However, it has been revealed in many studies that light fastness of many natural dyes are found to be poor to medium. From the obtained results, it was concluded that cellulose can be successfully dyed with the discarded peel of litchi fruit, giving acceptable fastness results, with or without mordants. Further researches can be done to explore the possibility of dyeing with litchi dye on other textile materials. Because only the discarded fruit peel was used for the purpose, its use will have no adverse effect on the bio-diversity. Researcher and scientists thus have a good opportunity to make pollution free environment by using these source on textile materials, as the processing of these dyes involved no toxic chemicals.

Jain (2013) extracted colourant from jamun leaves, bark, bark peel and fruit and dyeing was carried out on cotton premordanted with natural mordants: amar chal, arjun chal and babul barkat following conditions:

Dye extraction time : 45min.
Dye material concentration: 20ml/150mlof water
Mordanting time: 60 min.
Mordanting temperature: 60 °C
Dyeing time: 60 min.
Dyeing temperature: 60-75°C

Best shades on cotton fabric were obtained by using jamun leaves mordanted with babul bark, jamun fruit mordanted with arjun bark and jamun bark mordanted with amar stem gave good colour yield. Babul bark exhibited good light and wash fastness. And amar stem exhibited fair to good light fastness.

2.3.2 Natural dyes for protein fibre

Wool and silk are two important protein natural fibers obtained from animal and insect. Extensive literatures have been reviewed on dyeing of wool and silk with natural dyes. These studies mainly deal with dye extraction process, extraction time, concentration of dye, dyeing time, method of
mordanting, shades obtaining and colour fastness properties. Some important studies of natural dyes on wool and silk are summarised below.

The advent of natural dyes has necessitated search of new dye sources and natural mordants. Keeping this in consideration researchers (Gill and Singh, 2002) conducted a study to optimize the process of dyeing wool with gum from simal, *Bombax ceiba* Linn. syn. *Bombax malabaricum* DC. and application of natural mordants. During experiment natural dye was obtained by boiling 1g powder of the Semal bark in 50 ml water at seven different pH values, i.e. 4,5,6,7,8,9 and 10 for 45 minutes. natural mordants used for study were bark of arjun, Babool, Eucalyptus, Indian Blackberry, Mango tree, fruits of *Chebulic myrobalan* and Indian gooseberry and pomegranate fruit rind. These were used in dried and powder form. The results showed that Semal dye could be used on wool in combination with different natural mordants to produce different shades of pink (grayish pale red to light maderia). All natural mordants helped in increasing the colour strength of the dye on wool

Mathur and Gupta (2003) obtained natural mordant from concentrating the aqueous solution extract of banana flower petals under reduced pressure and evaporating it to dryness. Bharat merino sheep wool yarn dyed with turmeric (*Curcuma longa*) was subjected to mordanting separating with natural mordant and chromium under identical condition. Out of the different concentration of the mordants used 3.5% natural mordant and 1.55 % chromium on the weight of yarn show similar color fastness, reflectance, color shade and K/S values. The chromium mordant in high concentration damaged wool while natural mordant does not cause damage to wool. Since the nature of turmeric colourant and banana petals is ecofriendly, their use in dyeing and mordanting will not cause any harm to the environment.

Extraction of natural colourant from neem (*Azadirachta indica*) for dyeing of wool yarn was studied by Mehtab et al. (2003). Neem bark colourant showed two absorption maxima at 275 and 374 nm. Dyeing of wool yarn under the optimum conditions (pH, 4.5; colourant conc., 0.05g per gram of wool; treatment time, 60 min; and treatment temp., 97.5°C) showed very good light and wash fastness properties without deteriorating the quality of wool.
Paul et al. (2003) have described walnut bark as a good source of brown colour and relatively eco friendly. Application process is easy and so was found to be useful for rural population. Dyeing variables in using walnut dye to dye wool were tested, and the colourfastness of selected dye on woollen yarns was also investigated. Experiments were conducted to determine the optimization of dyeing variables - medium of dye extraction, and optimization of dye extraction time, dye concentration and dyeing time. Preparation of final samples and colourfastness testing were covered. Walnut bark was found to be a good source of brown colour, with a variety of fast shades using different mordants.

Agarwal and Gupta (2003) discussed the conditions for dyeing of wool with a vegetable dye from the roots of the herb Madder (*Rubia cordifolia*). The optimized conditions included the concentration of dye, extraction time, dyeing time, concentration of the mordants, and method of mordanting for wool fibers. The dyed samples were subjected to tests for fastness to light and washing. From optical density data, the optimum concentration of the dye was found to be 5 grams per 100 ml of water, while the optimum extraction and dyeing time were found to be 120 minutes and 90 minutes, respectively. Simultaneous method of mordanting was observed to give the best results in terms of luster, depth of shade, evenness of the dye, and the overall appearance.

Detailed work on wool dyeing using reinwardtia flowers and poplar leaves in the ratio of 50:50 each as natural dye was done by Garima et al. (2004). Different variables viz. wave length, dye material combination, dye extraction time, dye material concentration, dyeing time, pH and mordants were standardized. 7% dye material, extracted and dyed for 45 minutes each using 1% and 4% of copper sulphate, chrome and ferrous sulphate as mordants gave excellent colours ranging from yellow ochre to military green. The fastness grades in terms of washing as colour change were 3-4/5 and colour staining from 3-5, light fastness from 3/4 to 4/5, rubbing fastness 4-5 and perspiration from 3/4 to 4/5. Hence the source explored was found suitable for dyeing of wool.

Wool fabric was dyed with an aqueous extract from the bark of *Acacia pennata* containing tannin as the major colourant by Shukla et al. (2000).
Dyeing with the combination of extracts of *Acacia pennata* and banana stem has also been carried out and improvement in depth of colour without altering the tone was observed. The colour of the fabrics has been evaluated on computer colour matching system in terms of K/S and L* a* b* colour coordinates. The dyeing shows moderate to good fastness to washing, light and rubbing.

Bechtold et al. (2006) described that food and beverage industry releases considerable amounts of wastes which contain natural dyes. Such wastes could serve as a source for the extraction of natural dyes for textile dyeing operations. The extraction of brilliant yellow and red colours from fruits and vegetables is of particular interest. Wastes, e.g. pressed berries, pressed grapes, distillation residues from strong liquor production, and wastes and peels from vegetable processing, have been extracted with boiling water and test dyeing on wool yarn were performed. Colour strength, shade and fastness properties of the dyeing have been tested. The extracts were applied as direct dyes and in the presence of Fe$^{2+}$ and alum mordants. The results prove the potential of such wastes as a source for natural dyestuff extraction.

Das et al. (2006) studied the application of dye obtained from *Punica granatum* fruit rind on wool and silk fabric in the presence and absence of environment-friendly mordanting agents. The dyeing of wool and silk with pomegranate solution was found to be effectively accomplished at pH 4.0. Pre- and post-mordanting employing ferrous sulphate and aluminium sulphate improve the colour uptake, light fastness and colour retention repeated washing. The use of such mordants, however, does not improve wash fastness property of dyed substrates.

