Review of Literature

Prior to the synthesis of dyes from by-products of the petrochemical industry all colour was derived from natural sources, including plants. As the awareness of the need to preserve our natural resources increased and attitudes changes towards achieving this, interest is growing in finding renewable resources, which can be used as natural dyes.

2.1 Colour and Its Components

Natural dyes, like all natural products, have a very complex composition; therefore, they need sophisticated analytical methods for their identification. The characterization of the colouring agents in any dye or dye containing plant is a complex task due to the simultaneous presence of dyes, pigments, other minerals, polysaccharides, proteins, oils and/or resins in it. The combination of colorants, and the proportions in which they are present in each plant or animal dye source, form a kind of “fingerprint”. This can be different for every genus (Cardon, 2010).

According to review made by Degano et al., (2010) the identification of natural dyestuff is a challenging task, due to the complexity of their chemical composition and the possible presence of mixtures of chromophores and degradation products.

Natural Dyes have a long and rich history- all the drapes of past were dyed naturally. Specimens of textiles founds from Chaærchänn, dated at about 1000 BC was selected for dye analysis using newly developed protocols. A single blue (from an indigo plant), a red (from madder) and two yellow dyes detected, although the exact plant source for none could be identified with certainty (Zhang et al., 2008).
Analysis of main classes of natural dyes used in ancient times for dyeing textiles- red (anthraquinones), yellow (flavonoids), and known degradation products of flavonols hydrobenzoic acids has been carried out by Surowiec et al., (2007) in the dye extracts from archaeological samples.

Saidman et al., 2002 and Gulrajani et al., 1992 have reviewed the chemistry, chemical composition and chemical based classification of natural dyes having anthraquinone (madder), alpha napthoquinones (henna), flavones (weld), indigoids (indigo and tyrian purple), carotenoids (annatto, saffron), etc. which gave a basic understanding of chemical nature of such colorants.

The barks of Mimusops elengi and Terminalia arjuna have been extracted and the chemical constituents of the colour components responsible for dyeing were identified. The colour components isolated from the barks of these two plant varieties mainly contain flavonoid moiety (Bhuyan and Saikia, 2004).

Bhuyan et al., (2002) also studied the colour component extracted from the roots of Morinda angustifolia Rob using benzene extract and showed its melting point as 280 °C. The compound shows UV/Visible absorption at 446, 299, 291, 265.5 and 232 nm. Colourant is a morindone type of compound containing an anthraquinone group, using ethanol in a soxhlet apparatus and observed that the silk and cotton fabrics can be dyed with this colour component with and without using different mordant.

Extraction, spectroscopic and colouring potential studies of the dye in ginger rhizome (Zingiber officinale) were studied and reported by Popoola et al., (1994). This dye is soluble in hydroxyl based organic solvents and gives one homogenous component on chromatographic separation having λ_{Max} at 420 nm.

Samanta et al., (2008) have studied UV-vis spectra, DSC and FTIR of six selective natural dyes (red sandal wood, jackfruit, sappan wood, marigold, babool and
manjistha) and found that the babool and marigold show dominating UV-absorbance characteristics at 242-250 nm and 370-380 nm, with the 242-250 nm zone very predominant, while manjistha has no such preferential UV-absorbance peak at 242-370 nm zone except at 380 nm.

Samanta et al., (2007) studied the extraction of the dye from jackfruit wood under various pH conditions and reported that the optimum conditions for extraction of the colour component from jackfruit is achieved at pH 11, giving absorbance of colour component at 2.77 at 628 nm.

Samanta et al., (2006) studied extraction of red sandalwood under various pH condition and reported that the optimum conditions for extraction of colour component is achieved at pH 4, giving absorbance of colour component at 2.63 at 603 nm.

Dyeing studies with hydroxyanthraquinones extracted from Indian Madder were performed by Deepti gupta et al., (2001) Studies are being conducted on the dyeing properties of colorants present in Indian madder (Rubia cordifolia). Since the roots of R. cordifolia contains several anthraquinones based colour compounds studies have been performed separately, purify and characterize the major component of the root. It has been found that the roots contain little Alizarin, which is major component of European madder (R. tinctorium). It was found that R. cordifolia contains approximately 10 colorant. The major component is purpurin.

