CHAPTER I

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1.1. Textiles

From earliest times, people have used textiles of various types for covering, warmth, personal adornment, and even to display personal wealth. Today, textiles are still used for these purposes and everyone is an ultimate consumer. It begins in agriculture with fibre production of cotton, flax and other fibrous plants; in husbandry of sheep, other animals and silkworms; in mining of metals and minerals; in forestry for wood; in chemical research and production of synthetics. These fibres are processed into yarns and/or fabrics. The yarns are made into fabrics for industrial and consumer uses by various means, such as weaving and knitting. The fabrics are converted into finished cloths, which provide particular appearances and performances. These fabrics are made into end-use products, including apparel, home furnishings and various industrial applications.

1.2. Kinds of fibres

The textile industry uses many different kinds of fibres as its raw materials. Natural fibres that occur in nature can be classified as vegetable, animal and mineral. Vegetable fibres, found in the cell walls of plants, are cellulose in composition. Animal fibres produced by animals or insects, is
protein in composition. The mineral fibre, asbestos, is mined from certain types of rock. Manmade cellulosic fibres are derived from cotton linters and wood pulp. Noncellulosic polymer fibres are another group of manmade fibres. These synthetic fibres are synthesized by combining carbon, oxygen, hydrogen and other simple chemical elements into large, complex molecular combinations or structures called polymers. Manmade fibres created from other sources are mineral fibres, metallic fibres and rubber fibres.

1.2.1. Vegetable fibres

Cotton: It is composed of about 85% cellulose and about 6% moisture; the remainder consists of natural impurities. Cellulose contains a chain of linearly arranged biglucose units with ether bridge linkages. The side groups of these units are primary and secondary alcoholic hydroxyl groups that made the fibre hydrophilic and are responsible for dyeing. Adsorption, occlusion or reaction may do dyeing of cotton fibre with the hydroxyl groups.

Jute: It is composed of about 65% cellulose and about 10% moisture; the remainder consists of natural impurities. Jute fibre is obtained by retting. It is the cheapest textile fibre and is used as packaging material and textile fibre in great quantities. Because of its lack of strength, jute is difficult to bleach and can never be made pure white.
Sisal : It is extracted from the leaves of the plant Agave sisalana. The agaves have rosettes of fleshy leaves, usually long and narrow, which grow out from a central bud. As the leaves mature, they gradually spread out horizontally and are 1 - 2 meters long, 10 - 15 cm wide and 6 mm thick at the Centre. The fibres are embedded longitudinally in the leaves and are most abundant near the leaf surfaces. It is composed of about 65% cellulose and about 10% moisture; the remainder consists of natural impurities. It is used for ropes, twines and wrappings.

1.2.2. Animal fibre

Silk : It originates from the silkworm as continuous protein filament. The silkworm as a means of self-protection spins a cocoon around its body by extruding the contents of two silk glands through a spinneret at its mouth. The composition of silk principally consists of two portions (about 65% fibroin and about 25% sericin). The fibroin is the silk fibre, which is usually coated with the sericine, the silk gum. The fibroin is made up of a series of different amino acids. The structure is an extended form of the peptide chain in the CO-NH groups of the successive residues protrudes from opposite sides.

1.2.3. Synthetic fibre

Nylon : Nylon is a generic term for any long chain synthetic polymeric amide (polyamide) which has recurring amide groups (CO-NH) as an integral part of the main polymer chain. Nylon made from the condensation of a diamine
and a dicarboxylic acid is classified according to the number of carbon atom in the amine and acid respectively. The monomers for nylon 66 are hexamethylene diamine \((\text{H}_2\text{N}=[\text{CH}_2]_6\text{N}=\text{H}_2)\) and adipic acid \((\text{HOOC}=[\text{CH}_2]_4\text{COOH})\).

1.3. Textile wet processing

Wet processing operations like desizing, scouring, bleaching, dyeing, printing and finishing are commonly employed to produce textile goods for consumer demand.

Grey cotton cloth as woven on a loom is quite unattractive and contains natural and added components, which impart undesirable properties to the cloth and hinder the successful carrying out of the subsequent dyeing, printing, finishing processes etc. The very first operation of wet processing of cotton fabric is generally to remove the added size, which is known as desizing. Grey yarn or cloth after desizing contains fats and waxes that hinder the absorbency of the material leading to improper bleaching, dyeing, printing and finishing. These impurities are removed in the scouring process. The scouring process removes substantial quantities of wax and other impurities from cotton and leaves the material in a very absorbent condition. The natural coloring matter is still present in the cloth or yarn and has a creamy appearance. In order to obtain white material and facilitate the production of pale and bright shades, it is
necessary to decolorize the natural coloring matter in the yarn or cloth by a process known as bleaching. Further processing like dyeing and/or printing are done to provide lasting beauty and delight by adding color to the fabrics.

