Detection of Natural Dyes: Historical Importance of Indigo

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ABSTRACT: ***Many raw materials like fibres, employs either natural or chemical dyes for dyeing. Synthetic dyes are famous for their features like adhesion & resistance towards washing & chemicals but are marred by its mutagenic property on the environment. Natural dyes obtained from the natural world are not only quite tolerant to washing, having shown good adhesion and longevity is also environment friendly. In order to obtain information about the history and methods with types of natural dyes used, many analytical methods have been utilized. One of the natural dyes of historical importance is Indigo which is found in 3 forms, Indigo, Indirubin & the leuco or colourless form. The aim of this review paper is to have a brief understanding of the various detection methods for natural dyes in historical textiles and to understand how these techniques can be used for detection of the various forms and isomers of natural Indigo.***

KEYWORDS: Chromatography, Fibres, Mass spectrometers, Natural dyes, Synthetic dyes, Textiles

INTRODUCTION

The world of textiles employs raw materials including natural & synthetic dyes, with the different dyeing techniques which depend on various factors like the structure of the dye, fibre's origin and dye's solubility. Moreover, the textile industry is a known water guzzler and a pollutant of water. The textile industry uses both the natural dyes which are from plant or animal origin and are nontoxic for the environment while the synthetic dyes are toxic for the environment [1][2][3]. The natural dyes are derived from the natural origin and are not only resistant to washing, chemical treatments but are also safe for humans and for the environment. The natural dyes are from plants like henna for red, crocus for saffron colour etc. and from insects like lac for red & dark brown colours (Figure 1 and Figure 2). The aim is to have a brief understanding of the various detection methods for natural dyes in historical textiles and to understand how these techniques can be used for detection of the various forms and isomers of natural Indigo. In this review based on the available methods for detecting natural dyes, Indigo has been selectedbeing one of oldest natural dyes being used

Natural dyes are divided into 2 groups as per its attachment to the fibre: direct dyes that are chemically fixed sans admixture & mordant dyes, which needs fixation by a metal salt to prevent colour fading. Many natural dyes needs mordant where the Mordants for cellulose fibres (cotton, linen) need a basic dye bath, & mordant for proteins fibres requires dye bath of acid [4]. Till the 19^{th} century, Natural dyes held sway, but the discovery of mauveine or aniline purple had brought in the age of synthetic dyes. This coupled with the various limitations of the natural dyes made the synthetic dyes looked attractive. However, the toxic effects of the synthetic dyes have prompted resurgence in the usage of natural dyes.