Bhuyan and Saikia (2005) explored native dye yielding plants in Northeastern India. They extracted dye from stem of R. cordifolia Linn, roots of Morinda angustifolia, Leaves of Tectona grandis Linn, Barks of Mimusops elengi, bark of Terminalia arjuna. The colour components responsible for dyeing were isolated and their chemical constituents were established based on chemical and spectroscopic investigation. The plants with their principle colour components were
as, *Morinda angustifolia*, *Rubia cordifolia* and *Tectona grandis* found to contain anthraquinone moieties. Where as *Mimusops elengi* and *Terminalia arjuna* were found to contain flavonoid moieties in their molecules. The dye were used for dyeing of Milberry silk and cotton fibres.

**Fatahi N.et al., (2008)** extracted valuable pigments from petals of Safflower (*Carthamus tinctorus*) with sodium carbonate. Safflower is a essential dye stuff for preparing edible carthamin and safflower yellow dyes. A technique for the analysis of carthamin and *Carthamus* yellow is described. The techniques involves the following three steps, Extraction, measurement of visible absorption spectrum of the colour and thin layer chromatography. Dried safflower powder was used for extraction of water soluble yellow and water insoluble carthamin was obtainable through alkaline extraction, acidification and cellulose absorption. The water soluble safflower yellow showed 405 nm absorption maxima.

**Guinot P.et al., (2009)** extracted flavonoids luteolin-4-O-glucose and 3-methylquercetin first time in saw wort (*Serratula tinctoria*) it was found that it also contains high amount of luteolin and hence could be considered as good source of natural dye.

Oily natural dye for industrial application was made from extracted Sappon wood by using micro emulsion method. The absorbance of the dye extracted from sappon wood by distillation was measured with an ultraviolet/visible spectrometer, the highest absorbance was obtained from the mordant containing 2 weight% of Al. *(lee Dong-Kyu et al., 2008)*

Dye extraction was carried out with distilled water at pH 7 and temperature 70°C. The main component alizarin, purpurin and quinizarin of madder dye were identified by HPLC. Kinetics adsorption of the dye on wool was studied *(Farizadeh et al., 2020).*
The colour components extracted and isolated from the fruits of *Lagerstroemia indica* were characterized by NMR, Mass, IR and UV/Visible spectral techniques. The bio-colorants isolated were found to be quercetin and apigenin (Vinod *et al.*, 2010).

Combined application of various techniques gave valuable information helpful in the identification and characterization of natural colorant. The colour components extracted and isolated from weld plant were characterized by Column Chromatography, TLC, IR, NMR and mas spectrometric techniques. The natural dye extract obtained from the weld was used for the dyeing of wool fibre (Mirjaji *et al.*, 2011).

Saffron the oldest natural dyestuff is obtained from the stigma of *Crocus sativas*. The yellowness of saffron results from the presence of crocins, its main colouring compounds, which are examined by Lech *et al.*, (2009) in the crude methanol extracts by High Performance Liquid Chromatography coupled spectrophotometric and electrospray mass spectrometric detection (HPLC-UV-Vis-ESI MS).

Wool samples, dyed with madder and its principle components alizarin and purpurin were investigated using two complementary experimental techniques: Absorption and amission UV-VIS spectroscopy and chromatography (HPLC-PDA). Results showed that purpurin was the principle component responsible for the spectral and chromatic properties of madder as well as for its degradation products (Clemanti *et al.*, 2007).

The UV-Vis spectrum of morin in aqueous solution without pH control is characterized by two major absorption bands with maxima at 378nm and 261nm (Septhum, 2007).
The colour components from the flowers of Tabebuia argentea have been isolated and characterized by Konaghatta et al., 2011 using spectral techniques as, rutin and epigallocatechin gallate.

The concentrated dye mixtures obtained from flowers, foliage, fruit and branches of Safflower, Carthamus tinctorius, Sweet acacia, Sennacassia acutifolia were subjected to thin layer chromatography to separate the dyes using chloroform:methanol. The compounds of the dyes were detecting using tests to identify the presence of carbohydrate, steroids and terpenes, tannins, phenolic glycosides, anthraquinone glycosides, flavonoids, alalods, saponins and cardiac glycosides (El-Gamal, 1998).