1.4. Textiles and Ecology

With respect to textiles and ecology, the following aspects are considered:

- Production ecology, comprising
  
  (i) cultivation and harvesting of natural fibres
  
  (ii) manufacture of manmade fibres,
  
  (iii) manufacture of threads and fabrics
  
  (iv) bleaching, dyeing, printing and finishing of textiles
  
  (v) garment manufacture with the application of fertilizers, growth regulators, pesticides, dyes, pigments, textile chemical auxiliaries and finishing agents.

- User ecology, referring to the effects of clothing textiles and the substances that give them their beauty and performance characteristics on human beings during use, i.e. when the clothing is worn.
Disposal ecology, referring to the disposal of the textiles after use, i.e., recycling, composting, dumping or incinerating in a manner that ensures the least possible environmental impact.

The word 'Eco' is nothing but the ecology, which refers to the animals (including human beings) and plants in their relationship to each other and to their environment. The environment refers to the conditions surrounding us. With respect to human beings, it covers everything in the biosphere, oceans, fresh water, atmosphere, earth, rocks, soil organisms and so on. As such, any influence on the quality of environment has a direct bearing on the development, property and life of living beings including human beings. The human beings, who are the most intelligent among all animals, have been exploiting the nature, without any reference to its carrying capacity. There is a limit to everything and so with the carrying capacity of earth and the nature. The activities of human beings have become most damaging for themselves. The attacker himself is going to be the victim in the process.

Ecology is the study of interactions between living organisms and their environment, which includes atmosphere, water and pollutants. The pollutants in water and atmosphere are either present naturally (like microorganism) or introduced by man through industrial gases and effluents. These pollutants interfere with the natural growth of the living beings, including plants, animals and human beings. Insecticides, pesticides, herbicides, chemical wastes, gases
of nitrogen and sulfur oxides, formaldehyde, chlorine, oil spills and radioactive contaminants have a direct bearing on the ecology of a given area [1].

1.5. Textile Dyes

Natural dyes have been used since ancient times for coloring and printing fabrics. Until the middle of last century, most of the dyes were derived from plants or animals sources by long and elaborate processes. Picric acid (which was obtained by Wouif in 1771 by treating indigo with nitric acid) was used for dyeing silk but did not attain any significance. William H. Perkin produced the first synthetic organic dye.

The classification of dyes and pigments is as under:

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Synthetic</th>
<th>Water soluble</th>
<th>Direct, Acid, Basic, Reactive, Optical whiteners</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Water insoluble</td>
<td>Vat, Sulfur, Disperse</td>
</tr>
<tr>
<td></td>
<td>Ingrain</td>
<td></td>
<td>Azoic, Oxidation, Mineral</td>
</tr>
<tr>
<td>Pigments</td>
<td></td>
<td></td>
<td>Vat, Azoic, Phthalocyanine, Mineral</td>
</tr>
</tbody>
</table>

Nearly 4000 commercial dyestuffs are manufactured by the major dyestuff industries [2] in various countries including Germany, Switzerland, Italy, France, UK, USA, Japan, Russia, China and India. These dyestuffs include azo, anthraquinone, azine, oxazine, thiazine, stilbene etc., and the share of azo dye is highly significant. The chromophoric azo group (-N=N-) is found in many
classes of dyes (direct, acid, mordant, disperse, azoic, reactive and metal complex).

1.6. Textile chemicals and auxiliaries

The main raw materials used in the textile industry are the textile fibres, which are spun into yarns, and then woven into fabrics. They are further processed to get bleached, dyed, printed or finished before introduced to the consumer.

The textile chemicals are those, which are helpers or assistants and are added to the usual processing solutions (scouring, bleaching, dyeing, after treating, finishing etc.) for improving the efficiency of the process and/or the effect obtained on the textile materials being processed. Examples are: (i) stabilizers (sodium silicate, organophosphorous compounds and nitrogenous chelating agents) in hydrogen peroxide bleaching and (ii) formaldehyde based cationic dye-fixing agents in direct and reactive dyeing.

Inorganic and organic compounds commonly used in textile processing are as follows:

(i) Inorganic acids: sulfuric, hydrochloric etc.

(ii) Organic acids: formic, tartaric, citric, acetic, oxalic, tannic etc.
(iii) Alkalis: sodium hydroxide, sodium carbonate, potassium carbonate etc.

(iv) Salts: sodium chloride, sodium sulfate, diammonium phosphate, magnesium chloride, zinc chloride, zinc nitrate, zinc fluoroborate etc.

(v) Oxidizing agents: sodium hypochlorite, calcium hypochlorite, hydrogen peroxide, sodium chlorite, nitrous acid, peracetic acid, potassium chlorate etc.

