Chapter I

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Colouring yarn is a creative and lucrative art nurtured and patronized through centuries. Until the turn of the 19th century, fabrics were coloured using dye stuffs obtained from nature as they were the only colouring substances available at that time. The muted earth colours yielded by these natural dyestuffs were considered as harmonious as they go together giving pleasing results.

The history of natural dyes are more than 4000 years old. Colour in ancient times was considered a spiritual necessity of equal importance to the physical need of food. So in every civilization from the very early times to the present day, the art of applying colour through dyeing has played an important part in adding beauty to the world (D’Souza and Nandita, 1983). The dyes from natural sources like plants and animal, constituted the source of bio-colour (Das, 1992).

Dyes can be defined as organic chemical compounds, which have property of producing the phenomenon of colour by light absorption. Dyes are intensely coloured materials and are retained in substances by physical absorption, mechanical retention and by formation of covalent chemical bonds or complexes with salts or metals. The term ‘Dye’ includes natural dyes, synthetic dyes, pigments and whiteners. Chemically, a dye molecule is made up of two parts- chromophores and auxochromes.

The chromophores (Greek chroma - colour, phoros - bearer) are unsaturated groups, the presence of which makes the compounds coloured. The important chromophores bear the following groups in their structures.

\[
\begin{align*}
\text{C} = \text{C} & , \\
\text{C} = \text{O} & , \\
\text{C} = \text{S} & , \\
-\text{CH} = \text{N} - & , \\
-\text{N} = \text{O} & \\
-\text{N} = \text{N} - & , \\
-\text{N} = \text{O} & , \\
-\text{N} = \text{N} - & , \\
\end{align*}
\]
The auxochromes (Greek: auxo-increase, chroma - colour) are either acidic or basic in nature. These groups serve to deepen or intensify the colour in the presence of chromophores and hence they are known as auxochromes (colour intensifying groups). A chromogen without an auxochrome can never act as dye. Some examples of auxochrome groups are as below:

\[
\begin{align*}
-\text{OH}, & \quad -\text{OR}, \quad -\text{N}=\text{O}, \quad -\text{N}=\text{O} \\
-\text{NH}_2, & \quad -\text{NHR}, \quad -\text{C}=\text{R}, \quad -\text{C}≡\text{N}, \quad -\text{CH}=\text{CH}_2 \\
-\text{NR}_2, & \quad -\text{S}-\text{R}, \quad -\text{N}=\text{N}-\text{R}
\end{align*}
\]

Natural dyes can be defined as those colorants (dyes and pigments) obtained from animal and vegetable matters without processing. When used as textile dyes, they are mainly mordant dyes although some belong to other groups as well. Most of the historically important natural colorants are members of the anthraquinone, naphthoquinone, indigoid and carotenoid groups. According to the Society of Dyers and Colourists, UK, ‘Natural Dyes are those colourants which are obtained from plants, animal or mineral sources with little or no chemical processing at all. Most of these are mordant dyes, though some acid, vat and direct dyes are also known. There is only one basic dye in the whole range of natural dyes and there are no sulphur, azoic, reactive or disperse types of natural dyes (Gupta and Gulrajani, 1994 and Gupta, 1999).

Natural dyes can broadly be classified as organic dyestuff of vegetable, animal and mineral or inorganic pigments. Thus, the term ‘Natural dyes’ covers all the dyes derived from plants, insects and minerals, i.e., derived from natural sources
(Gupta, 1990). They can also be classified in various ways. Numerous methods of classification were adopted, which are:

* Classification based on their method of application.
* Classification based on chemical structure.
* Classification based on their origin or the sources from which they are obtained.
* Classification based on their colour.

Leaving aside other methods of classification, some details on classification based on their origin or the sources are given below.

Depending on the origin or sources from where they are produced, the natural dyes can be grouped into three distinct classes:

* Vegetable resources
* Insects as well as animal resources and
* Mineral resources.

Vegetable dyes are obtained from various parts of plants and herbs such as stem, wood, root, bark, leaf, flower, fruit and seed which produce distinct pale to dark shades on both natural as well as synthetic fibres. The prominent among them are indigo (Indigofera tinctoria Linn. and Isatis tinctoria Linn.), Turmeric (Curcuma longa Linn.), Annatto (Bixa orellana Linn.), Saffron (Crocus sativus Linn.), European Madder (Rubia tinctorum Linn.), Manjit (Rubia cordifolia Linn.), Brazil wood/Sappan-wood (Caesalpinia sappan Linn.), Morinda (Morinda eitrifolia Linn.), Lawson or Henna (Lawsonia inermis Linn.), Juglone (Juglans regia Linn.), Nyctanthin or α-Crocetin (Nyctanthes arbor-tristis Linn. and (Cedrela toona Roxb.), Barberry (Berberis aristata Linn.), Tesu flowers (Butea monosperma Lam.) etc.