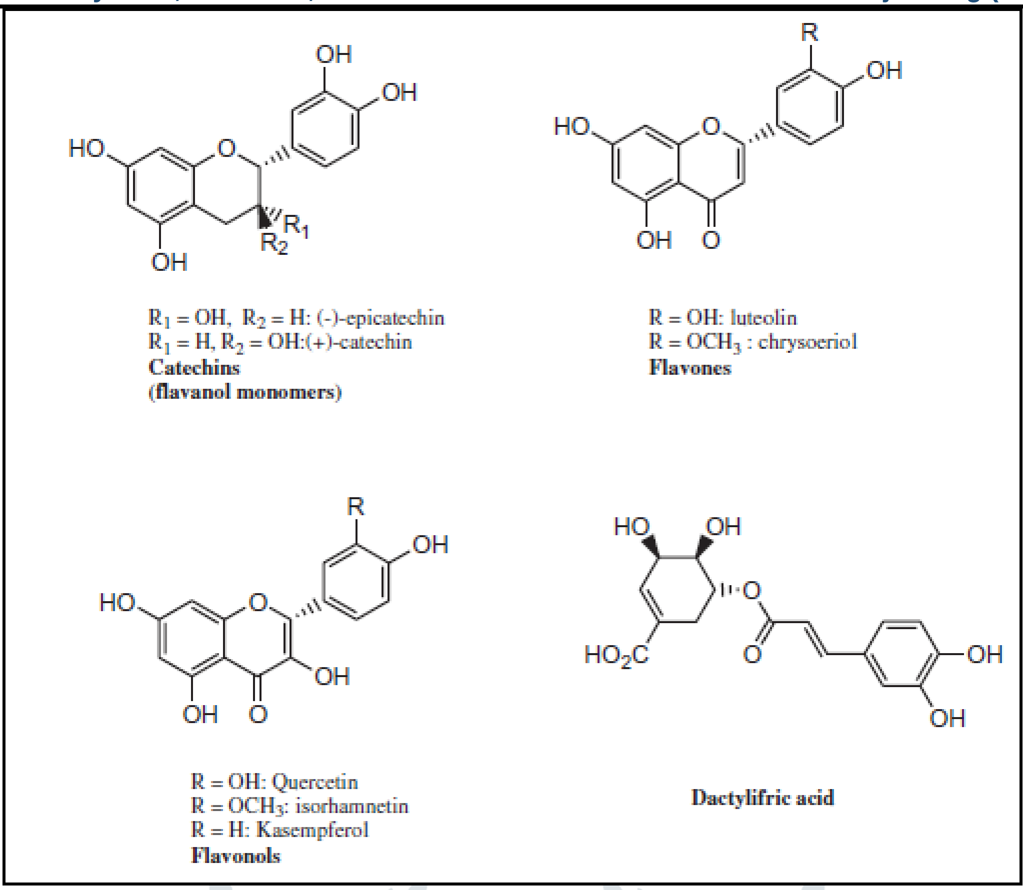

Figure 1: Molecular structure of some of the dyes found in dates.Dates are a source of nutrition and the presence of such constituents makes dates a valuable source of natural dyes as well. They are Catechins, Flavones, Flavonols and Dactylifric acid Figure courtesy.