(vi) Reducing agents: sodium hydrosulphite, sodium thiosulfate, sodium or zinc sulphoxylate formaldehyde, sodium sulfite, stannous chloride, stannous acetate, glucose, dextrin etc.

(vii) Sequestering agents: ethylene diaminetetraacetic acid, sodium hexametaphosphate etc.

Trichlorobenzene, Biphenyl, o-phenylphenol, p-phenylphenol, butyl benzoate, o-dichlorobenzene, methylnaphthalene, ethyl phthalimide etc. are the most commonly used commercial carriers in polyester dyeing. Manufacturers have withdrawn many of them from the market because of their carcinogenic, sensitizing or other toxic potentiality [3].

A broad outline of the existing non-ecofriendly chemicals used in textile processing with probable alternatives and their performance with respect to the currently used chemicals is given below.
<table>
<thead>
<tr>
<th>Non-ecofriendly chemical(s)</th>
<th>Use</th>
<th>Alternative chemical(s)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentachlorophenol, Formaldehyde</td>
<td>Size preservative</td>
<td>Sodium silicofluoride</td>
<td>Less effective</td>
</tr>
<tr>
<td>Nonyl phenyl ethylene-oxide adduct</td>
<td>Detergent, emulsifier</td>
<td>Fatty alcohol ethylene oxide adduct</td>
<td>More costly</td>
</tr>
<tr>
<td>Silicones and (monosilicones + APEO emulsifier)</td>
<td>Softening, Water repelling</td>
<td>Anionio / cationic softener, wax emulsion</td>
<td>Not permanent</td>
</tr>
<tr>
<td>Calcium hypochlorite, Sodium hypochlorite</td>
<td>Cotton bleaching</td>
<td>Hydrogen peroxide</td>
<td>More costly</td>
</tr>
<tr>
<td>Sodium silicate, Phosphorous-based compounds</td>
<td>Peroxide stabilizers</td>
<td>Nitrogenous stabilizers</td>
<td>Less efficient</td>
</tr>
<tr>
<td>Dichlorobenzene, Trichlorobenzene</td>
<td>Carriers in polyester dyeing</td>
<td>Butyl benzoate</td>
<td>less efficient</td>
</tr>
<tr>
<td>Kerosene</td>
<td>Emulsion thickener in pigment printing</td>
<td>Water-based thickener</td>
<td>Dull prints and harsh handle</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>Crease resisting of cotton and its blend fabrics</td>
<td>Polycarboxylic acids (Non-formaldehyde crosslinking agent)</td>
<td>Less effective, costly, yellowing, changing the tone of dyed fabrics, more strength loss of fabrics</td>
</tr>
<tr>
<td></td>
<td>Dye fixing for direct and reactive dyeing / printing</td>
<td>Non-formaldehyde based products</td>
<td>Tone difference and less effective</td>
</tr>
<tr>
<td></td>
<td>Dispersing agent for disperse dyeing and vat dyeing</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Reactive softener (Methylol stearamide type)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sodium dichromate</td>
<td>Vat dyeing</td>
<td>Hydrogen peroxide</td>
<td>Less effective in some cases</td>
</tr>
</tbody>
</table>
1.7. German Ban

In Germany, it was found that symptoms of cancer occurred among workers who handled benzidine in the production of azo dyes. Due to this, several European dye manufacturing companies stopped producing and marketing azo dyes based on benzidine in the 1970's. Later, several tests were conducted on azo dyes and it was found that azo dyes could be split under certain physiological condition to form carcinogenic amines.

In July 1994, Germany amended two laws that were significant for textile processing industries;

(i) The Fourth Federal Emission Protection Ordinance (its aim being to protect the environment from effluent of textile industry)
(ii) The Ordinance of Material and Articles (its aim being to protect the consumer).

This ban prohibits the use of certain azo dyes, which could split and give 20 amines proven or suspected to be carcinogenic. As per the German Legislation Consumer Goods Ordinance, "No articles of clothing or items which regularly come in contact with the human body may be put into circulation if they can release harmful amines due to the use of azo dyes, which are either known or suspected to be allergic, poisonous or carcinogenic. These dyes should not henceforth be used by any supplier of textiles or leather goods".
Red and Green lists have been prepared in most of the European countries. Green listed items are labeled as ecofriendly. Red listed items are either being banned or phased out. The list prepared by German Committee for testing the carcinogenic materials is called MAK list and is updated every year. The banned (red listed) dyes spread over six classes of dyes, viz., acid, azoic, basic (cationic), direct, disperse, oxidation bases and developers. These six classes are termed as "affected" classes of dyes. None of the dyes from the remaining classes of dyestuffs is banned, i.e., dyes belonging to reactive, vat, sulfur and natural dyes. These are termed as "unaffected" classes.

