1. INTRODUCTION

Colour is one of the elements of nature which made human life artistic and ravishing in the world. Dye is derived from the English word ‘Daeg’ or ‘Daeh’ means colour (Ravi Upadhyay and Mahendra Singh Choudhary, 2014). A dye or dyestuff is generally a coloured organic compound or mixture of compounds that impart colour to a substrate like cloth, paper, plastic or leather in a rationally enduring fashion. All the colouring substances are not dyes. The requisites to be a true dye are, it should have colour stability, it should be able to attach itself to the substrate material, must be soluble in water and it should have fastness property to washing, light, perspiration, heat, dry cleaning and other factors (Padma, 2007).

Natural dyes are obtained from plants, animals, insects and minerals (Mahabub Hasan et al., 2015). Dyes obtained from plants and animals are pigmentary molecules which impart colour to the substrates. These molecules have an aromatic ring structure with a side chain called chromophore which is needed for resonance and imparting colour. Auxochromes are functional groups which get attached with chromophore and thereby impart colour to fabrics (Shyam Vir Singh and Purohit, 2012). India is one of the world’s twelve mega diversity countries and one of the eight major centres of origin and diversification of domesticated taxa. It has approximately 490,000 plant species and harbours assets of useful germplasm resources and without doubt the plant kingdom is a treasure-house of varied natural products. One such product we obtain from nature is the dye (Shyam Vir Singh and Purohit, 2012). There are more than 450 dye yielding plants in India (Chandramouli, 1995).
The art of dyeing dates back to Bronze Age in Europe. All the dyestuffs were obtained from natural sources particularly from vegetable and animal matter until mid-19th century. The most famous and costly dye was tyrian purple which was obtained from spiny dye-murex shellfish which is noted in Bible. It was prepared by the Phoenician during seventh century. This dye was made from a clear fluid secreted by shellfish, which when oxidized produce red to bluish purple colour. Since the dye was difficult to get, it was used only in finest garments and became associated with royalty and aristocrats. Information of this Tyrian purple vanished during middle ages and was not rediscovered (Siva, 2007 and Belfer, 1972). The usage of natural dyeing materials during ancient times in India is very well evident from the wall paintings of Ajanta, Ellora and Sittannavasal (Ravi Upadhyay and Mahendra Singh Choudhary, 2014). Historical records show the use of natural colourants during Greco-Roman period. Extraction and application of natural dyes was thoroughly described in ancient Egyptian hieroglyphs. The coloured silk and muslin fabric of 16th and 17th centuries proved that natural dyes are in use since ancient times.

Different types of dyes derived from vegetable products and plants were used from the period of classical age (A.D. 300-700) to the medieval period of Indian history. The dyes include kampillaka (*Mallotus philippinensis*), abhaya (*Terminalia chebula*), pattanga (*Caesaplinia sappan*), amalaka (*Emblic myrobalan*), jatuka (a species of *Oldenlandia*), nila (*Indigofera tinctoria*), ayas (Iron), kesasa (sulphate of iron), anjana (sulphate of antimony), turrho (sulphate of copper) and sakala (black dye obtained from cowdung). The medieval period A.D 900 and late medieval period 18th century A.D. introduced the use of mordants such as tuvari (alum), iron mordant for fixing green, blue and violet dyes and aluminium mordant for fixing red dye. Kalamkari work of Machilipatnam and Sri Kalahasti and Tanjavur in eighteenth century used Chayroot and
indigo for cotton painting. There were about seventeen Neel Kuthis (Indigo houses) in Jessore and Nadia districts of West Bengal, which was later closed down with the introduction of synthetic indigo from Germany in 1864. Collection of 168 fabrics dyed by indigenous processes is displayed in Bengal Economic Museum, Calcutta. In Padmanabhapuram near Kanyakumari, Tamil Nadu, the wall paintings of the palace reports the use of vegetable colours in the 18th and 19th century A.D. (Padma, 2007).

The French Pyrene caves of Niaux and Spanish caves of Elcatillo and Altamira revealed the use of mineral earths and inorganic pigments like ferrous oxide for yellow, ferric oxide for red and copper carbonate for blue in their mural paintings (Valladas et al., 1992). Vedas described the use of different coloured dyes such as red dye from lac, safflower and madder, blue from indigo, yellow from turmeric and saffron and brown from cutch (Singh, 1985). India had a virtual monopoly in the production of textile materials which is painted, dyed and printed with natural dyes during 7th century (Parkes, 2002). People of Mohanjodaro (3000 B.C.) used natural dyes which were revealed during the excavation of ancient Happan sites, where a fragment of madder dyed cotton fabric was found (Padma 2007). Roman empire reported purple dyeing craft. The ancient Egyptian cuneiform texts were found which used natural colourants like madder, Tyrian purple Muex sp, *Indigofera* sp. etc (Puntener and Schlesinger, 2000; Zhang and Laursen, 2005). North Africa dyers used madder, cochineal and kermes as sources of colourants (Lucas and Harris, 1999; Crowfoot, 1944).