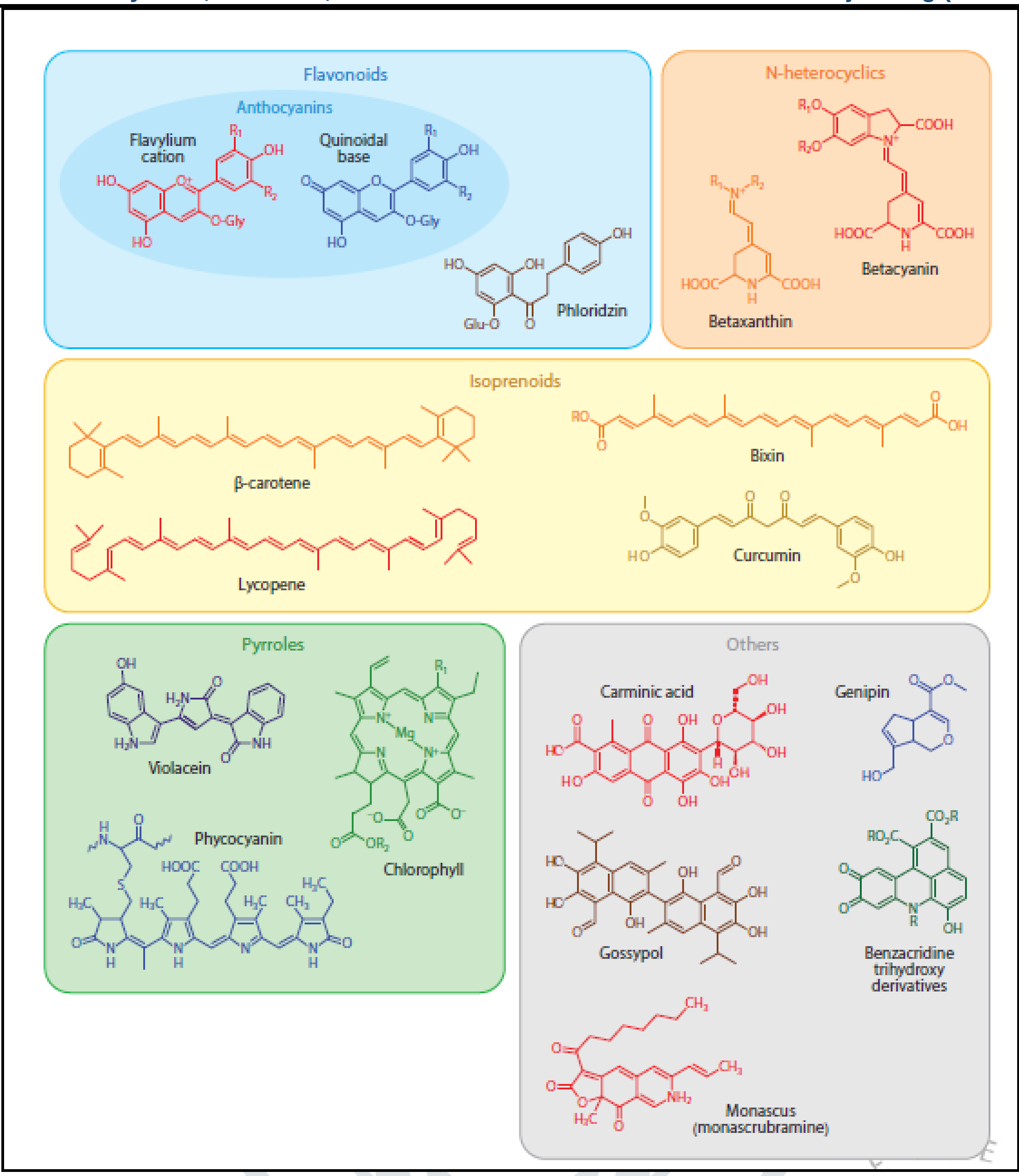

Figure 2: Chemical structure of naturally obtainable dyes which are also useful constituents in food sources. Most of such constituents have also medicinal uses along with their nutritional value Figure courtesy [6].

Synthetic dyes originate artificially from petroleum, having other mineral based components as well. These dyes have high longevity, high adhesion properties, resistant to washing and having low price but are now falling out of favour in the textile industry owing to its toxic effect on the environment [7]. This classification is adopted by considering the methods that is used to dye is dependent upon the fibre's chemical structure that is used for dying & also on the dyes which are applied (Fig. 3). Thereby, the same dye cannot be applied on other fibber types, such as protein, cellulose and polymer fibres. Several acid & base group exist throughout the structures of protein fibres, that serve as binding points for the dye's acid and base categories. Just favourable ether connections and hydrogen atoms serve as binding points for hydroxyl group in cellulose fibre clusters. Regarding polymers fibres, the method for dyeing is following the polymers' structures concerning varying polar groups. Moreover, a dye must become a component of the textile fibre & thereby provides resistances to various washing agent, etc. depending upon the physical/chemical bonds amongst useful group of dyes in addition to those present on surface of the textile fibre. In Figure 3, the types of textile fibres and the dyes applied on them has been illustrated whereas in Table 1, various characteristics of the textile dyes have been tabulated.