Vegetable colours have now entered a new era where they are sought and used for their many intrinsic values (Chattopadhaya, 1997). They are safe healthwise and can be used in foodstuff. They are gentle, soft and stubble and create a colourful
effect. In a world overpowered by synthetics, the urge for the natural intensifies. All interested in the development and wider use, need to actively encourage continuing research for more dye materials, for newer shades and also dissemination of the existing knowledge all over the globe (Gupta, 1996).

In the beginning, there were only dyes derived from natural sources. Throughout the centuries there occurred no change in the use of ancient dyestuff till the appearance of synthetic dyes in the mid 19th century A.D. With the accidental synthesis of mauveine by William Henry Perkin in 1856 and its subsequent commercialization has heralded the advent of coal tar dyes (synthetic dyes). Synthetic dyes are cheaper and are more readily available apart from imparting more reproducible shades with good fastness properties. These advantages of synthetic dyes have gradually diminished the importance of natural dyes (Gulrajani, 2001). Some synthetic dyes, particularly azo dyes (which are characterized by the presence of at least one azo [-N=N-] linkage in the chromophore, are prepared from α-aryl amines, which have been found to be potentially carcinogenic. They constitute nearly 70% of all the dye classes and are represented by acid, metal complex, mordant, direct and disperse application classes of dyes. The azo linkage is highly susceptible to reductive degradation to the two amines constituting the azo linkage (Fig. 1.1).

Distinct advantages of azo dyes are that they produce brilliant shades, are inexpensive and their application spectrum is broad and as such can be used for dyeing a wide range of natural as well as man-made fibres (Singh and Parmar, 1998). Thus during the late 1800 and early 1900's, the dye industry was the major synthetic
organic industry and was forerunner of the pharmaceutical and agricultural chemical industries as well as synthetic fibres, plastics and food industry (Simith and Wagner, 1991).

The German Government’s ban through the 40th amendment to Consumer Goods Ordinance on the import of textiles, leather and other items dyed with azo dyes based on 20 carcinogenic amines came into effect from April, 1996. Due to this, the application of much less hazardous eco-friendly natural dye, on cotton, silk, wool, jute, etc. is gaining popularity all over the world.

Thus, with the environmentally friendly products becoming a top priority in recent years, the dye industry has turned its attention to newer products which may cater to the fashion trend as well as to the environment and pollution control. Natural dyes/colourants derived from flora and fauna are believed to be safe because of their non-toxic, non-carcinogenic and biodegradable nature and can be blended very easily and safely.

It is improper to generalize all the synthetic dyestuffs as being harmful or the entire natural dyes as safe. For example, scarlet pimpernel and bracken used in food in the past were later found to be unsafe, the former causing anaemia and the latter containing a small quantity of carcinogen. On the other hand, the synthetic food colour Yellow 2G is non-toxic (Singh and Parmar, 1998). Further, sometimes the method of application of the colourant to the textiles using metallic mordant makes them non-eco-friendly and unsafe to human being and environment. The famous ‘German Ban’ has put the restrictions to the use of metal salts. Accordingly, the maximum permissible quantities of different metals in the ultimate product were fixed as: As - 1 ppm, Pb - 1 ppm, Cd - 2 ppm, Cr - 2 ppm, Co - 4 ppm, Cu - 50 ppm, Ni - 4 ppm, Zn - 20 ppm. There is however no upper limit on Al, Fe and Sn. The upper limit of Cu is also fairly high. Hence, one can safely use these salts for complexing and mordanting during dyeing process (Gulrajani, 2001).
Global consumption of textiles is estimated at around 30 million tonnes per annum and this is expected to further growth at the rate of 3% per annum. Colouration of this amount of textiles need around 70,000 tonnes of dye. So, use of this huge amount of textiles and its disposal would certainly add considerably to the environmental pollution and consequent health hazards associated with the use of disposal of these textiles. Inspite of all the efforts directed towards environmental safety, a number of classes of textile related allergies have been and are being reported in the newspapers and magazines in the European and other western countries. In order to ensure safety of the various textile goods used by the consumers, Germany has taken up initiative and announced a ban on the azo dyed textile goods which release harmful amines. The ban shall be extended to other chemicals used in the textile industry as well (Singh and Parmar, 1998).

Environmental consideration are now becoming an additional important factors during the selection of consumer goods including textiles all over the World. The world has become increasingly burdened with problems like the green house effect, ozone layer depletion, water pollution and waste disposal. The role of dyestuffs and dye industries in introducing harmful dye contaminants into the environment has been criticized. The acute ecological crisis has caused the environmentalists to ironic the call 'Go back to the nature'. Interest in natural products is gaining importance throughout the world and people are becoming aware of the need for ecofriendly materials to came up and dominate the scene. The revival of the use of natural dyes world-wide is primarily due to the increasing environmental consciousness today. Their non-toxic, biodegradable properties are making them exceedingly popular (Gulrajani and Maulik, 2002).