Egyptians used archil, which is a purple colour obtained from marine algae often found in rocks of Mediterranean sea, a red colour alkanet prepared from *Alkanna tinctoria* roots, red colour from *Rubia tinctorum*, indigo from *Indigofera* sp. leaves and a blue colour from fermentation of the leaves of *Isatis tinctoria* (Golyon, 1996; Redford, 2001 and Van et al., 1994). Leaves of *Lawsonia inermis* (Henna) was used to dye nails
of Egyptian mummies (Dawson, 2006 and Mohd Yusuf et al., 2015). Red coloured fabrics of King Tutankhamen of Egypt when subjected to chemical tests revealed the presence of alizarin, a pigment of madder plant. The mummies of Egypt were found wrapped with the naturally dyed cloth (Gulrajani, 1992). During wars and religious festivals primitive men used plant dyes to colour animal skin and also their own skin, because they believed that the colours give them magical powers and help them protect from evil things and can attain victory in the wars (Siva, 2003). The most important documentation in the dyeing history is Hudud-ul-Alam (982-983) which confirms the use of different colours such as red, blue, black, green, purple and shades of gold and pink with natural dyestuffs (Ferreira et al., 2004 ; Holme, 2006 and Mussak, 2009). In 1880 the revolution happened when madder and indigo dyestuffs were discovered. These two natural dyes were successfully synthesized and marketed in Germany.

Ancient dyeing method includes sticking the plants to the fabric and crushed pigments were rubbed to the textile materials. The technique has been improved with time by boiling the dye source with the fabric (Jothi, 2008). Although native knowledge system has been practiced over years, the use of natural dyes was declined over generations due to the lack of documentation and information available on databases. Due to the lack of accurate technical knowledge on extracting and dyeing technique, natural dyes have not been commercially succeeded like synthetic dyes (Shyam Vir Singh and Purohit, 2012).

William Henry Perkins in 1856 discovered the first synthetic dye while working with coal tar to find artificial quinine for treating malaria, which appeared violet in colour and he named it as ‘Mauve’. This declined the use of natural dyes tremendously because the natural dyes failed to accomplish the demand of the market (Shyam Vir Singh and Purohit, 2012). Magenta was discovered by Verguin in 1859. The first water
soluble acid dye was discovered by Nicholson. The diazo reaction upon the azo groups was discovered by Peter Greiss close to Nineteenth century (Anjali, 2003). Most of the synthetic dyes are aromatic organic compounds which are non-ionic, cationic or anionic. Methyl violet is a cationic dye and azo dyes are anionic dyes (Zollinger, 2003). Synthetic dyes have a broad spectrum of colours which can be easily and precisely reproduced, cost effective and more colour fast (Glover and Pierce, 1993). At present textile industry uses excessive amount of synthetic dyes due to their less cost, wider range of bright shades and significantly improved fastness properties, to meet the required global utilization of textile colouration (El-Nagar et al., 2005 and Iqbal et al., 2008). But synthetic dyes pose a threat to the environment due to their harmful effects on both the land and water bodies and also on human health. Textile industries have been categorized as most polluting sector by the Ministry of Environment and Forests, Government of India. When the toxicant enters the agriculture field they pollute the soil by rising heavy metal concentration and salinity that affects the plant growth adversely (Zahiruddin Shahin Banu and Kandasamy Murugesen, 2013).