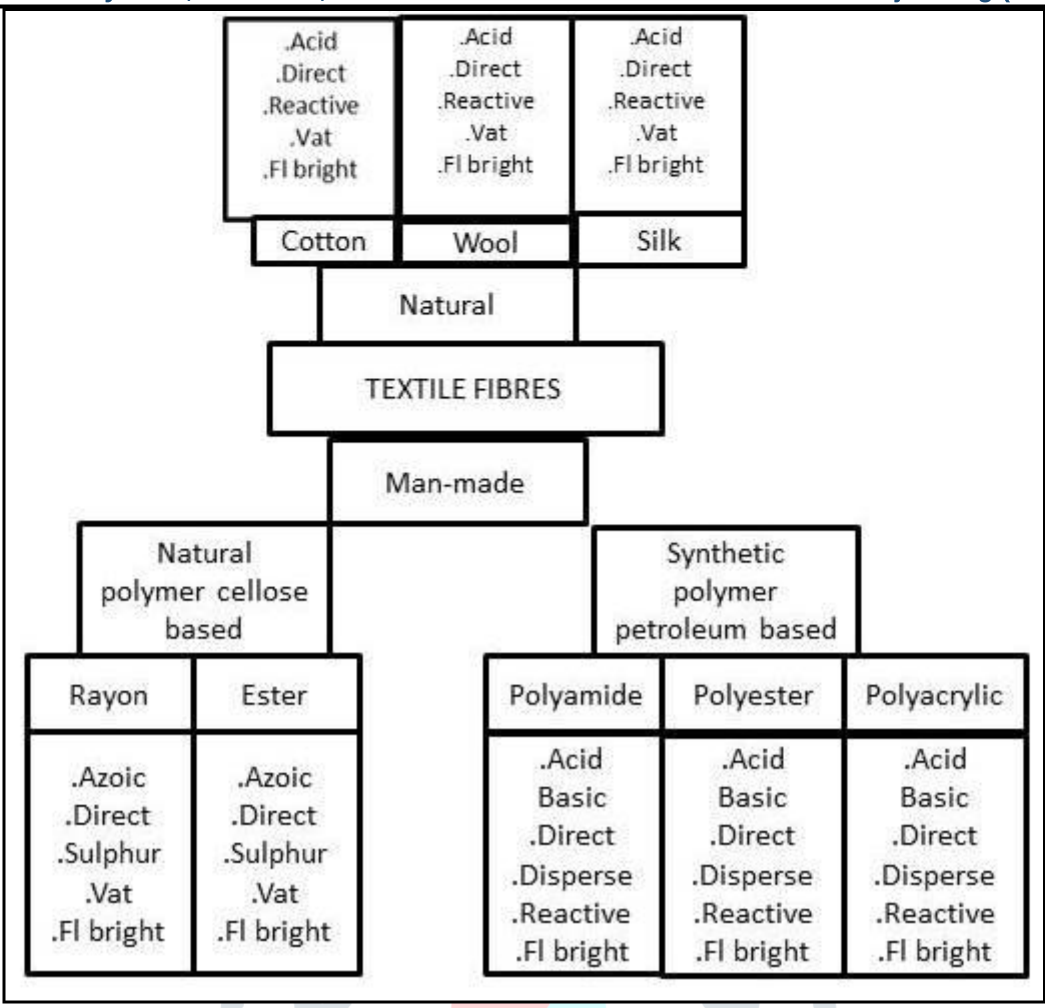

Figure 3: Textile dyes vs textile fibres. Cellulose esters are derivative of cellulose; Fluorescent brightener (Fl. Bright); Rayon is Redeveloped cellulose fibre. Both the textile fibres and the dyes assosciated with them has been divided into natural and synthetic ones [1].

Table 1: Different characteristics of the main classes of textile dyes. These are dependent **upon the textile fabric upon which the dye is to be applied [1]. Nylon is Polyamide fibre, Acyrlic is Polyacyrylonitrile fibre & Rayon is semisynthetic textile material [1].**

Chemical structure of dye	Textile fibre	Dye fibre linkage
	Acid dyes (anionic, water soluble)	
Nitroso, Xanthene	Wool, acrylic	Ionic bond
	Basic dyes (cationic, water soluble)	
Acridine, Xanthene	Wool, polyester	Ionic bond
	Direct dyes (anionic, water-soluble)	
Azo, stilbene	Cotton, nylon	Ionic and hydrogen bonds
	Reactive dyes (anionic, water soluble)	
Azo, oxazine	Cotton, nylon	Ether linkages
	Disperse dyes (non-ionic, water insoluble)	
Azo, nitro, styryl	Polyester, cellulose acetate	Van der waals, hydrogen bonds
	Sulphur dyes (insoluble in water)	
Undetermined structures	Cotton, rayon	Not established
	Vat dyes(water insoluble)	
Indigoids & Anthraquinones	Cotton, rayon	Chemical complex
	Fluorescent brighteners	
Stilbene, coumarine	All fibres	
	Azoic dyes	
Azo	Cotton, polyester	Covalent coordinate