The amines obtained after dye reduction (i.e. the reduction products) are electrophilic and are covalently bonded to the nucleic acid of DNA resulting in DNA damage and hence inducing cancer. Today, scientifically found evidence proves that four aromatic amines have carcinogenic effect on human. These are benzidine, 2-Naphthylamine, 4-Aminobiphenyl, 4-Chloro-o-toluidine. These four amines are listed as definitely carcinogenic and placed in group III A1 of German MAK list. The other listed amines are also carcinogenic under optimum condition of splitting and placed in group III A2 of MAK list.

Conditions that can cause reductive splitting of azo dyestuffs are:

(i) A reductive chemical medium (e.g., reduction stripping off dyestuff).
(ii) The human organism as a result of the action of intestinal bacteria or azo reductase in the liver on any azo dyestuffs in the body.

The mechanism of reduction cleavage and further action may be represented as follows:

(a) Reductive Cleavage:

\[ \text{R – N = N – R'} \quad \text{reductive condition} \quad \rightarrow \quad \text{R – NH}_2 + \text{R’ – NH}_2 \]

\[ \text{(Azo dyestuff)} \quad \text{(azo cleavage)} \quad \rightarrow \quad \text{Aromatic amines} \]

(b) Covalent bonding to the nucleic acid bases of DNA

\[ \text{R-NH}_2 \quad \xrightarrow{\text{Oxidation}} \quad \text{R-NHOH} \quad \xrightarrow{\text{pH < 7}} \quad \text{R-NOH} \quad \rightarrow \quad \text{R-NH}^+ \text{(covalent bonding)} \]

List of forbidden dyes based on benzidine type is as follows:

<table>
<thead>
<tr>
<th>Acid Orange 45</th>
<th>Direct Acid 44</th>
<th>Direct Brown 27</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Red 85</td>
<td>Direct Violet 1</td>
<td>Direct Brown 31</td>
</tr>
<tr>
<td>Acid Black 29</td>
<td>Direct Violet 12</td>
<td>Direct Brown 33</td>
</tr>
<tr>
<td>Acid Black 94</td>
<td>Direct Violet 22</td>
<td>Direct Brown 51</td>
</tr>
<tr>
<td>Azoic Diazo Comp 112</td>
<td>Direct Blue 2</td>
<td>Direct Brown 59</td>
</tr>
<tr>
<td>Direct Yellow 1</td>
<td>Direct Blue 6</td>
<td>Direct Brown 79</td>
</tr>
<tr>
<td>Direct Yellow 24</td>
<td>Direct Green 1</td>
<td>Direct Brown 95</td>
</tr>
<tr>
<td>Direct Orange 1</td>
<td>Direct Green 6</td>
<td>Direct Brown 101</td>
</tr>
<tr>
<td>Direct Orange 8</td>
<td>Direct Green 8</td>
<td>Direct Brown 154</td>
</tr>
<tr>
<td>Direct Red 1</td>
<td>Direct Green 8:1</td>
<td>Direct Black 4</td>
</tr>
<tr>
<td>Direct Red 10</td>
<td>Direct Brown 1</td>
<td>Direct Black 29</td>
</tr>
<tr>
<td>Direct Red 13</td>
<td>Direct Brown 1:2</td>
<td>Direct Black 38</td>
</tr>
<tr>
<td>Direct Red 17</td>
<td>Direct Brown 2</td>
<td></td>
</tr>
<tr>
<td>Direct Red 28</td>
<td>Direct Brown 6</td>
<td></td>
</tr>
<tr>
<td>Direct Red 37</td>
<td>Direct Brown 25</td>
<td></td>
</tr>
</tbody>
</table>
The list of banned azo dyes is as follows [4-6].