Bechtold et al. (2007) used the aqueous extract of ash-tree bark (*Fraxinus excelsior L.*) as a model to study the shade reproducibility of dyeing on wool. A meta-mordanting process using FeSO$_4$·7H$_2$O mordant was chosen as a system with particular potential for industrial application. The exhaust dyeing process with immediate use of the extracts as a dyebath and direct addition of FeSO$_4$·7H$_2$O stock solution as a meta-mordant process showed good shade reproducibility and satisfying levelness of the dyed material. An increase of Fe$^{2+}$ mordant above a dyebath concentration of 2-3 gm did not result in further colour depth. Extraction of 1-2 gm of bark was found sufficient to
dye 1 gm wool yarn to the darkest colour possible; use of higher amounts of bark did not yield substantially higher colour depth. The quality of bark and the extraction step were found to be of significant importance for the colour depth; thus, in an optimized process, conditions of extract formation have to be well controlled.

Koyuncu (2007) studied the dyeing of wool yarn using Rheum ribes roots as natural dye in conventional method. The effects of dyeing show higher colour strength values obtained by the latter. Dyeing with Rheum ribes roots has been shown to give good dyeing results. The results of washing fastness properties of the dyed wool yarn were fair to good. CIELAB values have also been evaluated.

Lu et al. (2007) performed experiment on dyeing wool fabric with sorghum red as natural dye by mordant dyeing method. The process conditions of premordant and post-mordant dyeing were determined in quadrature experiments. The experimental results were as follows: the consistency of the dye was the key factor on dyeing depth in pre-mordant process, the dyeing depth enhanced with consistency of the dye solution increase; the pH value was the second factor that affected the depth, the depth improved with the increase of pH value. The consistency of Fe$^{2+}$ played an important role in post-mordant dyeing process. The depth enhanced with the increase of consistency of Fe$^{2+}$. The depth improved with the temperature rising. The rubbing and washing color fastness of dyed wool fabric were all 4 or up to 4. It indicated that sorghum red dye was suitable to dye wool fabric.

Javalakshmi. and Amsamani (2008) applied annatto and catechu for dyeing wool using bio-mordants. The method of dyeing woollen yarn with annatto and catechu was standardized by determining the optimum dyeing conditions, namely dye material concentration, dye material extraction time, dyeing time, mordant concentration and mordanting method. Two bio mordants namely myrobalan and karavelum bark were used in 1% concentration and two natural fixing agents such as liquor of tamarindus indica linn. and boiled off liquor of green tea were used. Dye extracted from annatto and catechu were soaked 24 hours in aqueous medium. Mordanting and dyeing was carried out at room temperature for 30 minutes. Fixing treatment was given at room temperature for 10 minutes. The washing,
rubbing, light and perspiration fastness of the dyed samples was evaluated, giving fair to excellent fastness grades. Hence, an attempt by using natural Bio-Mordant and natural fixing agent has achieved both good wash fastness and good fastness to light.

An attempt was made by Gahlot et. al. (2008) to optimize various dyeing variables such as extraction medium, extraction time, dyeing time, mordants concentration and methods of mordanting for dyeing of wool and silk with jatropha flower dye. Four metallic mordant alum, chrome, copper sulphate and ferrous sulphate were used in various concentrations. Dyeing was carried out at optimized dyeing time (60 minute) and 4-6 pH. Various tones of different colours like peach, light peach, light brown and grey shade were obtained. The dyed materials had good colour fastness properties also. The processing of dye materials was easy as well as safe from the point of environment.

Comprehensive dyeing of wool using natural sources in alkaline condition was done by Raja, (2008). Fine wool from Bharat Merino sheep was dyed with seven different natural resources such as tanners senna bark, silver oak leaves, wattle myrobolan bark, myrobolan, carrot leave, indigo, and catechu at different pH conditions with different mordants(alum, aluminium sulphate, stannous chloride, ferrous sulphate, potassium dichromate) using post-mordanting technique. The shades obtained were grey, brown, yellow and light green with moderate high washing fastness. Selected dyed samples were tested for bundle strength to know the effect of alkaline pH on dyeing and concluded bundle strength was reduced. It was also concluded that wide range of shades except pure red and green can be developed using the above listed natural sources and mordants using the same recipe. If the pH conditions are changed probably more shades can be developed for wool in all cases fastness was satisfactory.

Optimization of dyeing procedure on wool yarn with *Pistacia integerrima* leaves dye using synthetic(alum, copper sulphate, stannous chloride) and natural mordant (*Alnus nepalensis*) was studied by Badoni (2009). Premordanted marino wool sample was treated in dyebath at room temperature for 45 minute. New colour shades like grey, yellow, dark golden, steel blue was obtained. He concluded that *P. integemma* (leaves) have
excellent dye property and can be utilized for commercial purposes. However, a number of color shades were obtained with different mordants that were found stable against light and washing factors. Moreover, the sample dyed with natural mordant was safer and eco-friendly and can be a source of mordant in textile industry.

In the study by Karolia (2010) dyeing of wool was done with natural dye extracted from bark, leaf, and fruit of walnut tree. From the study an interesting aspect was obtaining, an array of colors which could be easily done by varying different mordants (alum, copper sulphate, ferrous sulphate, tannic acid, tea, coffee, Pomegranate) and with change of pH. It was concluded that the colors produced by natural dyes—Walnut are interesting and attractive due to tonal effects created by them. Bark dyed samples had a mixture of yellow and green. Strong presence in the red and yellow quadrant was observed in acidic and self pH. In leaf dyed samples the shades obtained in self, alkaline pH were mostly green and yellow. In fruit dye, red–yellow was the dominant color quadrant. All the three pH gave mild shades and a strong presence of brown, showing the more of red being present. All colors showed fair to excellent wash, rub, and light fastness properties.

Khan et al., (2010) extracted natural dye from Acacia catechu. This dye was used for dyeing mordanted wool with eco-friendly mixture of mordants (Iron and Tin). By using different permutations and combinations of mordants with cutch, forty-eight shades were developed. Fastness properties (light, wash and rub/crocking) were studied on these samples. It was concluded that by changing the concentration of the dye and mordants, shade variation in wool sample was observed. Most of the dyed wool samples had fairly good to good fastness rating. It was concluded from the study that cutch can be used as an ecofriendly natural colourant for dyeing woolen yarn.

Khan et al., (2012) concluded that the colourant extracted from henna leaves was found to possess acceptable dyeing performance and produced orange yellow to reddish brown shades on woolen yarn. Dyeing was carried out by using 1%, 5%, 10%, and 20% of dye concentrations. Material to liquor (M:L) ratio was kept 1:40 maintaining neutral pH (7) at 30°C. Thirty-six shades with appreciable change in hue and tone were obtained by varying mordant combinations as well as dye concentrations. Dyeing of wool with
extract of henna leaves in the absence of mordent, displayed good light fastness, good to very good wash fastness but moderate fastness to rubbing. Mordanting with mixed mordant (5% alum + 2.5% iron and 2.5% iron+0.5% tin) does not have any significant effect on fastness property, depth of shades for both unmordanted as well as mordanted woollen yarn follow a commonly increasing trend with increasing concentration of dye. Dyeing on mordanted woollen yarns showed high colour strength which displayed good all-round fastness properties. It was also concluded from the study that extract of henna leaves applied on woollen yarns mordanted with mixed metal mordants can successfully be used to obtain a range of soft and soothing shades on woollen yarns.