Chromatographic Techniques

Separation & identification of dyes of textile from fabrics is performed by High Pressure Thin layer chromatography (HPTLC)/Thin layer chromatography (TLC)to High Pressure Liquid Chromatography & to Capillary Electrophoresis (CE) [1]. TLC including HPTLC provides minimum effort or instrumentation and ease of doing work. TLC needs very little clean-up, due to the characteristics of the plate used in TLC along with easy detection and separation of multiple compounds on the same TLC plate. Owing to these features TLC has been coupled with UV-VIS-IR spectrometers for the separation, detection and identification of dyes on textile fabrics [1]. HPLC has the capability to detect in one run compounds with various chemical & physical characteristics which makes it useful for detection of dyes used on textile fabrics for historical and forensic purposes. HPLC couple with UV-VIS spectroscopy and Mass spectrometer is used for peak identification including that of dyes used on textile fabrics [1]. LC linked to MS (LC-MS) or the tandem masses spectrometry (LC-MS/MS) is used for the detection of dyes used on textile owing to its good specificity & sensitivity. This is the reason why they are used in the analysis of dyes applied on textiles. In archaeology, analysis of textiles of the historical era has led to the discovery of the types and the patterns of dye used. Moreover, various degradation pathways of the dye once it's exposed to the environment can be determined by these methods [1].

Capillary zone electrophoresis (CZE) & capillary electrophoresis (CE) are separation methods using a high-power non-variant electric field which makes use of a molten silica capillary with diameter of 30–90 μm& 25–90 cm in length which is filled with electrolyte solution and is mainly used to separate ionic species. Nowadays CE/CE-MS techniques are used for detection of textile dyes for textile dye analysis which has been elaborated in Tables 2, 3 and 4. Moreover in Figure 4, various techniques for analysis of dyes have been illustrated [1].

Table 2: Natural dye of textiles analysed by historical textile. The historical textiles are dyed from natural dyes only [1].

Sample	Natural dye	Observations
Standard dyes: Historical silk & wool fibres	Insect dyes, Laocaic acids, Carminic acids	A group of 120 red samples from 100 historical textiles were characterized
Standard dyes: Historical wool fibres	Luteolin, Kaempferol	14 dyes confirmed from 4 sources
Religious embroideries	Alizarin, Rhamnetin	Lac dye, rhubarb detected
Chinese dyed silk	Gallnut, Gromwell	Chinese historical dyes detected
Dyed wool textile artefacts	Alizarin, Lucidin	Original dye profile detected
Chinese historical silk fibres	Rutin	3 types of natural dyes detected.

Table 3: Evaluation of artificial dye applied on both synthetic and natural fibres [1].

Matrix	Synthetic dye	Observation
Cotton, viscose	Direct Red, Solvent black	Dyes of single textile fibres identified
Textile samples	Disperse yellow, Disperse brown	Controls allergenic dyes in textiles
Acrylic fibres	Basic dyes	Method successfully applied in forensics
Acrylic fibres	Basic dyes	Utility of CE-MS was proved
Nylon fibres	Acid Blues, Acid Red	Utility of CE-DAD regarding acid dye analysis was noted.

Table 4: Textile dyes in environmental samples [1].

Matrix	Textile dye	Observations
Samples of waste-water	Acid green, basic red	MIP show it applicability for Acid green
Samples of waste-water	Reactive black, Reactive orange	Degradation products detected
Samples of waste-water	Auramine-O, Rhodamine B	Industrial wastes detected
Samples of surface-water	Disperse blue, Disperse yellow	Six dyes detected
Wastewater	Nylosan Red	Presence of dyes detected
Textile industry	Disperse blue, Disperse orange	Presence of dyes detected