<table>
<thead>
<tr>
<th>Azo Dye Code</th>
<th>Colour Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Red 4</td>
<td>Basic Red 111</td>
</tr>
<tr>
<td>Acid Red 5</td>
<td>Basic Red 42</td>
</tr>
<tr>
<td>Acid Red 24</td>
<td>Basic Brown 4</td>
</tr>
<tr>
<td>Acid Red 26</td>
<td>Oxidation Base 20</td>
</tr>
<tr>
<td>Acid Red 73</td>
<td>Direct Yellow 48</td>
</tr>
<tr>
<td>Acid Red 114</td>
<td>Direct Orange 6</td>
</tr>
<tr>
<td>Acid Red 115</td>
<td>Direct Orange 7</td>
</tr>
<tr>
<td>Acid Red 116</td>
<td>Direct Orange 10</td>
</tr>
<tr>
<td>Acid Red 128</td>
<td>Direct Orange 108</td>
</tr>
<tr>
<td>Acid Red 148</td>
<td>Direct Red 2</td>
</tr>
<tr>
<td>Acid Red 150</td>
<td>Direct Red 7</td>
</tr>
<tr>
<td>Acid Red 158</td>
<td>Direct Red 21</td>
</tr>
<tr>
<td>Acid Red 167</td>
<td>Direct Red 22</td>
</tr>
<tr>
<td>Acid Red 264</td>
<td>Direct Red 24</td>
</tr>
<tr>
<td>Acid Red 265</td>
<td>Direct Red 26</td>
</tr>
<tr>
<td>Acid Red 420</td>
<td>Direct Red 39</td>
</tr>
<tr>
<td>Acid Violet 12</td>
<td>Direct Red 46</td>
</tr>
<tr>
<td>Acid Brown 415</td>
<td>Direct Red 62</td>
</tr>
<tr>
<td>Acid Black 131</td>
<td>Direct Red 67</td>
</tr>
<tr>
<td>Acid Black 132</td>
<td>Direct Red 72</td>
</tr>
<tr>
<td>Acid Black 209</td>
<td>Direct Violet 21</td>
</tr>
<tr>
<td>Azoic Diazot Comp11</td>
<td>Direct Blue 1</td>
</tr>
<tr>
<td>Azoic Diazot Comp12</td>
<td>Direct Blue 3</td>
</tr>
<tr>
<td>Azoic Diazot Comp48</td>
<td>Direct Blue 8</td>
</tr>
<tr>
<td>Azoic Diazot Comp113</td>
<td>Direct Blue 9</td>
</tr>
</tbody>
</table>

After the prohibition of import and marketing of textiles (or allied articles containing azo dyes which on reductive cleavage release any of the twenty carcinogenic amines) by Germany, other countries also imposed similar restrictions [7]. These include Holland, Turkey, France and India, however, the approach in enforcing ban varied from one to another. The European union has banned around 300 textile dyes of suspected carcinogen [8].
1.8. Eco-processing of textiles

True Eco-textiles are those, which are biodegradable, and in their production no hazardous or toxic substances are used at any stage. Production of Eco-textiles is very difficult. Hence, at present, attention is focused on Ecofriendly textiles, which do not contain any hazardous or toxic substance and are biologically degradable, so that the damage to the environment and ecology is minimum [9].

Ecofriendly textile wet processing investigations reported in literature under different headings are as follows:

**Desizing**

Novel desizing method [10],
Desizing using potassium persulfate [11],
Persulfate and hydrogen peroxide desizing [12].

**Enzymatic desizing**

High frequency fields with enzymes and peroxide bleaching [13],
Thermostable lipolytic enzyme [14].

**Enzymatic scouring**

Scouring of cotton [15-18].
Bleaching

Novel bleaching method [19],
Biodegradable surfactants for bleaching [20].

Combined processes

One step process for desizing, scouring, bleaching of cotton [21],
One step desizing, scouring and peroxide bleaching [22],
Combined desizing and scouring using hydrogen peroxide [23, 24],
Single stage desizing, scouring and bleaching of cotton [25],
Solvent assisted single stage grey preparatory process [26],
Single stage desizing and bleaching [27-31],
Combined scouring and bleaching [32],
Use of smart rinsing systems and ultra-low liquor ratio machines [33],
Liquor ammonia mercerization of woven and knitted cotton fabrics [34],
Enzymatic and low temperature plasma treatment [35]

Dyeing, printing and finishing

Zero-dye and zero-salt effluent discharge in reactive dyeing [36,37],
Dyeing of cationic cotton without the electrolytes and fixation agents [38],
Use of organic bases in dyeing of indigo on cotton [39],
Six-dip, six-nip method for improved color yield [40],
Use of less quantity of sodium hydroxide in reactive dyeing [41],
Use of cellulase enzyme in finishing of cotton [42],
AATCC methods in cleaning and dyeing [43],
Liquid jaggery as an alternative to sodium sulfide for sulfur dyes [44],
Predyeing of cotton and acid cellulase enzymatic treatment [45],
Use of chitosan in finishing to improve the dyeability of cotton [46],
Ceric ion initiated graft copolymerization onto cannabis indica fibre [47],
Wet processing of wool [48],
1.9. Natural dyes

There are different sources (plant, animal, tissue culture by DNA transfer biotechnology) from which natural dyes are derived.

Advantages of natural dyes are:

(i) They are obtained from renewable natural resources,
(ii) no health hazards,
(iii) practically no or mild chemical reactions involved in their preparation and
(iv) no pollution problems.