Kaur et al. (2012) investigated the use of green tea as a natural colourant for dyeing of wool with good fastness results. The dyeing process was carried out with dye extracted from three different qualities of tea leaves using three solvent (Methanol, Acetone, Acetonitrile ). Washing fastness, light fastness, K/S and reflectance was measured. Colour yield and washing fastness properties are moderate to good, where as light fastness rating varies from 3-6.

In the study by Srivastava et al. (2012) litchi peels were utilized for imparting color on wool fabrics. Dyeing was done on the chosen fabrics with multiple trials, a series of experiments were conducted to determine the dyeing variables, such as extraction medium, optimum concentration of dye material, extraction time, and concentration of mordants and methods of mordanting. After the tests following recipe was finalized:

Dye materials : 5 gm
Water: 100 ml
Temperature : 60°C (as per the experiment conducted)
Time: 60 min. (as per the experiment conducted)
Mordants : ferrous sulphate, alum and tannic acid
Mordanting: Post mordanting for 45 min at 90 °C

During the study, a wide range of colors were obtained on wool fabric. Mordants were capable of improving the shades and the fastness in many of the cases. Litchi dye gave best fastness towards perspiration, crocking and then towards washing, while just satisfactory results for light fastness were achieved. However, it has been revealed in many studies that
light fastness of many natural dyes are found to be poor to medium. From the obtained results, it was concluded that wool fabric can be successfully dyed with the discarded peel of litchi fruit, giving acceptable fastness results, with or without mordants.

Dyeing of woolen yarn with lac dye has been studied using ferrous sulphate, stannous chloride and their combination by Mohammad et al., (2012). Eco-friendly mordants (5% Fe, 1% Sn) and their combination (2.5% Fe + 0.5% Sn) on the depth of shades, colour values and fastness properties of woolen yarns dyed with lac dye were measured. The temperature of mordant bath and dye bath was 91-93ºC with M:L ratio was 1:40. It was concluded that application of lac dye on wool substrate produces a range of fifty four shades varying from light orange-bright red-dark scarlet depending on the amount of lac dye, eco-friendly mordant and their combination used. Very good light fastness, good wash fastness and moderately good to good rubbing fastness properties were obtained.

Devi et al. (2002) identified Eclipta prostrata, a common weed found in most of the fields in Andhra Pradesh as a good source of natural dye for silk for production of green shades. Alkaline medium was suitable for extraction of dye from the plant and pleasant yellowish-green shades were obtained on silk. The extraction and dyeing procedures were standardized based on the optical density before and after dyeing silk and visual appearance judged by a panel of 30 scientists. All four mordants namely alum, chrome, copper sulphate and ferrous sulphate were found to be suitable for application on silk. 15% and 20% of alum, 3% of chrome, 2% of copper sulphate and 1 and 2% of ferrous sulphate were found to produce fast yellowish green shades on silk. Mostly dark shades were obtained by post mordanting method, followed by simultaneous and premordanting methods. Exposure to alkali had either deepened the hue or added green tinge to the silk samples when subjected to washing and alkali perspiration. Loss of colour was found with acidic perspiration. Excellent to outstanding fastness to sunlight was found in all mordanted samples. There was no absolute staining for washing. Colour change was not found in samples subjected to crocking in dry and wet conditions. Only slight staining was found. This dye can easily be recommended for use on silk fabrics for producing light green shades.
Phukan and Phukan (2004) standardized the condition of dyeing mulberry silk yarn with the bark of Arjun tree, *Terminalia Arjuna*. Mordants such as alum, chrome, copper sulfate, and ferrous sulfate were used for the study for the fixation of the dye molecule with the fiber. To remove the sericin, degumming was done before dyeing, with washing soda, alkaline and acidic methods were employed for dye extraction. Alum mordant and pre-mordanting method showed the best results in both alkaline and acidic medium of dye extraction. Yarns dyed with Arjun dyes showed color fastness to washing, rubbing, light, and perspiration.

The natural dyes which were selected for the study by Grover et al. (2005) included Jatropha, Lantana, Hamelia, Euphorbia, Kilmora, and Walnut. Silk was initially degummed prior to dyeing, to make the fabric free from sericin, which obstructs the penetration of dyestuffs into the fiber. A series of experiments were conducted to determine the dye-extraction medium, optimum concentration of dye, extraction time, dyeing time, mordant concentration, and methods of mordanting. The acidic media exhibited maximum percent absorption for Jatropha, Lantana, Hamelia, and Euphorbia dye, while Kilmora and Walnut dye showed good results in alkaline medium. The results obtained from different experiments lead to the optimization of a standard recipe for dyeing of silk with each dye source.

Silk yarn was dyed with Peach leaves by Mahajan et al. (2005) using six combinations of mordants namely Alum/Chrome, Alum/Copper Sulphate; Alum/Ferrous Sulphate; Chrome/Copper Sulphate; Chrome/Ferrous Sulphate and Copper Sulphate/Ferrous Sulphate in the ratio of 1:3, 1:1 and 3:1. Dyeing was carried out according to the optimized dyeing conditions, which were standardized beforehand. These optimized conditions were dye extraction time, dye concentration, dyeing medium, dyeing time etc. The dyeing was done using these optimized conditions and the abovementioned six combinations in three ratios with three mordanting methods namely pre, simultaneous and post mordanting. This resulted in a total of 54 shades. The dyed samples were then evaluated for colour fastness to washing, light, rubbing and perspiration fastness according to ISO standards. On evaluation it was concluded that silk dyed with Peach leaves showed excellent washing
fastness except for few samples, very good light fastness and fair to good rubbing and perspiration fastness.

Ukalkar and Karanjkar (2005) optimized dyeing variables of silk by using flame of forest flowers (*Butea monosperma*). The petals were selected as a dye source and were removed when the flowers were fresh and dried under shade. Optimization of dyeing silk comprised of optimization of dye material concentration, dyeing time and concentration of mordant. Based on percent dye absorption and visual appearance, aqueous medium was found to be most suitable for extraction of dye. The percent absorption increased with the increase in the concentration of flower petals from 1-5g and maximum percent absorption by 1 g of silk was obtained with 5g dye/100ml water. On the basis of percent dye absorption, optimized dye extraction time was 30 minutes, as optical density value was around 0.3. Higher dye absorption time was found after dying silk for 30 minutes. The 0.3 percent concentration of copper sulfate and ferrous sulfate, and 0.15 percent of alum gave higher percent dye absorption values in the three methods of mordanting.