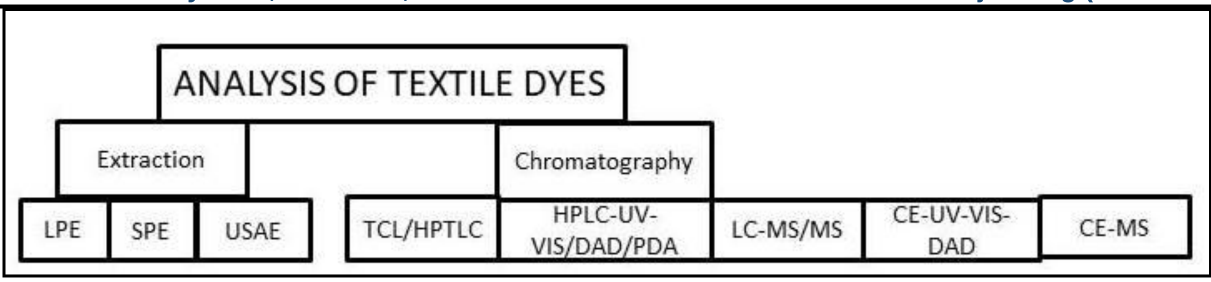

Figure 4: The analytical techniques that are utilized for evaluation of dye of textile are as follows: CE/MS: Capillary electrophoresis-mass spectroscopy, CE-UV-Vis/DAD is Capillary electrophoresis with ultraviolet-visible/diode-array detection; HPLC-UV-Vis/DAD/PDA is High performance liquid chromatography with ultraviolet-visible/diode-array/photodiode array detection; LC-MS is Liquid chromatography-mass spectroscopy; LC-MS/MS is Liquid chromatography-tandem mass spectrometry; LPE is Liquid phase extraction, SPE is Solid phase extraction, TLC/HPTLC is Thin layer chromatography/high performance thin layer chromatography; USAE is Ultra sound assisted extraction [1].

Natural Indigo (deep blue colour) which is extracted from the indigo plant has been used by man for centuries but the invention of the synthetic indigo had declined its demand. However, natural indigo is now in vogue owing to its environmental non-toxic nature. During the extraction process, Natural indigo gets oxidized to Indirubin (deep red colour) which is an isomer of indigo. Indirubin & Indigo are indeed dual indole compounds with the molecule $C_{16}H_{10}N_2O_2$ and the weight of 262.6 Dalton. Indigo is the molecule with a planar structure, a symmetrical transstructure, as well as durable conjugation effects. Amongst the adjacent imino & carbonyl group, 2 intra-molecular H-bond are forged. Indirubin is an indigo structural isomer generated by the condensation of two indole rings.

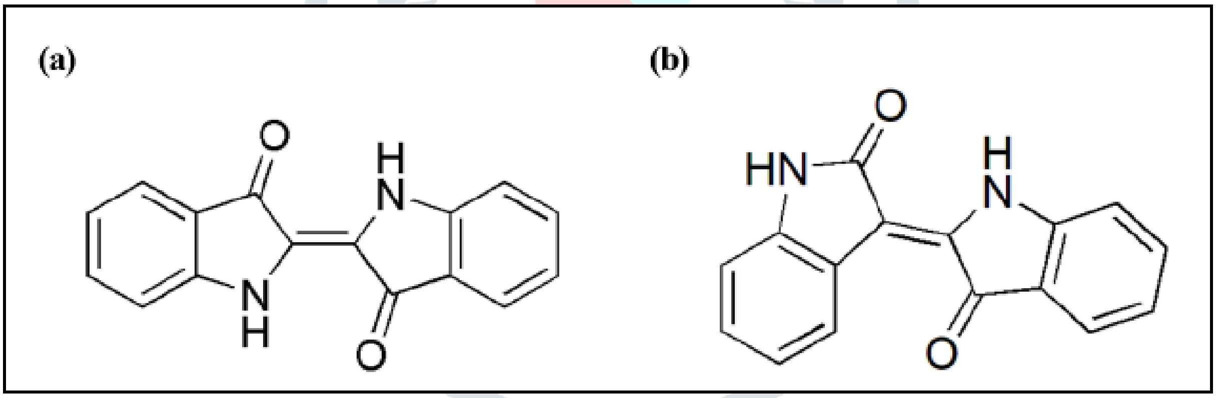

Figure 5: Both Indigo (deep blue colour) and Indirubin (deep red) are isomers (a) Chemical structure of Indigo (b) Indirubin Figure courtesy.