Limitations of natural dyes are:

(i) Tediums extraction of coloring component from the raw material,
(ii) low color value,
(iii) long dyeing time,
(iv) some of the natural dyes are fugitive and need a mordant for the enhancement of their fastness properties, and
(v) some of the metallic mordants are hazardous.
(vi) the cost of dyeing with natural dyes is considerably higher than with synthetic dyes.
Some of the natural dye source materials and mordants used are as follows:

<table>
<thead>
<tr>
<th>Dye color</th>
<th>Source</th>
<th>Botanical Name</th>
<th>Parts Used</th>
<th>Mordant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red</td>
<td>Safflower</td>
<td>Carthamus tinctorious</td>
<td>Flower</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Caesalpina</td>
<td>Casealpinia sappan</td>
<td>Wood chips</td>
<td>Alum</td>
</tr>
<tr>
<td></td>
<td>Madder</td>
<td>Rubia tinctorium</td>
<td>Wood</td>
<td>Alum</td>
</tr>
<tr>
<td></td>
<td>Lac</td>
<td>Coccus lacca (insect)</td>
<td>Twigs</td>
<td>SnCl₂</td>
</tr>
<tr>
<td>Yellow</td>
<td>Bougainvillea</td>
<td>Bougainvillea glabra</td>
<td>Flower</td>
<td>Tin</td>
</tr>
<tr>
<td></td>
<td>Golden rod</td>
<td>Slidago grandis</td>
<td>Flower</td>
<td>Alum</td>
</tr>
<tr>
<td></td>
<td>Teak</td>
<td>Tectona grandis</td>
<td>Leaves</td>
<td>Alum</td>
</tr>
<tr>
<td></td>
<td>Marigold</td>
<td>Tagetes species</td>
<td>Flower</td>
<td>Chrome</td>
</tr>
<tr>
<td></td>
<td>Parijata</td>
<td>Nyctanthes arbor-tristis</td>
<td>Flower</td>
<td>Chrome</td>
</tr>
<tr>
<td>Blue</td>
<td>Indigo</td>
<td>Indigofera tinctoria</td>
<td>Leaves</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Woad</td>
<td>Isatis tinctoria</td>
<td>Leaves</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Sunberry</td>
<td>Acacia nilotica</td>
<td>Seed pods</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Piyet</td>
<td>Ligustrum vulgare</td>
<td>Mature berries</td>
<td>Alum, iron</td>
</tr>
<tr>
<td></td>
<td>Water lily</td>
<td>Nymphaea alba</td>
<td>Rhizomes</td>
<td>Iron, acid</td>
</tr>
<tr>
<td>Black</td>
<td>Lac</td>
<td>Coccus lacca (insect)</td>
<td>Twigs</td>
<td>FeSO₄</td>
</tr>
<tr>
<td></td>
<td>Alder</td>
<td>Alinus glutinosa</td>
<td>Bark</td>
<td>FeSO₄</td>
</tr>
<tr>
<td></td>
<td>Rofblamala</td>
<td>Loranthus pentapetalus</td>
<td>Leaves</td>
<td>FeSO₄</td>
</tr>
<tr>
<td></td>
<td>Custard apple</td>
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<td>Caesalpina</td>
<td>Casealpinia sappan</td>
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<td>Flower</td>
<td>FeSO₄ + Acid</td>
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<tr>
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<td>Flower</td>
<td>Alum.</td>
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<tr>
<td></td>
<td>Marigold</td>
<td>Tagetes species</td>
<td>Flower</td>
<td>Chrome</td>
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<td>Rubus fruticosus</td>
<td>Berries</td>
<td>Iron</td>
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<td>Tulsi</td>
<td>Ocimum sanctum</td>
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<td>FeSO₄</td>
</tr>
<tr>
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<td>Bougainvillea glabra</td>
<td>Flower</td>
<td>Alum + Base</td>
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<tr>
<td></td>
<td>Lily</td>
<td>Convolvulaira majalis</td>
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<td>Nettles</td>
<td>Urtica dioica</td>
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<tr>
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<td>Bougainvillea glabra</td>
<td>Flower</td>
<td>SnCl₂ + Acid</td>
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<td>Impatiens balsamina</td>
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<td>Tin</td>
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<tr>
<td></td>
<td>Dahlia</td>
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<td>Flower</td>
<td>Alum / Chrome</td>
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<tr>
<td></td>
<td>Annatto</td>
<td>Bixa orellana</td>
<td>Seeds</td>
<td>-</td>
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</table>

Natural dyes are classified based on their structure, source, method of application, color etc.
• Based on chemical structure: Indigoid, carotenoids, flavones, dihydropyrans, anthraquinone, α-hydroxy-naphthoquinones and anthocyananidins.

• Based on color: Various natural dyes could present all the colors of the visible spectrum. Treating with metal salts can alter the natural color and hue of a dye. If the dye is of plant origin, the color may vary depending on the soil properties, part of the plant, season of harvesting, cultivation practices etc.