Rawat et al. (2005) studied the application of poinsettia leaf dye, an environmental friendly natural dye, on silk fabric. The fastness properties were found satisfactory. Silk fabric, which was degummed using a solution of genteel and water, was dyed with poinsettia leaves and the dyed fabric was subjected to color fastness testing. During the colorfastness test, the samples were washed in a Laundrometer for 45 minutes at a constant temperature of 50° C. The colorfastness of the dyed samples to acidic solution was found much better than the alkaline solution. The dye may be useful in imparting number of fast shades on silk using common mordants such as FeSO₄ and CuSO₄ with good fastness properties except alkaline perspiration.

Sudhakar et al. (2006) extracted natural dye from the nuts of *Areca catechu* grown abundantly in India and utilized for coloration of silk fabric. Different mordants at varying concentrations were used on silk for pre-mordanting to study their effect on the colour value and fastness properties of the dyed samples. Silk fabrics were also dyed with different mordanting techniques using lowest concentration of mordants. Colour values with respect to K/S, L*, a* b* and fastness properties were found to be influenced by the
type of mordant and technique of mordanting with very low concentrations of the mordant.

An attempt was made to extract natural dye from coffee-seeds for its application in dyeing silk by Teli and Paul (2006). Dye extract was filtered after boiling the coffee-seed coat in 5 liter water for 4 hours and kept overnight. Dyeing was carried out by pre-mordanting, meta-mordanting and post-mordanting, using several mordants including myrobolan and ferrous sulphate. The fastness properties of dyeing are continuously achieving the range of satisfactory level and give different tones and higher depth of dyeing. The result indicated that coffee-seed extract develops a range of shades with good fastness properties on silk.

Lee (2007) extracted natural colorant from Coffea arabica L., using water as extradant at 90°C for 90 min. Studies were made on the dyeing, color fastness, and deodorization properties of silk fabric dyed with Coffea arabica L. extract solutions. The best mordants were found to be FeSO₄, CuSO₄, and SnSO₄ for improving the color strength (K/S) of silk, fabric MnSO₄ showing rating of 3. It was found that FeSO₄ and CuSO₄ were the best mordants for the improvements of color strength (K/S) and light fastness for silk fabric. In addition, it was found that silk fabrics dyed with the Coffea arabica L. extract showed good deodorization performance.

Shanker and Vankar (2007) extracted natural dye of Hibiscus mutabilis (Gulzuba)/Cotton rose belonging to family Malvaceae which was used for dyeing textiles. Aqueous extract of Gulzuba flowers yielded shades with good fastness properties. In the present study dyeing with gulzuba has been shown to give good dyeing results. Pretreatment with 2-4 % metal mordants and keeping M:L ratio as 1:40 for the weight of the fabric to plant extract is optimum showing very good fastness properties for silk. The dye has good scope in the commercial dyeing of silk for garment industry.

Sharma et al. (2007) explored the herbaceous plant Eupatorium adenophorum as a very good green color source for dyeing of silk yarn with excellent fastness properties. Leaves of the Eupatorium plants were collected and shade dried, crushed and packed. Sericin was removed from silk fabric so as not to interfere with luster and dye absorption. The dye material was entered into the dye liquor and boiled. Four mordants were used with three
methods of mordanting. A mordant ranged from 1-5% was selected for the study. The concentration of dye material was optimized by taking seven concentration prepared by boiling. Yarn was dyed in the dye bath for varying time. The time at which the absorption high was selected as optimum dyeing time and then evaluated for color fastness. Results show that 10% alum with post mordanting method has yielded yellowish green shade while with 4% chrome in pre-mordanting sap green color has been obtained. Light army green and dark army green shades on silk were obtained with 4% CuSO$_4$ and 4% FeSO$_4$ using post-mordanting method. Excellent fastness to light and outstanding fastness to washing was shown by dyed silk yarn using 4% chrome. Little noticeable staining and color change was found for dry and wet crocking samples.

Vankar and Shanker (2008) studied ultrasonic dyeing of silk with *Nerium oleander* flower. Mordanting with metal salts such as FeSO$_4$, SnCl$_2$, CuSO$_4$, SnCl$_4$, K$_2$Cr$_2$O$_7$ and alum was carried out at 60°C for 30 minute. Silk was dyed with dye extract, keeping M:L ratio as 1:40 and pH was maintained at 4 by adding buffer solution. It was concluded that aqueous extract of nerium flowers yield cream to green to purple shades on silk fabrics with good fastness properties the colour strength (K/S value) were good particularly for silk mordanted by ferrous sulphate. The dye showed good scope in commercial dyeing of silk fabric for garment industry.

Sidhu and Jastesh, (2008) studied silk dyeing with Goldendrop (*Onosma echioides*) dye. Dyeing of silk was done using four mordants namely alum, chrome, copper sulphate and ferrous sulphate in three concentration each. For 100 gram degummed silk 5, 10, 15 grams alum and 1, 2, 3 gm chrome, copper sulphate and ferrous sulphate were used. Optimum dye: material concentration was 1gm/1gm silk. Dyeing was carried out at room temperature for 45 minute. It was found that goldendrop dye can be successfully used for dyeing of silk to obtain a wide range of soft, pastel and bright colours such as olive green, light and dark grey, brownish, bronze and blackish brown. With regards to colour fastness test, samples exhibited excellent fastness to washing; poor to fairly good fastness to light; fair to excellent fastness to rubbing and good to excellent fastness to perspiration in both acidic and alkaline medium.
Prusti, et al (2009), have studied *Terminalia catappa* as a suitable natural dye for silk yarn. Process development for the extraction of natural dye in pure form, from the waste leaves of Indian almond (*Terminalia catappa*) and its application on different yarns have been carried out successfully. Silk yarn was treated with mordant such as alum, turmeric powder, alum + turmeric powder, ferrous sulphate, stannous chloride, copper sulphate, potassium dichromate; then mordanted silk yarn was dyed at 80ºC-90ºC. Golden yellow, slate gray, pale yellow, brown colour shades were obtained. It is possible to obtain various intensities of colour shades for silk yarn by using a known quantity of isolated dye materials, which is not possible in case of the traditional method. Different colour shades have been achieved for silk materials using different mordants.

Washing fastness of natural colourant is comparatively low so attempt was made to improve the fastness properties of natural dyes with the help of mordant on silk fabric by Sundrarajan et al. (2009). Three natural colourant (Hibiscus flower, Onion skin, and Eucalyptus bark) were selected for dyeing silk fabric and fastness was improved with the use of synthetic mordants: Alum, copper sulphate and potassium dichromate and natural mordant: Pomegranate rind and tannin. Dyeing was done at optimized condition (6% dye solution at 80ºC for 45 minute). Combinations of two and three mordants were also used. Yellow brown and green shades were obtained on silk fabric. It was concluded that premordanted fabrics produced good dye uptake and wash fastness than the unmordanted fabric. Two and three combinations mordanted fabrics produced better dye uptake and also better washing fastness than single mordanted and unmordanted fabrics. Three colorants produced better improvement in washing fastness property with tannin and pomegranate mordants. Combinations of two and three mordants gave almost same results.