The chief component of Turmeric is curcumin along with other related curcumoids. Curcumin is actually responsible for the yellow colour of the dye (Kakate et al., 2007).

### 2.2 Natural Dyes in Textile Dyeing

Natural dyes are known for their use in colouring of food substrate, leather as well as natural protein fibres like wool, silk and cotton as major areas of application since pre-historic time. India is rich in natural wealth and there are ample scope to explore and revive application of natural dyes on textile, having more scientific knowledge base available (Mohanty et al., 1987). There has been a growing interest since the beginning of the 1990s, in the re-introduction of natural dyes and the dye–yielding plants for textile application.

Dayal and Dobhal (2001) extracted colorants from the leaves of Eucalyptus hybrid, seeds of Cassia tora and Grewia optiva by using aqueous medium under varying condition. These dyes impart fast shades on silk, cotton and jute fabrics. These dyes may help in enhancing the export of silk, wool, cotton and jute garments dyes with natural dye to countries where the use of azo dyes has been banned.
Pan et al., (2003) dyed the grey jute fabric with extracts from deodar leaf, jackfruit leaf and eucalyptus leaf by soaking it in soft water and boiling for 4 hours separately. Lighter shades were obtained after dyeing of bleached jute fabric with the above extracts without applying mordant. Dye uptake increased with the increase in mordant concentration. The use of mordant in the dyeing of jute fabric resulted in deeper shade with goos fastness.

Aqueous extraction of saffron yields a yellow dye with medium wash fastness on wool and poor wash fastness on cotton, but the wash fastness can be improved by treatment with metal salts before dyeing, as studied and reported by Tsatsaroni et al., (1994).

Dixit and Jahan (2005) extracted euphorbia leaves under acidic pH by adding hydrochloric acid, under alkaline pH using sodium carbonate and under aqueous medium, it was observed that the silk fabric dyed under acidic medium produced best shades.

Purohit et al., (2007) extracted natural dyes from different flower parts of Gulmohar Delonix regia and used the dye for dyeing of silk and cotton, extraction were performed with pure methanol.

Extraction of dye from eucalyptus was done by Ali et al., (2007). This work concerned with extraction of dye and its application on cotton fibre, in an endeavour to investigate optimal extraction and application conditions to attain desirable fastness properties.

The alkaline conditions for extraction of natural dye from Henna leaves were optimized and the resulting extract was used to further optimize its dyeing conditions on cotton. Dyeing without any mordant were compared with those obtained with premordanting and postmordanting with alum and iron. It was found that dyeing produced with alkaline extracts of henna leaves have better colour strength than the
dye extracts obtained in distilled water. Furthermore dyeing with alkaline extracts have moderate to good fastness properties and that mordanting did not result in any significant improvement in fastness properties. *(Shaukat Ali et al., 2009)*

The dyeing of cotton and jute with tea as natural dye has been studied by Deo and Desai (1999) and tannins was described as main colouring agent. Dyeing was carried out with and without metal salts as mordants using three different dyeing methods. The colour of the fabrics was investigated on computer colour matching system in terms of K/S, and CIE L a* b* colour –difference value.

*Nishida* and *Kobayashi* (1992) reported properties of natural dye on silk, cotton and cashmilon using alum or ferrous sulphate mordants. The dyeing properties of three natural dyes from vegetable sources were evaluated. Colourfastness to light, colourfastness to washing, exhaustion, and colour strength were compared for Ukon (*Curcuma longa*), Ouren (*Coptis japonica* Makino), and Kariyasu (*Miscanthus tincrrius* Hack) dyes. The light fastness of Kariyasu was very high compared with the other dyes.

Colours were extracted from Hibiscus mutabilis flower with water. The colorant show one major peak at 585 nm. Dyeing parameters were further optimized for textiles dyeing *(Shankar and Vankar, 2007)*. Aqueous extract yields shades with good fastness properties.

Air dried power of the roots of Morinda angustifolia was extracted with ethanol in a soxhlet extractor for 10 hours. The ethanol was then removed under reduced pressure to get a solid mass, which was then extracted with petrileun ether, benzene and methanol. Further the dyeing behaviour of the colouring component on wool in aqueous medium was evaluated *(Bhuyan et al., 2003)*.

