CHAPTER-I

INTRODUCTION

1.1 Historical background:

Colour is one of the elements of nature that has made human living more aesthetic and fascinating in the world. They are supposed to be associated with emotions, human qualities, seasons, festivals and passion in our life. In the past at the dawn of the civilization, people tried to ornament their surrounding similar to that of natural colours observed in plant, soil, sky and other sources. This gave birth to science of colours from natural origin. All over the world, natural colours and strains have been obtained from plant and animal kingdom and also from mineral sources.

Dyeing was practiced as early as 3000 BC in China and Egypt. The earliest records of Indian textiles belong to the period of about 2500 BC and they contained references of coloured silk and gold brocades. By about 1450 BC the Egyptians were making textile material of astonishing delicate structure and were able to dye them in a whole range of colours (Trotman, 1975).

The art of dyeing is as old as human civilization. From the historical records, it is learnt that natural colourants were available to people during Greco-Roman periods. Our Vedas, the aharvedas carries description of natural dyes. The use of natural dyeing material is evident with the wall painting of Ajanta, Ellora and Sithanvasal. The excavations of Harapan culture at Mohenjo-Daro have yielded a cloth which carries evidence of red dye (like madder). In the epic period there are frequent references of 'Pitambar' a yellow garment used by Gods. The evidence of use of natural dyes during pre Muslim and Muslim period of Indian history is much better preserved in the form of dresses, manuscripts and paintings. The coloured exquisite silk and muslin fabrics of India had acquired fame throughout the world during 16th and 17th centuries(Srivastava, 1989).

Ancient Egyptian hieroglyphs contain a thorough description of the extraction of natural dyes and their application in dyeing. Further developments extending over many thousands of years led to rather complicated dyeing process and high quality dyeing.
Natural dyes are known for their use in colouring of food substrate, leather, wood as well as natural fibers like wool, silk, cotton and flax as major areas of application since ancient times. Natural dyes may have a wide range of shades, and can be obtained from various parts of plants including roots, bark, leaves, flowers, and fruit (Allen, 1971). Since the advent of widely available and cheaper synthetic dyes in 1856 having moderate to excellent colour fastness properties, the use of natural dyes having poor to moderate wash and light fastness has declined to a great extent. However, recently there has been revival of the growing interest on the application of natural dyes on natural fibers due to worldwide environmental consciousness (Samanta and Agarwal, 2009).

Although this ancient art of dyeing with natural dyes withstood the ravages of time, a rapid decline in natural dyeing continued due to the wide availability of synthetic dyes at an economical price. However, even after one and a half century, the use of natural dyes has not eroded completely and they are still being used. Thus, natural dyeing of different textiles and leathers has been continued mainly in the decentralized sector for specialty products along with the use of synthetic dyes in the large scale sector for general textiles owing to the specific advantages and limitations of both natural dyes and synthetic dyes.

1.2 Synthetic dyes and pollution:

Textile processing industry is one of the major environmental polluters. In order to process a ton of textile, one might have to use as much as 230 to 270 tons of water. The effluent generated by this much water would pollute the environment as it contains a heavy load of chemicals including dyes used during textile processing. Over $7 \times 10^5$ tones and approximately 10,000 different types of dyes and pigments are produced world-wide annually. It is estimated that 10-15% of the dye is lost in the effluent during the dyeing process (Iqbal and Ashiq, 2007).

The textile industry plays a major role in the economy of Asian and other countries. In India, it accounts for the largest consumption of dyestuffs about ~80% (Mathur et al., 2003), taking in every type of dye and pigment produced, this amounts to close to 80,000 tones. India is the second largest exporter of dyestuffs, after China. Worldwide, ~$10^6$ tons of synthetic dyes are
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produced annually, of which 1-1.5 x 10^5 tons are released into the environment in wastewaters (Zollinger, 1987). This release is because not all dye binds to the fabric during the dyeing processes; depending on the class of the dye, the losses in wastewaters can vary from 2% for basic dyes to as high as 50% for reactive dyes, leading to severe contamination of surface and ground waters in the vicinity of dyeing industries (O'Neill et al. 1999). It is estimated that globally 2,80,000 tons of textile dyes are discharged in textile industrial effluent every year (Jin et al. 2007).