Abu Sayeed et al. (2009) isolated natural dye (2-hydroxy 1,4 napthoquinone) from the leaves of *Lawsonia Inermis Linn*. The dye was characterized by chemical analysis and spectroscopic analysis like FTIR, $^1$H NMR and $^{13}$C NMR. The isolated dye was applied on degummed silk fiber with alum mordant at 80ºC and pH-3 for 60 minute in M:L ratio 1:40. The colour of dyed silk was deep orange yellow. It was concluded that leaves of
heena contain extractible dye constituents which is more than 0.923% on the wet basis. Dyeability of degummed silk fiber with dye was very good in aqueous medium. The colour of dyed silk fabric was pleasant and fast to sunlight, detergent wash, organic acid and alkalis.

Process development for the extraction of natural dyes from the waste leaves of jack fruit plant (Artocarphs heterophyllus) and their application on silk yarns have been carried out successfully by Purohit, et al (2009). Silk yarns was premordanted with alum, alum + turmeric powder, alum + NaNO₂, alum + FeSO₄, alum + (NH₄)₂SO₄, alum + K₂Cr₂O₇ for 30-45 minute at 50-60°C, then air dried for 15 minutes. The mordanted silk yarn was then dyed for 45-60 minute at 50-60°C with extract from leaves of jack fruit plant. The dyed yarn was left for 30 minutes for air oxidation. The various fastness studies such as washing, rubbing, perspiration and light fastness was carried out. It was observed from the above experiments that the traditional way of dyeing is a time consuming and laborious method, whereas the isolated dye obtained from the waste leaves of jack fruit plant and its applications on textiles is economical, time saving and easy to handle. It is possible to obtain various intensities of colours shades such as golden yellow, orange yellow, maroon, slate grey, chocolate, brown for silk yarns, which are not possible in case of the traditional method. Further the present investigation deals with the waste utilization of natural resources.

Goel et. al. (2010) extracted dye from onion peals in acidic medium for dyeing mulberry and tussah silk. Metallic mordants (alum, ferrous sulphate and stannous chloride) were used to enhance colourfastness of dyed silk yarns. Brown, rust green, dark green and golden yellow shades were obtained. Colourfastness was evaluated against washing, rubbing, perspiration and light according to ISO standards. It was concluded that for all the dyed yarns, mordants improved the colourfastness properties.

Waste leaves of Tectonagrandis as a suitable natural dye for textile has been studied by Prusti et. al. (2010). Process development for the extraction of natural dye from the waste leaves of teak plant (Tectona grandis) and their application on silk yarns has been carried out successfully using following condition. Silk yarn (0.5 g) was treated in 20 ml of prepared mordant solution
at 1:30 MLR (material to liquor ratio) at 60-70 °C for 30-45 min. Then the mordanted yarn was air dried for 15 minutes.

Light salmon and maroon colour shade for silk yarns has been achieved using the isolated colouring materials. The dying experiments were carried out adopting premordanting technique using different parameters with silk yarns. It was observed that the isolated colouring material produces excellent shade on silk yarn. The solvent used for the extraction process can be recovered and reused for subsequent extraction. They concluded that the dyeing procedure is time saving and economical as compared to the traditional way of dyeing. In this method, it is possible to obtain various intensities of colour shades for silk yarns by using known quantity of dye materials, which is not possible in case of the traditional method. It is also observed that different shade: light salmon and maroon are achieved without any mordant. while, brick red, brown, golden red, slate grey and olive were obtained by different mordents.

Kumaresan et al. (2011) studied application of eco-friendly natural dye on silk using combination of mordant such as myrobolan+nickel sulphate, myrobolan+aluminium sulphate, myrobolan+potassium dichromate, myrobolan+ferrous sulphate, myrobolan+stannous chloride. They found that flower of Cordia Sebestena can be successfully used for dyeing of silk to obtain a wide range of soft and light brown shade by using combination of mordants; with regards to colour fastness, test samples exhibited excellent fastness to washing (except for pre-mordanting using myrobolan + Potassium dichromate combination); excellent fastness to rubbing (except for pre-mordanting using Myrobolan + Potassium dichromate combination); good to excellent fastness to perspiration in both acidic and alkaline media and fairly good fastness to light.

In the study by Rastogi & Rastogi (2012) one co-friendly dyeing with ayurvedic herbs on silk fabric revealed that sandalwood and manjistha gave good colour on silk fabrics, while sandalwood and neem gave good colorfastness on silk fabrics. On the other hand alum produced very even and deep shades on fabric in comparison with MgCl₂. Ironing and washing fastness of all the dyes on silk fabrics with all mordants gave excellent results. Light fastness of sandalwood and neem gave better fastness as compared to
Sandalwood and manjistha. Rubbing fastness of all herbs was found very good to excellent. Thus it was concluded that alum could be used as a better substitute for MgCl₂ to improve colorfastness of Ayurvedic herbs.

2.3.3 Natural dyes for polyamide fibre

Nylon is synthetic fiber containing amide link known as polyamide fiber. Literature has been reviewed has shown limited studies on dyeing of nylon with natural dyes. Studies mainly deal with extraction process, dyeing process, method of mordanting, shades obtained and colour fastness properties. Some important studies of natural dyes on nylon are presented below:

Gulrajni (2001) demonstrated possibilities of nylon dyeing by using vegetable dyes like Annatto, Ratanjot and Berberine. Furthermore evaluation of sample fastness and colour value was undertaken. Anlab Colour Space plots for each dye was prepared by plotting their a*b* values. K/S values were discussed and the percentage exhaustion dye absorbance reported. Wash fastness was good for Rajantot, very good for Annatto and poor for Berberine. Light fastness values were included. Nylon could be dyed with these vegetable dyes at pH 4 (Rajanot), 6 (Annatto) and 9 (Berberine). Good to moderate light and wash fastness resulted.

Gupta (2004) purified two components of Indian madder, purpurin (1,2,4-trihydroxyanthraquinone) and munjistin (1,3-dihydroxy-2-carboxyanthraquinone) and dyed nylon fabric with these two component. The light and wash fastness of dyed and mordanted samples has been studied. Purpurin showed much better resistance to photo fading than munjistin. It was found that the type of mordant and the method of mordanting significantly affected the rate and extent of photo fading. The use of copper or ferrous sulphate gave high resistance to fading, whereas stannous chloride or alum did not. On the other hand, light fastness was improved when post mordanting was conducted with copper or ferrous iron, but pre-mordanting was superior in the case of stannous chloride and alum.

Mashaly (2006) studied dyeing of nylon fabrics using lac as a natural dye in both conventional and ultrasonic techniques. The extractability of lac dye from natural origin using power ultrasonic was also evaluated in
comparison with conventional heating. The results of dye extraction indicate that power ultrasonic is rather effective than conventional heating at low temperature and short time. The effect of dye bath pH, salt concentration, ultrasonic power, dyeing time and temperature were studied and the resulting shades obtained by dyeing with ultrasonic and conventional techniques were compared. Colour strength values obtained were found to be higher with ultrasonic than with conventional heating. The results of fastness properties of the dyed fabrics were good to very good. Dyeing kinetics of nylon fibre with lac dye using conventional and ultrasonic conditions was compared. The time/dye-uptake isotherms revealed enhanced dye-uptake in the second phase of dyeing (diffusion phase). The values of dyeing rate constant, half-time of dyeing and standard affinity and ultrasonic efficiency have been calculated and discussed.