The use of natural dyes has increased substantially during the last couple of years. According to Singh and Parmar (1998), natural dyes have certain advantages like:
In India, dyes from natural sources have a long history and can be traced to antiquity. It is interesting to note that India is one of the few civilizations to perfect the art of fixing natural dyes to the cloth. Indian textiles were greatly valued and sought after for their colours and enduring qualities. Like most ancient Indian arts and crafts, the knowledge and expertise of natural dyes was traditionally passed down from the master craftsman to his disciples. It can be seen that, scientist have paid considerable attention in the post independence period to study the plants in relation to their pharmaceutical use, but very little attention has been given to study the plants as source of dyes and colourants.

The sub-Himalayan region of North-eastern India particularly Assam and Arunachal Pradesh are the treasure house of wide varieties of plant species. Due to the varied topographic and climatic conditions, various types of flora with their own distinctive characteristics are available in this part of the country. Many of the plant species have medicinal & aromatic value, while some plant species contain natural colouring matters in their leaves, fruits, roots, flowers, seeds or barks. The practice of extraction of colouring matters from plant sources is in vogue in this part of the country from very ancient time. Conventionally, some rural people of NE region extract dyes either from leaves, roots, flowers, seeds or bark of some selected plant species, adopting their own methods of extractions. These methods
mostly involves boiling, scraping, powdering and mixing with other materials to get desired colour. Sometimes fermentation processes are also involved in extraction of dyes. In most cases, the dyes are extracted and used fresh for colouring textile materials.

The fact that the extraction of dyes from natural plant sources and their utilization have been localized in the areas of availability, therefore the methodologies adopted for extraction of dyes and their utilization are mainly oriented to the manufacture of specific items of local importance.

Apart from a few conventionally used plant materials for extraction of dyes by rural folks, many dye yielding plants remain unutilized due to ignorance and also due to non availability of R &D data on their quality and quantity. Thus it has become essential to screen out the potential plant sources of natural dyes available in the forest zones of NE region and to develop scientific methods for extraction of dyes from them.

In spite of several advantages natural dyes have over synthetic dyes, the use of natural colour is still very limited due to non availability of standard shade card, precise and specific ways of application and standard norms. The appropriate technical knowledge of colour extraction, purification and standardization of dyeing techniques is of immense value and requires detailed scientific study. Besides the focus is on increasing export of textile goods and the use of natural colours for dyeing textile materials may enhance export prospects as there is a growing interest for textiles dyed with natural dyes among foreign buyers.

The amount of research done in this field is negligible. Limited sources of natural dyes are familiar at present and therefore, efforts are required to identify more dye sources to meet the increased demand. There is plenty of scope for R&D work in cultivation, production and processing in natural dye sector. Generation of new informations on dye quality of less known but potential natural sources may directly help in the evolution of natural dye industries in the unexplored NE region. The information about dyeing properties of natural dyes, if available, would facilitate
the scientific use of these natural dyes, which are safer than synthetic products. Moreover any variation in the time of harvesting the plant material, period of extraction of dyes, the amount of dye, concentration of mordant and the time and temperature of dyeing gives greatly varied results. It greatly reflects the need for proper knowledge of these variables so as to get satisfactory results with natural dyes. Authentic information about dyeing properties would facilitate better and fuller use of these natural products. The appropriate technical knowledge of colour extraction, purification and standardization of dyeing techniques is, therefore, of immense value for this new dye sector.

Though a number of natural dye are used in the NE region to dye silk and cotton yarn, detailed information on the dyeing technique is not available and a proper scientific study has not been initiated. ‘Muga’ and ‘pat’ are two famous silk produced in Assam, and a sizeable amount is exported to other countries. In the present situation it is expected that these yarn dyed with natural dyes will fetch better demand and price in national and international market. Keeping these in view, the present investigation has been undertaken with the following objectives:

1. To select out certain most potential dye yielding plant species of Assam for standardizing processes for extraction and application of dye on two different types of yarns (mulberry silk and cotton) and evaluation of dyed product.
2. To study parameters that determine the extraction of dye from raw materials and to develop a standard extraction process.
3. To study various parameters of dyeing silk and cotton yarn with the four selected dyes for developing useful shades.
4. To develop and evaluate mordanting process and standardize various parameters.
5. To evaluate the quality of the dyed yarn using recognized procedure.
6. To standardize uniform dyeing technique for each dye to adopt at commercial level.