*Mathur et al.,* (2001), extracted dye from beet sugar, the colotant was obtained by concentrating beet sugar juice under reduced pressure and evaporating it.
to dryness. It showed three absorption band at 220, 0280, and 530 nm. Colourant was used for dyeing of wool. The optimum concentration of colourant for dyeing was found to be 0.03 per gram of wool at pH 4.5 and temperature 97.5°C.

Wool yarn has been dyed with natural dye extracted from neem bark. The colorant showed two absorption maxima at 275 nm and 374 nm. Dyeing of wool yarn under optimum conditions (pH 4.5, colourant concentration 0.05 gram per gram of wool, treatment time 60 minutes and temperature 97.5°C) shows very good light and wash fastness. (Mathur et al., 2003).

The colouring component of red sandalwood were extracted with organic as well as aqueous alkaline solution from the sandalwood and the physiochemical properties of the extracts were evaluated. The extracted dye was applied on wool and nylon with and without mordant. The fastness of the sample to light and washing studied. (Gulrajani et al., 2003).

The colorimetric properties of a range of yellow dyes, including henna, dolu, kamala, onion skins and turmeric, with various mordants have been studied by Gulrajani et al., (1992).

Bixa Orellana fruits were peeled off to collect seeds. The seeds were then dried and powdered. The extraction of the dye from powdered seed were obtained by using four different solvents namely acetone, ethanol, water and hexane with different polarity. Solvent extraction were performed. Four sample were died with and without use of mordants, washing fastness and light fastness were determined. (Meena Devi, et al., 2013)

Singh Shyam vir et al., (2012) extracted dye from flowers of Erythrina suberosa. A known quantity of flowere were dried, Podered and soaked in warm water overnight. The extract was obtained by boiling it in the same water and after filtration used for dyeing. The dyeing was carried out at optimized dyeing condition.
namely dye extraction time 60 minutes, material to liquor ratio 1:20, dyeing time 50 minutes. Potassium dichromate, ferrous sulphate, stannous chloride with lemon juice were used as mordant.

Eco-friendly natural dyes derived from the plants- Bridelia retusa (bark) and Parkia javanica (skin of fruit pods). The dyeing properties was found to be from the content of anthraquinones, tannins and flavonoid moieties. Dyes were extracted with methanol. Extracted dyes were tried on silk and cotton fabrics, effect of dye concentration on % dye absorption and K/S value was observed. Fastness of the dyes were increased by adding mordants such as CuSO$_4$-5H$_2$O, K$_2$Cr$_2$O$_7$, SnCl$_2$ and Al(NH$_4$)(SO$_4$). The fibres dyed and postmordanted with CuSO$_4$-5H$_2$O and K$_2$Cr$_2$O$_7$ showed deeper shades. (Laitonjam et al., 2014)

Natural dye was extracted from green chilli. The main coloring component in chilli is oleoresin. The dye was extracted with ethanol- water via solvent extraction method. 100g sample was extracted with 500ml of solvent. The material was heated in water bath at 60°C for 60 minutes. Extracted dye was purified and used for dyeing of cotton fabric. Two mordants CuSO$_4$ and FeSO$_4$ were used. Good light fastness, good rub fastness and moderate wash fastness was observed in fabric dyes. (Kulkarni et al., 2011)

Silk and wool fabrics have been dyed with colorant extracted from Rheum emodi in the absence and presence of magnesium sulphate, aluminium sulphate and ferrous sulphate mordants for producing shades of different colours, ranging from yellow to olive green. Coloring component has close resemblance with a anthraquinonoid disperse dye. Colour uptake, rate of dyeing and affinity of colour are found to be more on silk than that for wool under all the conditions studied. Coloured fibres show a common light fastness and wash fastness rating of 4 and 3 respectively (Debashish Das, 2008).
A mixture of two natural dyes namely Terminalia arjuna (fruit) and cochneal in different percentages (80:20, 70:30, 50:50 %) was extracted with water. High colour strength was obtained when using 1g of dye mixture/100 ml water and dyeing the wool fabric for 60 minutes at boil without using salt (Kamel et al., 2001).

Water soluble yellow dye was extracted from turmeric rhizomes (curcuma longa) through aqueous/ solvent extraction procedure. Numerous Shades were obtained with good wash fastness properties (Sachan and Kapoor, 2007).