Production of synthetic dyes is dependent on petrochemical source, and some of synthetic dyes contain toxic or carcinogenic amines which are not eco-friendly (Hunger, 2003). Moreover, the global consumption of textiles is estimated at around 30 million tones, which is expected to grow at the rate of 3% per annum. The colouration of this huge quantity of textiles needs around 700,000 tones of dyes which causes release of a vast amount of unused and unfixed synthetic colourants into the environment (Samanta and Agarwal, 2009).

Some of the synthetic dyes are not good due to their toxic effect. Some synthetic dyes create allergic reaction to skin and also cause pollution. Thus revival of natural dyeing technique as one of the alternative is being emphasized for this purpose. Many natural resources which are being wasted indiscriminately or thrown away as waste product contain useful dye and pigment. Earlier studies have revealed that waste contain many flavones can be effectively used as dyes(Chai-Ming & Chun-Nan, 1994 and Lin et al.,1995).

Thus, there are two main ways to limit the environmental impact of textile processing. One is to construct sufficiently large and highly effective effluent treatment plants, and the other way is to make use of dyes and chemicals that are environment friendly.

1.3 Renewed interest in natural dyes:

A renewed international interest has arisen in natural dyes due to increased awareness of the environmental and health hazards associated with the synthesis, processing and use of synthetic dyes. Natural dyes comprise colourants that are obtained from animal or vegetable matter without any chemical processing. During the last decade the use of natural dyes, obtained
from animal or vegetable matter without any chemical processing, has gained momentum due to increased demand for these dyes by the food, pharmaceutical, cosmetic as well as the textile colouration industry.

Samanta and Agarwal (2009), Bechtold and Mussak, (2009), Vankar, (2007) are of the opinion that the use of non-toxic and eco-friendly natural dyes on textiles has become a matter of significant importance because of the increased environmental awareness in order to avoid some hazardous synthetic dyes. However, worldwide the use of natural dyes for the colouration of textiles has mainly been confined to craftsmen, small scale dyers and printers as well as small scale exporters and producers dealing with high valued eco-friendly textile production and sales. 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). Natural dyes produce very uncommon, soothing and soft shades as compared to synthetic dyes. On the other hand, synthetic dyes are widely available at an economical price and produce a wide variety of colours; these dyes however produce skin allergy, toxic wastes and are harmful to human body.

There are a small number of companies that are known to produce natural dyes commercially. For example, De la Robbia, which began in 1992 in Milan, produces water extracts of natural dyes such as weld, chlorophyll, logwood, and cochineal under the Eco-Tex certifying system, and supplies these to textile industry. In USA, Allegro Natural Dyes produces natural dyes under the Ecolour label for textile industry (Hwang et al. 2008). Aware of the Toxic Substance Act and the Environmental Protection Agency, they claim to have developed a mordant using a non-toxic aluminum formulation and biodegradable auxiliary substance. Companies in Germany, France, Netherland also manufactures and sells vegetable/natural dyes.

It is observed that there are many companies in India also known to produce natural dyes commercially. Alps Industries is one major natural dye producing company. The company has a production capacity of around 300 tones per year (Gulrajani, 2001). Other Indian companies are: A.M.A. Herbal Laboratories Private Limited in Lucknow; Kirpal Export Overseas in New
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Delhi; K. M. A. Exports in Tindivanam; Saboo Coatings Limited in Dera Bassi (Punjab); Tulip Trade link Private Limited in Ahmadabad Gujarat etc.

For successful commercial use of natural dyes, the appropriate and standardized dyeing techniques need to be adopted without scarifying required quality of dyed textiles materials. Therefore, to obtain newer shades with acceptable colour fastness behavior and reproducible colour yield, appropriate scientific techniques or producers need to be derived from scientific studies on dyeing methods, dyeing process variable, dyeing kinetics and compatibility of selective natural dyes. A need has also been felt to re-investigate and re-build the traditional processes of natural dyeing to control each treatment and pre-dyeing process (preparation, mordanting) and dyeing process variables for producing uncommon shades with balanced colour fastness and eco-performing textiles.