Two different natural dyes extracted from vegetable sources, namely: *Calendula* and *Casuarina*. were selected by Mohamed (2009) and applied as a dye on polyamide fibre, i.e. nylon 6 successfully. He concluded that the behavior of natural dyes during dyeing of nylon fabric was similar to that of acid dyes. The rate of dyeing was found to increase as the temperature, increased till it reached its maximum at boiling for the two applied natural dyes. Temperature breaks down the aggregate of dyes and increases their solubility as well as opening up the fibre structure and thus accelerates the diffusion of dye molecules inside the fibre. The pH of dyeing was found to play a great role since maximum colour strength was achieved at strong acidic medium which may be attributed to the high electrostatic attraction between positively charged basic groups in the nylon fibre and the dye anions.

Teli et al. (2010) have studied dyeing of nylon with natural colourants, the research mainly focuses on application of natural dyes such as turmeric, madder, catechu, Indian rhubarb, heena, tea and pomegranate rind on nylon. Three different methods of application namely pre-mordanting, meta-mordanting and post-mordanting were used in which case contribution of copper sulphate, ferrous sulphate, Potassium dichromate and Tannic acids was studied in terms of enhancement in depth of dying. These dyes have affinity for nylon and bright deep shades of yellow, grey, and black were obtained. They concluded that most suited mordants in general are ferrous sulphate and
tannic acid. Moreover, toxicity of ferrous sulphate as compared to copper sulphate and potassium dichromate is very less and tannic acid is also biodegradable in nature. Therefore in other words the process of dying of synthetic fibers with selected natural dyes has potential of becoming environmentally safe process.

2.3.4 Natural dyes for printing

Tawfik (2002) explained the suitability of turmeric in the fine powder form as natural dye in printing cotton, polyester and their blended fabrics using pigment-printing technique. Variable studied included concentration of the colour, nature of thickening agent, type of fixation and pH of the printing paste. The printed goods were evaluated by measuring the K/S and the overall fastness properties. The data obtained indicated that regardless of the nature of the fabrics used, type of fixation or of the time elapsed before commencing printing, the K/S increased by increasing the concentration of turmeric and/or decreasing the pH to 6.3. Thermo fixation is more suitable than steaming. It can be concluded that turmeric can be used as natural dye for printing successfully.

Maulik and Mandal (2010) reported printing of handloom cotton fabric with vegetable colourants in presence of different inorganic salts, like aluminium sulphate, ferrous sulphate and copper sulphate and to assess different colourfastness properties of printed textile. *Camellia sinensis* (tea leaf), *Allium cepa* (onion skin), *Tagetes erecta* (marigold flower) and *Butea monosperma* (palas flower) were used as vegetable colourant. Aqueous solution was prepared by adding 50 g of dried vegetable matter boiled for 60 minutes, allowed to stand for 15 minutes and filtered through nylon bolting cloth. Evaporated water was replaced by fresh water. Dyeing was carried out by pad-dry technique at nearly 100% wet pick-up in a laboratory model two bowl padding mangle. The impregnated fabrics were then dried at room temperature before printing. Printing of cotton fabrics treated with natural colourant was carried out with the help of print paste containing inorganic salts (5 g/l) and gum indulka thickener. The impressions were made with the help of wooden blocks of various designs. After printing the fabrics were dried at room temperature, followed by steaming for 15 minutes at a temperature of 102°C in a cottage steamer. After steaming the printed fabrics were
immediately washed with 2 g/l non-ionic detergent at 60°C for 10 minutes in order to remove gum and the strong mineral acid (sulphuric acid) produced during the steaming process. After soaping the printed fabrics were washed with hot water, followed by cold wash and finally dried in air. It was concluded that in presence of different inorganic salts with the objectives of achieving an improvement in the fastness properties of the printed materials, making them higher performing and enhancing scope for their use in different value-added niche handloom products. Ferrous sulphate, aluminium sulphate and copper sulphate when used as inorganic salts produce most balance improvements in colourfastness of the printed cotton fabrics.

In the study by Jayalakshmi and Varshitha (2010) bleached woven organic cotton fabric was block printed with vegetable dyes and treated with mintage wash, crushing process and gulf voll wash to adhere strongly, improve the general appearance of the fabric and impart wrinkled effect to organic cotton fabric. Vegetable dyes were extracted by combination of carrot, beetroot and red cabbage each of 200 gms were taken, boiled, smashed and added in 1:40 ml of M: L ratio maintaining a temperature of 60°C for a duration of 1 hour. Later it was dried, filtered and the thick dye solution was extracted. Printing paste was prepared by mixing one kg of binder, two gms of prepared thick vegetable dye colour. On the previous day of printing, hundred gms of gum were diluted with 4-5 liters of water in a big trough so as to make the water into a thick viscous solution. Later, a minimum amount of three gms of binder was mixed with this diluted gum solution. The binder acts as the medium which is sometimes replaced by kerosene. The ratio of binder to kerosene is 1: 8 for good quality of print. Printing operation was carried out at room temperature following the block printing procedure. The treated organic cotton fabric was converted into garment and wear study revealed that it was comfortable during wear, without creating any irritation to the skin.

Maulik and Biswas(2011) research on dyeing and printing of jute yarn/fabric with *Camellia sinensis* (tea leaf), *Tagetes erecta* (Marigold), *Rubia tinctorum* (Manjistha), *Cedrela toona* (Mahogany), *Terminalia chebula* (Harda) and *Acacia catechu* (Khair) in absence and presence of different inorganic salts with the objectives of achieving an improvement in the fastness properties of the printed materials, making them higher performing
and enhancing scope for their use in different value-added jute diversified products. Extraction was done by adding 100 g of each vegetable matters to one liter of water. The mixture was stirred, heated and kept at boiling point for 45 min, allowed to stand for 15 min and finally filtered through nylon bolting cloth. Dyeing of jute with vegetable colour in absence of inorganic salt at a material to liquor ratio of 1:20. The dye bath temperature was kept at 80\(^{\circ}\)C for 45 min. The dyed materials were then washed with 2 g/l non-ionic detergent at 60\(^{\circ}\)C for 10 min, Dyeing was also carried out in presence of inorganic salt such as aluminium sulphate and ferrous sulphate by post-mordanting method at 80\(^{\circ}\)C for 45 min followed by cold wash and finally dried. Printing of jute fabrics dyed with vegetable colourants was carried out with the help of print paste containing inorganic salts (5 g/1000 g of print paste) and gum indulka thickener, whereas for printing on bleached jute fabric the print paste was prepared by mixing inorganic salts, vegetable colourants and gum indulka thickener. The impressions were made with the help of wooden blocks and the fabrics were dried at room temperature, followed by steaming for 10 min at a temperature of 100\(^{\circ}\)C in a cottage steamer. The fabrics were then immediately washed with 2 g/l non-ionic detergent at 50\(^{\circ}\)C for 10 min in order to remove the gum and the strong mineral acid (Sulphuric acid) produced during the steaming process. After soaping the printed fabrics were further washed with cold water and finally dried in air. Colourfastness of the printed jute fabrics was improved by inorganic salts such as ferrous sulphate and aluminium sulphate.