The optimum dyeing conditions for Henna on to the wool fabrics were investigated. Wool fabrics were dyed with Henna at various time, temperature, concentration and pH conditions. The optimum dyeing conditions for henna on to the wool fabrics are 60°C, pH 7.2, and 45 minutes of dyeing (Park et al., 2004).

A dyeing process was development for two natural dyes extracted from the leaves of teak and the bark of chir on wool is reported by Vedner et al., (1990).

The dyeing substances present in Madder plant were extracted by using solvent extraction method and the woollen fabrics were dyed with both the new madder and extracted madder dye. The colour strength of the extracted dye on woollen fabrics with the raw madder’s colour was also studied through spectrophotometer. It was found that the K/S of extracted madder dye is more than raw madder (Goodarzian and Ekrami, 2010).

In order to explore the role of mordant dyeing on wool fabric by natural plant dyes, such as Semen arecae, Rhizome curcumae longae, Radix rubiae, Pericarpium granati, Fructus gardenia, Lignum sappan and Flos carthami have been carried out. The result showed that the chroma and brightness of colour were promoted by using one kind or two kind of mordants. Additionally mordant played an important role in dye-uptake and dye fastness. But the colour-fastness to sunlight of natural dyestuffs did not meet the criteria of wearable textiles (Takekawa, 2007).
Bleached jute fabric was mordanted with different concentration of potash alum mordant. The mordanted fabrics were dyed with dyed with natural dyes extracted from deodar leaf (*Cedrus deodara*) and eucalyptus leaf (*Eucalyptus globulus*). Natural colour dyed jute fabric premordanted with 8% potash alum showed increased colour yield without affecting the brightness or wash fastness (Zekik and luka, 2001).

Dyed cotton and silk fabric using dyed material (stalk of parijataka flower’s pigment) with the help of selected mordants (alum, FeSO$_4$, CuSO$_4$ and AL,FeSO$_4$) offered golden yellow, golden brown, buff yellow and yellow. It was found that an increase tensile strength and abrasion resistance of dyed fabric after mordant use was observed (Siddiqui et al., 2009).

A study has been conducted on five dye sources namely, Cutch wood, Annato seeds, Coleus leaves, Wallnut bark and Kilmora roots, as a potential material for design in various applications by Varma et al., (2008). After the evaluation, it was found that a natural dye exhibit many pleasant colour combinations, which could probably increase demand of natural dyes in market.

Dyeing of silk with mango, Manjista and marigold- based natural dyes was attempted by Mitsuo et al., (1997). Dyeing with a mixture of these dyes yielded satisfactory colour fastness values even after washing with detergent or soap.

Moiz et al., (2010) used aqueous extract of tea to dye on the wool fabric to produce different shade with different mordants salts like Alum, CuSO$_4$ and FeSO$_4$. The colour of fabric was investigated on Data Colour matching system in terms of K/S and CIE Lab- colour values. Pre, meta and post mordanting methods were followed. Copper was found as good mordant to achieve the best results being a transition metal ion, the effect of good light fastness and wash fastness properties was achieved.
The dried Achillea was used for dyeing Iranian wool yarns. Achillea found to have good agronomic potential as a natural dye in Iran. Dyeing with Achillea in conjunction with metal mordants showed enhancements in its fastness properties. It shows commercial capability for dyeing wool yarns which was mainly used as Pursian carpet piles (Kiumarsi et al., 2009).

The dye obtained from turmeric was used to dye cotton at different dyeing conditions. It has been observed that when dyeing is implemented with mordants, washing and light fastness properties show improvement while rubbing fastness exhibits deterioration (Umbreen et al., 2008).

The four natural dyes such as safflower yellow, gardenia blue, cabbage red and gardenia yellow on wool were studied. The various colour fastness of the dyed samples was good and over 4 grade, but the fastness to light was of 3 grades (Zhang et al., 2006).

Waheed and Alam, (2004) used aqueous extract of Kikar bark (Acacia arabica) and madder barl (Rubia cardifolia) to dye silk fabric by using various metal sulphates as mordants. The fastness properties of dyed samples were determined and comparison was made for control and samples were found to be in the range of good to excellent. The effect of different metal ions has been studied with respect to their influence on colour shade and fastness properties.