Natural dyes do not combine directly with the material they are intended to color. They are substantive, requiring a mordant to fix to the fabric, and prevent the color from either fading with exposure to light or washing out. These mordanting compounds bind the natural dyes to the fabric.

Natural dyes work best with natural fibres such as cotton, linen, wool, silk, jute, ramie and sisal. Among these, wool takes up dyes most easily followed by cotton, linen, silk, sisal and jute. Nearly all of them require some sort of a mordant. The trick is to choose the right dye from the right source that gives not only beautiful tones, but colorfast shades as well.

The chemistry of bonding of natural dyes to fibre is complex. It involves through the formation of direct chemical bonding, hydrogen bonding and some
hydrophobic interactions. Mordants help binding of dyes to fabric by forming a chemical bridge between dye and fibre, thus improving the staining ability of a dye along with increasing its fastness properties. Mordants form insoluble compounds of the dye within the fibre. The presence of certain functional groups in suitable positions in the dye molecule causes its coordination to the metal ion. Generally, two hydroxyl groups or a hydroxyl group with a carbonyl, nitroso or azo group in adjacent positions are responsible for coordination. The mordant dyes produce a wide range of hues of remarkable resistance to wet treatments, but the shades lack brilliancy. An example is the chromium-alizarin complex. A chromium ion can combine with alizarin by covalently and/or coordinately to form the 'Lake'. Chromium being trivalent combines with three molecules of alizarin.

Wool and silk retain the dye through hydrogen bonding between the polypeptide linkages and the dye. An example of alizarin is given to show the nature of bonding with Nylon 6, which also has peptide linkages.
Poor light fastness of some of the natural dyes is due to the photooxidation of the chromophore. To prevent / minimize such photooxidation, a complex has to be formed between the dye and transition metal.

\[
\begin{align*}
\text{CH}_2 & \quad C = O \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{N} & \quad \text{H} \\
\end{align*}
\]

Hydrogen bonded dye interaction with Nylon 6

Treatment with metal salts alters the light absorption characteristics of tannins in addition to making them insoluble in water with the fabric acquiring washing fastness [51].

Many investigations have been reported in literature on natural dyeing. A few of them are as follows:

**Natural dye extraction and dyeing of natural fibres**

Cotton dyeing with canna using ecofriendly mordants [52],
Naturally colored cotton [53],
Dyeing with sulfur dyes [54],
Dye extraction from stems, leaves, barks of selected plants [55],
Use of supercritical fluid extraction for extraction [56],
Plant dyes for dyeing silk fabrics [57],
Mordanting techniques on the dyeing of jute and cotton [58].

**Dyeing of synthetic fibres**

Natural dye is not a viable alternative to synthetic dyes [59],
Poor dyeing of natural dye on polyester, polyacrylonitrile, nylon 66 [60].

**Instrumental analysis of natural dyes**

TLC, UV-Visible, DSC for natural dyes [61]
Spectro fluorimetry [62,63]
HPLC [64]
Mass spectrometry [65, 66]
Liquid chromatography [67]
3D fluorescence spectra [68].

**Brief list of natural sources used for dye extraction [69-101].**

<table>
<thead>
<tr>
<th>Plant</th>
<th>Plant</th>
<th>Plant</th>
<th>Plant</th>
</tr>
</thead>
<tbody>
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<td>Croton</td>
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<td>Chestnut</td>
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<td>Onion</td>
<td>Paprika</td>
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<td>Dolu</td>
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<td>Mugwort grass</td>
<td>Birch</td>
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<td>Indigo</td>
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<td>Brazil wood</td>
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<td>Henna</td>
<td>Sappan wood</td>
<td>Madder</td>
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<tr>
<td>Clyers broom</td>
<td>Nut tree</td>
<td>Chamomile</td>
<td>Beed</td>
</tr>
<tr>
<td>Golden Shower</td>
<td>Mast wood</td>
<td>Manjeet</td>
<td>Myrobolan</td>
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</table>
1.10. Textile Color analysis

Practical applications based on "Lab" and "LCH" system

A color could be specified objectively in terms of tristimulus values X, Y, Z or trichromatic coordinates x, y. Mathematically, chroma \( C = \sqrt{a^2 + b^2} \) and hue \( H = \arctan \left( \frac{b}{a} \right) \) are essentially the polar coordinates calculated from the cartesian coordinates 'a' and 'b'. The hue angle tells us about the color itself, i.e., whether the color is red, yellow, green, blue or purple. The chroma tells us about the purity of color. \( Da \) and \( Db \) (i.e. difference in 'a' and in 'b' between two pairs of colors) have the great deal of relevance in calculating color difference. The 'a' and 'b' coordinates representing redness (+a) or greenness (-a) and yellowness (+b) or blueness (-b) respectively.