2.4 Details of dyes used in the study

Waste material of four plants namely Tropical almond (waste leaves), Shimalo (Bark), Asopalav (waste leaves), Neem (waste leaves) were selected for the present research study. General information, brief introduction, physical appearance, chemical composition of plant waste is given below.
2.4.1 Tropical Almond or Indian Almond (*Terminalia Catappa*)

**General information:**

<table>
<thead>
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<th>Family:</th>
<th>Combretaceae</th>
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<tbody>
<tr>
<td>Scientific/Botanical name:</td>
<td>Terminalia catappa</td>
</tr>
<tr>
<td>English name:</td>
<td>Tropical-Almond, Indian-Almond</td>
</tr>
<tr>
<td>Common name(s):</td>
<td>Badamlili, Desi badam</td>
</tr>
<tr>
<td>Part used as dye:</td>
<td>Waste leaves</td>
</tr>
</tbody>
</table>

**Brief introduction:**

It is a large, spreading tree now distributed throughout the tropics in coastal environments. It grows to about 35 meter tall, with an upright structure. During the dry season (autumn), the leaves turn into colours of red, copper, gold. The tree usually sheds all its leaves twice a year in January-February and July-August. The tree first drops its leaves when it reaches 3-4 years old and then every year.

The leaves are large, 15–25 centimeters (5.9–9.8 inch) long and 10–14 centimeters (3.9–5.5 inch) broad, ovoid, glossy dark green and leathery. Before falling, they turn pinkish-red or yellow-brown, due to pigments such as violaxanthin, lutein, and zeaxanthin. The leaves contain several flavonoids (like kaempferol or quercetin), several tannins (such as punicalin, punicalagin or tercatin), saponines and phytosterols.

The leaves are found to have strong anti-bacterial properties and promote fish breeding, curing sick fish and speed up healing of damage. The dried leaves act as a "black water extract" which gradually turns the water brown like tea and effectively reduces the pH levels in water, releasing organic compounds such as humic acids, flavanoids and tannins into the water which absorb harmful chemicals. (Thomson and Evans, 2006).
2.4.2 Malabar semul or red cotton tree (*Bombax Ceiba*)

![Malabar semul or red cotton tree (*Bombax Ceiba*)](image)

Tree | Stem with conical prickle | Conical prickle
--- | --- | ---

Source of images: Google Images

**General information:**

<table>
<thead>
<tr>
<th>Family:</th>
<th>Bombacaceae</th>
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<tbody>
<tr>
<td>Scientific/Botanical name:</td>
<td>Bombax ceiba Linn</td>
</tr>
<tr>
<td>English name:</td>
<td>Malabar semul, Red cotton tree, Indian kapok tree</td>
</tr>
<tr>
<td>Common name(s):</td>
<td>Shimalo, Semal</td>
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<tr>
<td>Part used as dye</td>
<td>Dry bark with trunk</td>
</tr>
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</table>

**Brief introduction:**

It is the large beautiful and deciduous tree found throughout India and other parts of tropical and sub-tropical Asia, Australia and Africa. The tree is mentioned in Mahabharata proving its presence since a long time.

The tree is large sized, tall, deciduous, having straight, buttressed trunk with a clear bole and widespread branches. The trunk and branch bark is gray in colour having hard, sharp and conical prickles.

Preliminary tests show the presence of glycosides and tannins from root, stem and leaf. In the stem some alkaloids and in root proteins are identified. The stem bark contains lupeol and b-sitostrol. (Jain et al., 2009)
2.4.3 Mast tree or Asopalav (*Polyalthia longifolia*)

<table>
<thead>
<tr>
<th>Photograph-2.3 Mast tree or Asopalav (<em>Polyalthia longifolia</em>)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Mast tree or Asopalav" /></td>
</tr>
<tr>
<td><img src="image2" alt="Asopalav close view" /></td>
</tr>
<tr>
<td><img src="image3" alt="Asopalav leaves" /></td>
</tr>
</tbody>
</table>

**Asopalav whole tree** | **Asopalav close view** | **Asopalav leaves**

Source of images: Google Images

**General information:**

<table>
<thead>
<tr>
<th>Family:</th>
<th>Annonaceae</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scientific/Botanical name:</td>
<td><em>Polyalthia longifolia</em></td>
</tr>
<tr>
<td>English name:</td>
<td>Mast tree</td>
</tr>
<tr>
<td>Common name(s):</td>
<td>Asopalav</td>
</tr>
<tr>
<td>Part used as dye</td>
<td>Dry leaves</td>
</tr>
</tbody>
</table>

**Brief introduction:**

It is a lofty evergreen tree, native to India and Sri Lanka, commonly planted due to its effectiveness in alleviating noise pollution. It is introduced in gardens in many tropical countries around the world. It exhibits symmetrical pyramidal growth with willowy weeping pendulous branches and long narrow lanceolate leaves with undulate margins. The tree is known to grow over 30 ft in height. It grows naturally (without trimming the branches out for decorative reasons) into a normal large tree with plenty of shade. The plant was found to contain alkaloids, flavonoids, saponins, carbohydrates, fats and oils, tannins, steroids and terpenoids. (Chen et al., 2000)

Fresh leaves are a coppery brown colour and are soft and delicate to touch, as the leaves grow older the color becomes a light green and finally a dark green. The leaves are shaped like a lance and have wavy edges. The leaves are use for ornamental decoration and are used in festivals. In past, the flexible, straight and light-weight trunks were used in the making of masts for sailing ships. That is why the tree is also known as the Mast Tree.
2.4.4 Neem tree (*Azadirachta indica*)

<table>
<thead>
<tr>
<th>Photograph-2.4Neem tree(<em>Azadirachta indica</em>)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neem whole tree</td>
</tr>
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</table>

General information:

<table>
<thead>
<tr>
<th>Family:</th>
<th>Meliaceae</th>
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</thead>
<tbody>
<tr>
<td>Scientific/Botanical name:</td>
<td><em>Azadirachta indica</em></td>
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<tr>
<td>English name:</td>
<td>Neem tree</td>
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<tr>
<td>Common name(s):</td>
<td>Limdo, Neem</td>
</tr>
<tr>
<td>Part used as dye:</td>
<td>Dry leaves</td>
</tr>
</tbody>
</table>

Brief introduction:

*Azadirachta indica* (neem) belonging to *Meliaceae* family is very important medicinal plant which is traditionally used to treat different diseases. It is a large evergreen tree, 12 to 18 meter in height and 1.8 to 2.4 meter in girth with a straight bole and long spreading branches forming a broad crown as much as 20 meters across, commonly found throughout greater parts of India. Neem is a native tree of India, found in every part in India especially in semi-arid conditions. The Neem Tree is an incredible plant that has been declared the "Tree of the 21st century" by the United Nations. It is one of the major components in Ayurvedic medicine. The neem is an ancient Indian cure-all due to its antibacterial, antifungal, antiviral, antihistamine and antiseptic properties. In fact the people of India call the Neem Tree "The Village Pharmacy".