Garg and Shinde (1991) reported that premordanting is better rather than post mordanting in case of dyeing carried out with Tesu flowers. Dyes obtained from saponwood and turmeric has been evaluated in terms of premordanting and post mordanting conditions.

lee Young-he et al., (2009), extracted dyes from peony, pomegranate, clove, Coptis chinensis and galnut. Further the dyes were used for dyeing of cotton, silk and
wool fabrics. Antibacterial activities of these fabrics were also checked and were found to be good.

Extraction of dyes from walnut using soxhlet apparatus has been studied. The colour components extracted and isolated from walnut shells were characterized. Extract obtained was used in dyeing polyamide fabrics with different mordants. Results indicate that the dyed material displayed excellent antibacterial activity in presence of ferric sulphate, cupric sulphate and exhibited good and durable fastness properties (Mohammad et al., 2013).

2.3 New Extraction Techniques

Dye extraction is also an important phenomenon as it depends on a number of variations including dye source, solvent time and method by which colorant should be extracted. Many investigations have been carried out for the extraction of colourant from different parts of the plant and their chemical identification. Various studies are reported, where ultrasonic assisted extraction have been used to improve the yield.

Guillaume Cuoco et al., (2009) developed a central composite design for ultrasound assisted extraction of the dye from madder root. The optimal experimental conditions are 18 of extraction, temperature was 36°C and 37/63 MeOH / H2O.

Ultrasound assisted extraction of rutin and quercetin from Euonymus was investigated by Yi Yang et al., (2008). The influence of four extraction variables on extraction yield of rutin and quercetin was discussed. The optimum extraction conditions found were 70% aqueous ethanol, Solvent sample ratio 40:1 (V/W), Extraction time 3x30 minutes.

The influence of ultrasound on natural colorant extraction from dye yielding plants has been studied in comparison with magnetic stirring process. The plant material used are Green wattle bark, Marigold flower, pomegranate rind, 4’o clock
plant flowers and cocks comb flowers. The result indicate there was a significant 13-100% improvement in the extraction efficiency of the colorant obtained from plant materials due to use of ultrasound. (Sivakumar et al., 2011)

The use of Enzyme Assisted Extraction shown increase in yield in the extraction of various natural products. The process was commonly used for food colours and small handicraft and cottage industry, however very limited studies are available on its implication in natural textile industries.

Reverse phase C$_{30}$ HPLC was applied to study the identity of lutein isomers and to monitor the effects of solid contents and elimination of water soluble substances on the isomeric carotenoid profiles of marigold samples treated with enzymes. Enzymatic treatment on a 5% solids slurry produced the marigold meal with highest all trans lutein content (25.1 g/kg dry weight). (Vargas et al., 1997)

According to Vargas et al., 1997 fresh marigold treated with enzymes showed a higher susceptibility to pigment extraction than untreated samples, and the highest carotenoids yield were obtained using the ECONASE-CAP. This enzyme at 0.1% w/w increased extraction from marigold from 1.7 to 7.4 g/kg of marigold flower in dry weight. Such treatments may enhance carotenoid extraction at industrial level as well.

The effect of enzymatic treatment using a commercial enzyme (ECONASE-CAP at pH 5.0 and 0.1% w/w concentration) at different levels of dehydrated marigold meal (5, 10, 15, 20% dry weight), to enhance carotenoid extraction, was evaluated. The measurement of carotenoid was also carried out in samples in which the water soluble compounds were previously eliminated. Total carotenoids ranged from 11.4 to 17.4 g/kg and 18 to 24.7 g/kg of control and treated marigold meal respectively. Highest amount of carotenoids were noted when 5% level of treated material was used. (Vargas et al., 1997)
Barzana et al., 2002, proposed an alternative extraction process for carotenoids, consisting of a simultaneous enzymatic treatment and solvent extraction. The proposed process employs milled fresh flower directly as raw material, eliminating the inefficient silage and drying operation as well as the generation of hard to deal with aqueous effluents present in traditional processes. The process developed was tested at the 80L scale, where under optimal conditions a carotenoid recovery yield of 97% was obtained.