Until the latter half of the 19th century people were using natural dyes (Parkes, 2002) for colouring textile fibre 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. Some synthetic dyes are hazardous, carcinogenic and also release vast amount of pollutant in the environment during their manufacturing (Nagia and Mohamedy, 2007; Gulrajani and Gupta, 2001; Shanker and Vankar, 2007).

India has a very rich tradition of using natural dyes. The art and craft of producing natural dyed textiles is being practiced in many villages and by some craftsmen in the country, but there is no organized effort to revive and improve the methods of dyeing and printing with natural dyes. India being tropical country has a good resource of plant dyes which can be easily integrated into textile manufacturing.

Natural dyes serve dual purposes of catering to fashion trends as well as being environment friendly. In this context, India is at an advantageous position since the country holds a rich reservoir of natural resources with potential products. According to recent studies the present Indian flora is estimated to contain about 50,000 species (Dayal and Dobhal, 1999).
1.4 Statement of the problem:

Owing to increase in awareness about health, safety and environment, within the last few years numerous research studies on natural dyes have been reported. These studies mainly deal with application of natural dyes with pre, post or simultaneous mordanting in order to make the fabric receptive to the dye or to improve its fastness and characteristics to get more number of shades (Dayal and Dobhal, 1999; Goel and Chauhan, 1996; Gulrajani, et. al., 1992).

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.

India being a tropical country, cotton is the most extensively used and preferred fabric, followed by wool and silk. Amongst synthetics, popular ones are nylon, polyester and acrylic. For the study three natural and one synthetic fabric were taken, i.e. cotton, wool, silk, and nylon.

Cotton fabrics, however, have a tendency to wrinkle badly and have poor smooth drying properties after laundering. Under distortion and moist conditions, the hydrogen bonds that hold the cellulose chains together are ruptured, and then the chains slide to minimize the stress within the fibers. This phenomenon causes the hydrogen bonds to reform in a new position after removal of the distorting force. The rupture and reformation of hydrogen bonds cause wrinkle problems on cotton or cotton-blend fabrics (Andrews, 1992, 1995; Cooke & Weighmann, 1982 a&b; Smith & Block, 1982 a&b).

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, which can covalently crosslink with the adjacent cellulose chains within cotton fibers. The new crosslinking bonds formed in the durable press chemical finishing process are stronger than the former hydrogen bonds. The new crosslink hold when the fabric is under distortion and moist conditions; the bonds pull the cellulose chains back into position after removal of a distorting force so that the fabric resists wrinkling.

The most widely used crosslinking agents in DP finishes have been N-methylol agents or N-methylolamides because of their efficiency and low price. These reactants fall in the category of formaldehyde reactants (Cooke
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&Weigmann, 1982a). To achieve the best DP finishes and the least formaldehyde release of N-methylol compounds, all these factors must be controlled carefully.

The formaldehyde reactants have two serious disadvantages (Choi, 1992). First, they release formaldehyde vapors during DP finishing, storage, and consumer use. The Occupational Safety and Health Administration (OSHA) lists formaldehyde as a hazardous and toxic substance (Andrews, 1995), and has set the upper limit for formaldehyde in air at 0.75 parts per million average over an eight-hour work shift. Several studies by the Chemical Industry Institute of Toxicology show that formaldehyde is a carcinogen to animals. To humans, it is a severe eye irritant, a mucous membrane irritant, and a skin irritant, and it is toxic if ingested (Cooke & Weigmann, 1982a). Secondly, formaldehyde treated fabrics suffer a major loss of such mechanical properties as tensile strength, tear strength, and abrasion resistance due to two key contributing factors. One factor is the fiber degradation caused by the acid catalysts at elevated temperatures. The other is the restriction of stress distribution within the fibers due to the cross linked sites. The loss of mechanical properties also occurs with some nonformaldehyde reactants, such as polycarboxylic acids.