If 'a' and 'b' are both positive, then the color shades are red, yellow, orange, brown and yellow khaki.

If 'a' and 'b' are both negative, then the color shades are greenish blue, turquoise blue, blue and greenish navy.

If 'a' is negative and 'b' is positive, then the color shades are yellowish green, greenish yellow, olive green and greenish khaki.
If ‘a’ is positive and ‘b’ is negative, then the color shades are purple, royal blue, violet and reddish navy blue.

Hue circle envisages three primary colors viz. Yellow (H = 70 – 105), Red (H = 350 – 35) and Blue (H = 195 – 285); and three secondary colors viz. Green (H = 105 – 195), Violet (H = 285 – 350) and Orange (H = 35 – 70).

The ‘L’ representing the third coordinate in the three-dimensional color space and indicating lightness or darkness (a perfect black has L=0, whereas a perfect white has L=100).

These enable one to understand the specified color better than is possible using trichromatic coordinates. Thus ‘Lab’ or ‘LCH’ color specifications are able to define any color in a meaningful manner compared to the tristimulus values or trichromatic coordinates. The equidistance of ‘a’ and ‘b’ coordinates in Lab color space facilitates computation of color difference [102].

‘LCH’ and ‘Lab’ color specification is able to define any color in a meaningful manner compared to the tristimulus value or trichromatic coordinates. Important application of colorimetry by difference from a spectrally similar standard is the solution of problem as the color changes produced by the application. In these, the color standard is for the original specimen and
color sample is for the original specimen and color sample is for the produced (treated) specimen.

1.10.1. Color difference

Important application of colorimetry by difference from a spectrally similar standard is the solution of problems as the color changes produced by various deteriorative agents (weathering, heat, salt spray, acid, alkali, abrasion, etc.) or those produced admixture of a dye or toner. In these problems, the color standard is the original unexposed or untoned specimen; and the chief concern is to evaluate the character and amount of color differences, the absolute evaluation of the color being of secondary interest, or required only approximately. For these applications, colorimetry by difference would be used in preference to absolute colorimetry.

Another application of colorimetry by difference is in the measurement of color changes in nonturbid solutions. In these applications, generally the color changes of interest arise from alteration of the amount of one of the constituents in the solution. If the standard is a solution of known concentration of the constituents of interest, spectral similarity between standard and unknown is assured, and colorimetry by difference may be used to evaluate the concentration of the constituent of the unknown solution [103].
Color difference concept is based on determining the cumulative effect of differences in the individual components of the color, viz. lightness (DL), red-greenness (Da), yellow-blueness (Db), or alternatively in chroma (DC) and hue (DH). The color difference (DE) can be computed from its components DL, Da and Db as

\[
DE = (DL^2 + Da^2 + Db^2)^{1/2},
\]

where DL = L (sample) – L (standard),
Da = a (sample) – a (standard) and
Db = b (sample) – b (standard).

DH can be calculated indirectly from DE, DL and DC as

\[
DH = (DE^2 - DL^2 - DC^2)^{1/2}
\]
and it is not just a difference in hue angles.

While comparing any sample with the standard,

if DL < 0, then the sample is darker than the standard,
if DL > 0, then the sample is lighter than the standard,
if Da < 0, then the sample is greener than the standard,
if Da > 0, then the sample is redder than the standard,
if Db < 0, then the sample is bluer than the standard,
if Db > 0, then the sample is yellower than the standard,
if DC < 0, then the sample is duller than the standard and
if DC > 0, then the sample is brighter than the standard [104].
For color difference measurement, any color difference method (Lab, LCH, Luv, etc.) can be applied. It is not possible to find any precise correlation between color differences by different methods. Thus, the exact method of computing color difference must be mentioned. Cross evaluation of the objective assessment against visual judgement may be done.

1.11. Summary

Due to the environmental problems, ecofriendly materials and methods are to be used in textiles. Different authors carried out various studies and they have been reported in different literatures. From the literature survey, it is clear that some of the textile operations employed today are under challenge to meet out the legislation laid by different agencies.

For textiles today, any new investigation has to be focused on the ecofriendly manner. The material and methods to be investigated should be preferably in this ecofriendly area. Literature reports on the textile wet processing operations were analyzed. Based on these details, a work plan for this investigation has been arrived at. They are; (i) Investigation on the application of biodegradable bleaches for cellulosics, (ii) investigation on the exploitation of exhausting agent which can produce good dye uptake with lower TDS in dyeing, (iii) investigation on the exploitation of natural dye for dyeing, (iv) investigation on the modification of natural fibres by ecofriendly modifiers, and (v) investigation on the application of ‘Lab’ color analysis, K/S color strength and exhaustion measurements in dyeing.
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