Bolanos et al., 2004, studied the effect of non-commercial preparation on xanthophyll extraction from marigold flower. The enzymatic extracts was synthesized by endogenous microorganism. The result show that the extraction yield depends directly on the extent of enzymatic hydrolysis of cell walls in the flower petals and then it is possible to reach yields in excess of those previously reported for treatments with commercially available enzymes (29.3g/kg of dry weight). The enhanced extraction system appears to be very competitive when compared to the traditional process and current alternatives.

Inci Cinar (2004) has done enzymatic extraction of carotenoid from orange peel, sweet potato and using different concentrations of Cellulase and Pectinase combinations. The high cost of enzymes can greatly be reduced by extending the extraction time for the same level of the colour yield. Stability of enzyme extracted pigments were much higher than solvent extracted pigments for all treatments under all storage conditions.

Although dyeing of textile fabrics with natural dyes has been extensively investigated, little information is available on the new techniques, which involves a environment friendly extraction processes, so as to avail their use for industrial application. The commercialization of natural dyes can be successful only with a systematic scientific approach to extraction, purification and chemical characterization of unexplored dye sources.
In order to explore newer natural dye sources, for getting variety in colour range and to explore their extraction processes four plants material have been chosen.

- Pomegranate (*Punica granatum*) rind.
- Marigold (*Tagets erecta*) flower petals
- Red onion (*Allium cepa*) peels
- Dahlia (Arabian night) flower petals

**Pomegranate Rind**

The principal colouring components from pomegranate (*Punica granatum*) rind are tannins and flavonols. Pomegranate rind has been known to be very rich in hydrolysable tannins, mainly Punicalin, Penduculagin, and Punicalagin (*Seeram et al.*, 2005). (Fig. 2.1)

![Chemical structure of a.Punicalin, b. Penduculagin, c. Punicalagin](image)

**Fig. 2.1:** Chemical structure of a. Punicalin, b. Penduculagin, c. Punicalagin
Anthocyanins present in pomegranate rind are mainly cyanidin, pelargonidin, and delphinidin (Noda et al., 2002). Flavonoids present in pomegranate rinds are kaempferol, luteolin and quercetin (Van.Elswijk et al., 2004).

It is interesting that though the pomegranate peels have been used since antiquity in the Middle East as colorant for textiles because of their high tannin and phenolic contents the literature is rare.

Kulkarni et al., 2011, reported N-methyl granatonine as the main coloring agent in pomegranate rind. Dye was extracted with solvent extraction method by using ethanol water (40:60) at 60 °C and extraction time was 60 minutes. Cotton fabric was dyed using mordants copper sulphate and ferrous sulphate.

Goodarzian et al., 2010, extracted dye from pomegranate rind with solvent extraction process separately by using water and ethanol and termed them as raw and extracted dye respectively. Both were used for dyeing of woolen fabric, it was found that the colour strength of extracted dye is more than that of its raw dye.

Dye was extracted from pomegranate rind with water and further used for dyeing of Pashmina wool at acidic pH. Isolation and then structural determination of seven colouring components of dye were also performed by Chhagan et al., 2011.

Marigold Flowers

The Marigold flowers contain flavonols-quercetagetol which is derivative of quercetol. It is accompanied by two of its glucosides and lutein. It also contains patulutol and some ellagic acid which acts as mordant. Flavonoids, such as kaempferol or quercetin-like structures, have already been reported (Ivancheva et al., 1993). Furthermore Tarpo (1967, 1968, 1969) and Bhardwaj et al., (1990) reported the presence of patuletin 7-0 glucoside (patulitrin) and of patuletin, Quercetagetin, quercetagetin 7-o glucoside and luteolin, but no structural evidence was provided to confirm the structure of patulitrin and patuletin. Then Guinot et al., (2008) extracted
flavonoids from marigold flowers and were investigated for their dyeing potential. Patulitrin and Patuletin were isolated and established their structure using NMR and HPLC-MS. Patulitrin and Patuletin were identified as the main flavonoids present in dyeing bath. Several solvents were tested for their potential to extract the flavonoids, the use of a water-ethanol mixture gave a high extraction efficiency and allowed selective extraction of patulitrins and patuletin.