Identification and characterization of chemical compounds in crude extracts from leaves of Omani neem has been carried out by Hossain et al., (2013). The crude extracts of the leaves contain normal hydrocarbons, phenolic compounds, terpenioids, alkaloids and glycosides.(Bukhari et al.,2014) The
important chemical constituents were present in the leaf crude extracts of neem that can be endorsed to cultivation on a domestic plantation.

2.5 Studies of ecofriendly finishes on dyed fabric

Textile fiber or fabrics are deficient in one or more properties or improved properties are desired for the fiber or fabric. Textile finishing provides a method whereby deficiencies in the textile can be corrected or specific properties can be introduced. A finish is a treatment given to a fabric, to change its appearance, handling /touch or performance. Its purpose is to make the fabric more suitable for its end use (Jahid & Pervez, 2015).

To improve those performance properties, cotton fabric often are given a chemical treatment called durable press finishing. This treatment involves the use of crosslinking agents. Most important ecofriendly crosslinking agents are butanetetracarboxylic acid (BTCA) and citric acid (CA). Many research studies on durable press finishing with ecofriendly crosslinking agents have been carried out. Few studies are given below.

Schramm et al. (2002) used polycarboxylic acids 1,2,3,4-butanetetracarboxylic acid and citric acid as non-formaldehyde durable press finishing agents instead of formaldehyde-releasing N-methylol compounds. In this study, isocratic HPLC is applied in an attempt to quantify the polycarboxylic acids that react with cellulosic material dyed with CI Reactive Red 195, CI Reactive Yellow 145 and CI Reactive Blue 221. Subsequently, the fabrics were cured with formulations containing butanetetracarboxylic acid and citric acid or a combination of both. The pre-weighed, dyed fabric was impregnated in a treatment bath containing a crosslinking agent and a catalyst. No softener was used. The catalyst was added to the formulation immediately before application. Subsequently, the sample (30 × 50 cm) was passed through a two-roll laboratory padder (air pressure 1 bar, fabric speed 3 m/min). This treatment gave a wet pick-up of about 100–109%, depending on the original weight of the fabric treated. After drying (2 min, 100 °C) the fabric was cured for a specified time at 180 °C in a laboratory dryer, washed with occasional stirring (sodium carbonate 1 g/l, 10 min, 50 °C, wash liquor 1 l) and finally dried again (3 min, 80 °C). The chromatographic determination reveals that an increase in the depth of shade results in a decrease of the amount of
butanetetracarboxylic acid, except in the case when cotton is dyed with CI Reactive Blue 221, a copper formazan complex-based dyestuff. Colour measurements indicate that the $\Delta E^*$ values decrease in the order CI Reactive Yellow 145, CI Reactive Red 195 and CI Reactive Blue 221. The dyestuffs react with the hydroxyl groups of the cellulose and consequently fewer hydroxyl groups are available for the esterification reaction with polycarboxylic acids. This phenomenon is confirmed by the fact that the application of higher depths of shade results in a decrease in the amount of cotton-bound PCA, except with CI Reactive Blue 221.

Concurrent dyeing and finishing of cotton with natural colour and citric acid in the presence of NaH$_2$PO$_4$ as catalyst under thermal treatment by Maulik et al. (2011) has been reported. Cotton fabric was simultaneously modified and dyed with citric acid and *Camellia sinensis*, and citric acid and *Punica granatum* in the presence of sodium di-hydrogen phosphate (NaH$_2$PO$_4$) as the catalyst using a pad–dry–cure technique. Treatment with 10% citric acid, 15% NaH$_2$PO$_4$ and dye at 100% wet pickup, followed by drying at 95°C for 5 min and curing of the dried fabric at 140°C for 5 min produced most balanced improvements in respect of the depth of shade, wrinkle recovery and colour fastness to light, wash and rubbing with retention of more than 70% of the original strength. Infrared analysis of the dyed cotton fabric indicated that the treatment of cotton with citric acid and either *Camellia sinensis* or *Punica granatum* under the influence of an esterification catalyst led to the esterification of carboxyl groups of citric acid and of hydroxyl groups of cotton cellulose and with that of both the dyes. The said process also led to some degree of cross-linking of polymeric chains of cotton.

Effect of different cross-linking agents on cotton fabric dyed with caspian natural dyes was studied by Sheth et al. (2003). Mill bleached mercerized cotton fabric was used. The fabric was pretreated with potash alum, stannous chloride or tartaric acid at 80°C for 30 minutes at M:L 1:20. Undyed and dyed fabrics were padded with conventionally used dimethyl dihydroxyethylene urea. Color depth and color difference of dyed and cross-linked fabric was measured on a Macbeth Colour Eye 7000A. The results observed that the color difference of differently cross-linked fabric was comparable of slightly higher than that for conventionally used DMDHEU.
cross-linked fabric. Trisuccinimidyl citrate (TSC) fabrics showed drastic change in shade, while very low formaldehyde (VLF) cross-linked fabric showed less comparable color difference to that of DMDHEU depending on type of mordant used during dyeing. Wrinkle recovery angle was found to be between 233-258. While tear and tensile strength retention was between 51-100 depending on type of mordant used during dyeing and type of cross-linking agent applied. Generally, from the results obtained it was found that in case of most of the natural dyes and different mordants when dyed on cotton fabric and cross-linked with organic acid in presence of trisodium citrate, color difference was higher than that for conventionally used cross-linked fabric.

Influence of microwaves on non-formaldehyde DP finished dyed cotton fabrics has been reported by Vukusic et al. (2003). An alternative approach to the application of formaldehyde releasing conventional N-methylol compounds is based upon the use of non-formaldehyde Durable Press (DP) finishing agents – polycarboxlic acids (PCA). The application of microwave energy to impart durable crease resistance to dyed cotton fabric. Bifunctional dyes: C.I. Reactive Red 195, C.I. Reactive Yellow 145 and C.I. Reactive Blue 221 were applied in the study. Isocratic HPLC method was applied to quantify the PCA reacted with the cellulosic material under two different curing procedures. Microwave way of curing imparts higher levels of wrinkle resistance of dyed as well as of undyed cotton materials treated with PCA. General trend noticed when microwave curing is used a lower amount of PCA bound. This opposite trend between elastic recovery and quantity of PCA bound can be attributed to a greater number of least di-ester linkages which can improve DP properties and cannot be distinguished from mono-ester linkages with the HPLC technique. The chromatographic determination reveals the decrease in PCA, in almost all the cases studied, caused by the increase in shade depth with both ways of curing. These results confirmed the reduced cellulose affinity for further crosslinking with PCA molecules, because of the partial blockage of cellulose reactive groups with the dye molecules. Regarding the evaluation of the color differences, they are more prominent when microwave treatment is included in the experiment. Shade changes are primarily caused by the catalyst applied, which is a strong reducing agent. Azo chromogen is decomposed by the action of the reducing
agent, which causes most prominent shade changes, particulary with yellow hue. Primarily in the wrinkle recovery and resistance to deformation, microwave way of curing offers much better results.