Largely because of concern about formaldehyde hazards to workers in the textile industry and also to consumers, formaldehyde-free crosslinking agents for producing durable press properties are of interest to replace DMDHEU, the conventional finishing agent for DP finishes. Polycarboxylic acids (PCA), which are nonformaldehyde reactants, are possible replacements for the conventional finishing reactant. The main advantages of PCA are that they are formaldehyde-free, do not have a bad odor, and produce a very soft fabric hand. Loss of mechanical properties is a problem, however.

Research at SRRC has shown that the most important PCA reactants for the textile industry today are butanetetracarboxylic acid (BTCA) and citric acid (CA). The best results in DP finishes with PCA have been obtained with BTCA in the presence of sodium hypophosphite as the catalyst (Welch, 1988; Welch & Andrews, 1989 a&b). BTCA, in the presence of sodium hypophosphite, provides the same level of durable press performance and finish durability in laundering as does the conventional DMDHEU reactant.
Yet, the high cost of BTCA is an obstacle to mills' decisions to use BTCA as replacement for conventional DP reactants.

Citric acid (CA) is another compound to replace DMDHEU. The advantages of CA over other PCA are low cost, proven lack of toxicity, and ready availability (Andrews, 1989, 1990). PCA reactants can solve the problem of formaldehyde release from finished cotton fabrics. Further research is needed to bring about reduction in the cost of DP finishing with BTCA and CA and in the loss of mechanical properties of cotton fabrics treated with PCA reactants.

Durable press finishing agents can be applied on cotton fabrics by a technique called the pad-dry-cure method. Pad-dry-cure is the conventional technique for applying durable press finishing agents to cotton fabrics because of its simplicity and ease. The fabric is immersed, for 5-10 minutes, in the aqueous solution containing a DP finish, curing catalyst, fabric softener, wetting agent, and water. Then, the fabric is padded through squeeze rolls to give a specified wet pick-up, reported as percent on weight of fabric. After that, the fabric is dried and cured for a specified time at a specified temperature. The pad-dry-cure technique results in fabric with good DP properties.

A number of investigations have been undertaken in order to study the effects of crosslinking on the properties of dyed fabrics. The treatment of dyed fabrics with PCA also gives rise to coloration changes that can be balanced to some extent if a single dyestuff is employed.

Polycarboxylic acids (PCAs), especially 1,2,3,4-butanetetra-carboxylic acid (BTCA) or citric acid (CA) in combination with phosphorus-containing catalysts, such as sodium hypophosphite (SHP), have proven to be the most effective substitutes for the formaldehyde-releasing crosslinking agents such as the N-methylol compound dimethyloldihydroxyethylene urea (DMDHEU)(Schramm et al,2002)

Thus for the present study PCAs were used for the post treatment to determine whether dyed cotton fabric has been able to increase the DP or not. Study of washing fastness properties of post treated dyed fabric was carried out. The absorption of finish by dyed cotton dyed fabric has also been evaluated by stiffness test and crease recovery test. To determine the influence
of finish on dye with reference to fastness has been determine by washing fastness.

Thus by keeping in view all above advantages of natural dyes, this study was undertaken with following objectives.

**Objective of study:**

**Broad objective:**

- Use of eco-friendly dyes and textile auxiliaries on various textile fibers.

**Specific objectives:**

- Identification of locally available plant waste rich in natural dye content but having no other important property except use as a fuel and fertilizer.
- Identification of colourants (dye(s) and/or pigment(s)) through isolation using spectral analysis.
- Extraction and application of identified natural dyes from plant waste for dyeing of cotton, wool, silk and nylon using ecofriendly mordants for pretreatment and development of shade.
- To study colour characteristics (mainly colour strength and fastness property) using different mordants for dyeing of cotton, wool, silk and nylon fabric.
- Shade, colour strength and colour fastness comparison between ecofriendly and non ecofriendly mordants used as pretreatment to determine phasing out of non ecofriendly mordants for dyeing with natural dyes.
- To study influence on washing using post treatment on premordanted dyed cotton fabric.
- To study use of natural dyes from waste leaves for block printing application on cotton fabric.