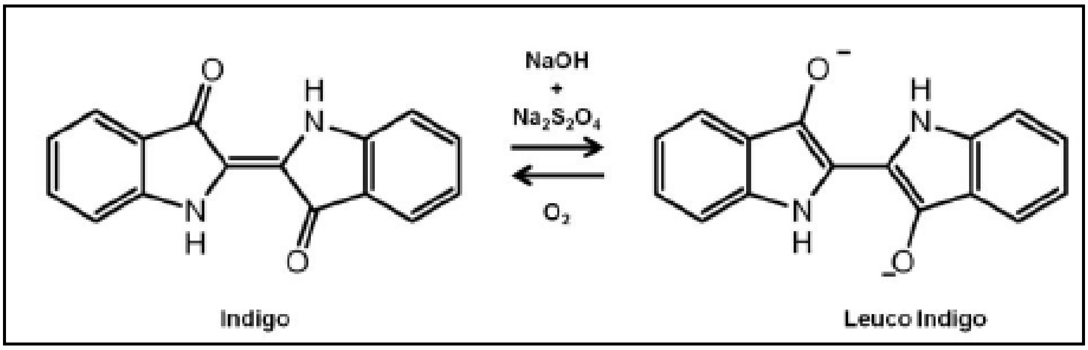

Figure 6: Chemically Structured indigo dye & the colourless form. The water insoluble deep blue coloured indigo converts into a colourless leuco form upon contact with air Figure courtesy.

One of the major cons of indigo is its rapid oxidation into the colourless form once gas is contacted hence most of the industrial dyeing is conducted in a neutral environment. Moreover the amount of Indigo undergoing transformation to its leuco form must be regulated in an industrial setting In Figure 5, chemically structured Indigo and Indirubin have been illustrated and in Figure 6, the chemically structured Indigo & the colourless form has been illustrated.

DISCUSSION

The dyeing industry is dependent upon the role of dyes. The dyes exist either as natural or as synthetic form. Synthetic dyes has all the properties of a dye should have like having longevity, adhesion to textile fibres, resistant to washing and chemical treatment and should fade once the textiles fabrics are exposed to the sun or to the air for a longer period of time and must be cheap to produce at an industrial level. For example the production of commercial Indigo in 1897 meant that dyers were not to be dependent upon the production of Indigo from the Indigo plant, rather they got a cheap source of dye. However, synthetic dyes come with a rider, that they are highly toxic to the environment. The synthetic dyes tend to accumulate in the food chain causing bio-magnification i.e. the concentration of the synthetic dye increases upon increase in the level of the food chain. One of the major reasons for bio-magnification is that synthetic dyes are not bio-degradable which can potentially cause mutations in the organisms inhabiting a particular ecosystem including that of humans.

Natural dyes tend to lose out on some of the property of the synthetic dyes but are considered safe to the environment as they are bio-degradable. Nowadays most of the industrial dyers are now shifting to the usage of natural dyes. One of the problems associated with the extraction of natural dyes that during the extraction, there may be loss of bioactivity, which needs to be further looked into. There are many chromatographic techniques which are linked with mass spectroscopy which not only help to separation of the dye from the textile fibre sample but also help to identify it. One of the dyes in question in this paper is Indigo which is dark blue in colour. Its isomer is Indirubin which is deep red in colour. Moreover, during extraction, the Indigo tends to turn into its colourless leuco form. Thereby care should be taken and the dyeing process should be monitored for potential non-essential colour forms. Moreover, the role of chromatography and mass spectroscopy is essential for determining any dye that has been used to dye a fabric and also to detect alternate form of the same dye that has been used.

CONCLUSION

The dyeing industry is dependent upon natural or on the synthetic form of dye. Synthetic dyes though having properties which makes it commercially attractive is bad for the environment. This has led to the increase in demand for natural origin dyes. Natural dyes are safe for the environment. Moreover, there is a historical interest in deciphering the historical origin of natural dyes on textiles and the fact that natural Indigo being used for many years is found in 3 forms, Indigo, its leuco form &Indirubin makes it an attractive topic for this review paper to be deliberated upon. Various techniques like chromatography which is then linked to mass spectrometer are being used for isolation, separation and the subsequent identification of the dye from the environment. Moreover in the case of Indigo which either has an isomer, Indirubin or its leuco form the detection of this dye is important during the dyeing process and also to observe its presence in textile fabrics of historical value.

The dyeing industry is a multi-million dollar industry where quality is given paramount importance. One of the methods of quality control is analysis of the dyes during and after the dyeing process. Thereby faster and quicker methods of detection must be developed for quick identification of the dye. Moreover, the historians in collaboration with chemists can be expected to devise protocols for quicker detection of the various forms of Indigo on textiles of historical importance. Thus, the present study provides a brief understanding of the various detection methods for natural dyes in historical textiles and explains how these techniques can be used for detection of the various forms and isomers of natural Indigo.

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