![Chemical structure of patulitrin (1), patuletin (2)](image)

**Fig. 2.2:** Chemical structure of patulitrin (1), patuletin (2)

*Montazer et al., (2007)* performed dyeing of wool with marigold as a source of yellow colour. To do this, wool yarns treated with alum dyed with marigold and then pre-treated with different percentages of ammonia solution. There is no difference between the wash fastness of untreated and the ammonia treated dyed yarns. The colour of the marigold dyed wool was changed after wash fastness test. This created a colour hue on the samples with higher absorbance. The result of the light fastness also showed a fading of the marigold dyed yarns.
An experiment was conducted to study the use of an extract isolated from marigold as a natural dye. The dye potential of the extract was evaluated by dyeing using the flower, in 100% cotton and silk fabrics under normal dyeing conditions. Studies of the dyeability, wash fastness, light fastness and colour hue were undertaken. ThwL, a and b values of dyed material were also studied. (Jothi 2008)

Sarkar et al., (2005) worked on three varieties of fresh marigold flowers viz lemon yellow, golden yellow and maroon yellow as raw materials for natural dyeing of cotton, wool and silk textiles. Material to liquor ratio and extraction time were optimized. Material were dyed with use of mordants.

Red Onion Peels

In Fruits and vegetables, flavonols and their glycosides are found predominantly in the skin where they serve , among others, as ultraviolet protection. Although the onion bulb grows under the soil at least partly, its skin- the non edible dry peel, is also richer in total flavonoids compared to the edible flesh. Nine major compounds were found in dry onion skin with two dominating :quercetin aglycone and quercetin 4′-glucoside (Suh et al., 1999, Ly et al., 2005).

Flavonoids are generally found at higher concentrations in the outer layers of fruits and vegetables (Tsushid and Suzuki, 1996). The flavonoids present in the peel are mainly aglycons due to flavonols glucoside hydrolysis during the peel formation. (Pricr and Rhodes 1997, Takhama and Hirola 2000)

The red –purple colour of red onion is given by the presence of anthocyanins in epidermal cells of the scale leaves in the form of four major anthocyanins cyanidin -3- glucoside, cyanidine-3-laminariboside, cyanidin-3-malonylglicoside and cyanidin-3- malonylaminariboside. (Donner et al., Wu and Prior, 2005)

Besides cyanidin derivatives constituting over 50% of the total anthocyanins, further delphinidin and petunidin derivatives were detected in the Tropea red onion
(Allium cepa) (Gennaro et al., 2002). From the pigmented scales of red onion quercetin-3,7,4′-triglucoside was isolated and a dihydro-flavonols, taxifolin-4′-glucoside was detected. (Fossen et al., 1998)

Quercetin is concentrated in dry skin of most onions, where its oxidation products 3,4 dihydroxy benzoic acid and 2,4,6-trihydroxyphenyl glycosylic acid imparts the brown colour.

![Quercetin](image.png)

**Fig. 2.3 : Chemical structure of Quercetin**

Innovative dyeing with onion has been shown to give good dyeing result. Pretreatment with 2% metal mordant and using 5% of plant extract was found to be optimum and showed very good fastness properties for cotton, wool and silk dyed fabric. The dye has good potential of uptake, adherence to the fabric and has good wash and light fastness. (Venkar P.S. et al., 2009)

**Dahlia flower**

Dahlia flowers are rich in anthocyanins. In early 1915, Willstatter et al., reported that the chief anthocyanins of Dahlia are 3:5 diglucosides cyanidin and pelargondin and the flavones are apigenin and a yellow isomeric tri-hydroxy compound. In 1990 Kasumov et.al. reported anthocyanins contained are pelargonidin,
delphinidin-3,5-diglucoside, malvidin, and cyanidin-3-glucoside. The flower-colour range results from the mixture of the flavone and anthocyanin pigments in varying proportions and intensities. Thus, anthocyanin with yellow flavone appears orange to scarlet according to the intensity of the anthocyanin. Similarly anthocyanin with ivory flavone gives magenta and purple colors. The ivory-colored flavone, occurring in the dahlia has the property of changing the anthocyanin colour in the direction of blue (Lawrence, 1932, Halbwirth et al., 2008). The deep red dahlia contains 19.4 % of cyanin in the dried flower (Mallison, 1915).

Suzuki et al., 2002, have even used dahlia anthocyanins for cDNA cloning. Dahlia colorant are also suitable for colouring confectionery, bakery products, syrups, beverages, and other food products (Blank, 1947).