100,00 synthetic dyes are commercially available with a production rate of over 7x10^5 to 1x 10^6 per year and 10-15% of those used dyes enter the environment through effluents (Gupta and Suhas 2009; Mondal 2008). Global consumption of textiles has been estimated around 30 million tonnes and about the rate of 3% per annum has been expected to increase (Rajendran and Thamarai, 2014). For colouring such a huge quantity of textile materials 700,000 tonnes of different dyes are required (Rungruangkitkrai and Mongkolrattanasit, 2012). Most of the synthetic colours are manufactured from petrochemical sources with hazardous chemicals which pollute the environment adversely through their wastes (Ashis and Adwaita, 2011). The synthetic dye residues affect the photosynthetic activity in aquatic life by preventing the light
penetration and the toxic chemicals produced have a deleterious effect on flora, fauna and human beings (Chen et al., 2003 and O’Mahony et al., 2002). Effluent from textile dye industry contains complex mixture of different polluting substances from organochloride based waste to heavy metals due to dye and dyeing process (Correia et al., 1994). The European Economic Community (EEC), Germany, USA, Holland, Canada, India and few environmental agencies like Environmental Protection Agency (EPA), Food and Agriculture Organization (FAO) have recently banned the use of azo dyes, which is a highly pollutant and toxic dye and other synthetic food and textile colourants, thereby increasing the scope of natural dyes (Sivakumar et al., 2010 and Muneer et al., 2010).

Natural dyes are non-toxic, less polluting, non-carcinogenic and non-poisonous. They produce soft, lustrous and soothing shades to human eye. Natural dyes are used in food, textile, cosmetic and pharmaceutical industries. They are used as hair dye and also in dyeing of plastics. They not only provide unique colours but also give antimicrobial, deodourizing and UV-protective functions to the textile materials. In addition to their dye-yielding quality, some of the plants also possess medicinal properties and few of them are Curcuma longa (Turmeric), Crocus sativus (Saffron), Carthamus tinctorius (Safflower), Bixa orellana (Annato), Punica granatum (Pomegranate), Lawsonia inermis (Henna) and Rubia cordifolia (Chengaiah et al., 2010). Natural dye’s global demand per year is around 10,000 tonnes which equals to 1% of the world’s synthetic dye consumption (Sivakumar et al., 2010). Nowadays textile materials dyed with natural dyestuffs are available in market with antimicrobial finishing, UV protective finishing, deodourizing finish and insect-repellent finishing (Mohammad Shahid et al., 2013). Natural dyes are used in solar cells as an eco-friendly and cost effective alternative for complex dye like ruthenium which are commonly called dye-sensitized
solar cell (DSSC), which is another scope of natural dyes to work with (Narayan, 2012 and Patrocinio et al., 2009). The growing concern for food safety and quality has increased the use of natural dyes in food industries to replace the harmful synthetic food colour (Mohammad Shahid et al., 2013). Exports of natural dyes have grown to a remarkable annual rate of 181.0% between January and September 2010 (Shyam Vir Singh and Purohit, 2012). Technology for natural dye production has improved from simple aqueous to complicated solvent systems to sophisticated supercritical fluid extraction system (Siva, 2007). Like synthetic dyes, natural dyes were also used to dye textile materials at every stage like fibre, yarn and fabric and different vessels such as aluminium, iron, stainless steel and copper were used for natural dyeing process (Sujata Saxena and Raja, 2014).

Few companies that produce natural dyes commercially include De la Robbia in Milan, Allegro Natural Dyes in USA, Livos Pflanzenchemie Forschungs- und Entwicklungs- GmbH in Germany, Bleu de Pastel in France and Rubia Pigmenta Naturalia in Netherlands (Hwang et al., 2008 and Padma, 2007). Alps industry is one of the major natural dyes producing industry in India. The production capacity of the industry is 300 tonnes per year. Other Indian companies include Satal Katha, Sam and Ram, A.M. A. Herbal, D. Manohar Lal, etc (Gulrajani, 2001).

Natural dyes have no disposal problems but have problems such as colour yield, availability, reproduction of shades, stability and complexity of dyeing process (Prabhu and Bhute, 2012). Tedious extraction process, low colour value and increased time hikes the cost of dyeing with natural dyes compared to synthetic dyes. Other problems include difficulty in collecting plants, lack of standardization of the extraction and dyeing process, lack of technical knowledge and availability of species. In order to get 14 gm of Tyrian purple dye, about 1200 molluses were needed, so the availability of
species in abundant is required. Detailed studies are needed to explore the potential and easily reproducible dye-yielding plants. There is an immediate need for collection, assessment and characterization of dye-yielding plants and the dye obtained from them and most importantly the documentation of such plants and the standardization methods to overcome the drawbacks of natural dyes (Siva, 2007). Since natural dyes are renewable and easily biodegradable, they are sustainable but could not fulfill the massive demand of the textile sector. Over exploitation of natural resources may lead to deforestation and threaten endangered species. To avoid such problems, Global Organic Textiles Standard (GOTS) permitted the use of safe synthetic dyes and prohibited the natural dyes from endangered species (Sujata Saxena and Raja, 2014).

A limitation in the use of natural dyes in textile dyeing is inadequate fastness properties. To overcome this problem, chemical called mordant was used. The word mordant comes from Latin word “mordere” which means “to bite”. A mordant is a chemical that produce an affinity between the textile material and the dye by forming a chemical bond with the colourant, thereby enhancing the dye fixation and improving the colour shade and fastness properties (Padma, 2000). Although metal mordants improve the affinity and fastness properties, the effluent generated contains residual toxic metal ions which bring out negative impact on the environment (Zheng et al., 2011 and Li et al., 2016). So recently there is an extensive research going on to discover safe, non-toxic mordants from natural sources and they are called as biomordants.

The availability of natural dyes can be increased to a different level in future by biotechnological interventions like tissue culture or genetic engineering resulting in mass production of these dyes at low cost thereby their usage can become sustainable for mainstream textile processing (Sujata Saxena and Raja, 2014). Recently, the interest towards the development and applications of natural colourants including different
features like identifying new sources, extraction, formulation, purification and stability were increased. Though detailed studies were carried out in this area, the socio-economic capability of production of natural dye and its commercial application for sustainable utilization as bio-resources have a great future scope for the identification of natural pigments having wide industrial applications. More experimental observations should be concentrated to acquire novel techniques for producing natural colourants as a compatible, eco-friendly alternative for synthetic colourants for making greener world (Mohd Yusuf et al., 2017).

1.1 SIGNIFICANCE OF THE STUDY

The use of non-toxic and eco-friendly natural dyes on textile industry has become a matter of significant importance because of the increased environmental awareness to avoid hazardous synthetic dyes. Synthetic dyes pose a threat to the environment due to their harmful effects on both the land and water bodies and also on human health. Most of the synthetic colours are manufactured from petrochemical sources with hazardous chemicals which pollute the environment adversely through their waste released. Natural dyes produce very uncommon, soothing and soft shades as compared to synthetic dyes. Therefore, in the present study natural dyes were extracted from leaves of *Acalypha wilkesiana*, flowers of *Torenia fournieri* and fruit rind (agrowaste) of *Punica granatum*. The plants used in the study were common ornamental plants and agrowaste. There is a lack of technical knowledge of standardisation of extraction and dyeing technique in case of natural dyes. So, the aqueous extraction of dye from all three plant sources was optimised to yield maximum amount of dye. Dyeing of cotton and silk yarn was optimised for the better dye uptake. The use of harmful chemical mordants also contributes to the toxicity of the effluent released from textile industries. Biomordant has been gaining interest recently to avoid the pollution
caused by harmful chemical mordants. In the present study, chemical mordant alum which is less toxic and biomordant tannin obtained from bark of *Peltophorum pterocarpum* and seed coat of *Tamarindus indica* were used for better dye uptake and colour fastness. Ultrasound is efficient and energy conservative which makes the dyeing much faster and less time consuming, cost effective and also provides better fastness properties. Both conventional and sonicator (ultrasound) dyeing showed good dye uptake and colour fastness, however sonicator showed comparatively better results than conventional method of dyeing. Dyes that are obtained from natural sources like plants, animals and insects are pigmentary molecules that are responsible for the colour. The dye extracts were characterized to study the pigment and stability of the dye powder for a period of one month proves that the dye can be stored effectively and used commercially by the textile industries. The dye effluent released from textile industries affects the agricultural crops, organisms in water bodies and also human beings. Effluents are discharged in the agricultural fields without treatment of water. Even if treated in few cases, the residue of toxins still remains in the effluent thereby affecting the crops and soil directly. Germination, growth and yield of the important cereal crop *Oryza sativa* L. was not affected by the dye effluents obtained from the present study when compared to the industrial effluent collected from Kancheepuram which contains synthetic dye and harmful chemicals. Thus, these non-toxic, easily biodegradable, eco-friendly dyes can be potentially used by the textile industries in large scale without polluting the environment.

### 1.2 OBJECTIVES

- Extraction of dye from leaves of *Acalypha wilkesiana*, flowers of *Torenia fournieri*, fruit rind of *Punica granatum* (pomegranate).
- Optimisation of aqueous extraction of dye.
- Optimisation of chemical and biomordants.
• Optimisation of dyeing of cotton and silk yarn with dye extracts using conventional and sonicator methods.
• Characterization of dyes with the help of spectroscopic and chromatographic techniques.
• Study of stability of dye powder for a period of 30 days.
• Study on effect of dye effluent on commercially important crop plant (Oryza sativa L.) in pot culture experiment.