

**APPRAISAL OF FASTNESS AND TENSILE PROPERTIES
OF COTTON FABRIC DYED WITH NATURAL
COLOURANTS BY PAD-STEAM METHOD**



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**COLLEGE OF HOME ECONOMICS
UNIVERSITY OF PESHAWAR**

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Shahnaz Parveen Khattak

**A dissertation submitted to University of Peshawar for the partial fulfillment of the
requirements for the degree of Doctor of Philosophy in
Home Economics (Textiles & Clothing)**

**COLLEGE OF HOME ECONOMICS
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CERTIFICATE OF APPROVAL

This dissertation titled “*Appraisal of Fastness and Tensile Properties of Cotton Fabric Dyed with Natural Colourants by Pad-Steam Method*” submitted to University of Peshawar by Shahnaz Parveen Khattak is hereby approved and recommended as partial fulfillment for the award of Degree of Doctor of Philosophy in Home Economics (Textiles & Clothing).

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Dedication

This dissertation is dedicated to

My father,

Prof. Dr. Iqbal Nasim Khattak:

My source of inspiration for higher studies

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Shahnaz Khattak
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ABSTRACT

This study was conducted to appraise the fastness properties of some natural dyes of plant origin on cotton fabric. Owing to the growing trend of going “green” throughout the world, a renewed international interest has developed in the dyeing of textiles with natural colourants. These dyes exhibit better biodegradability and are usually well compatible with the environment. They contain natural colouring matter which is generally non-allergic, non-toxic, non-carcinogenic and non-hazardous to the user and environment. Common drawbacks of natural dyes are their non-uniform shades and poor to moderate colourfastness. In this research project, solvent extracted dyes from alkanet (*Alkana tinctoria*), cutch (*Acacia catechu*), madder (*Rubia tinctorum*) and ready to use dyes from marigold flower (*Tegetes erecta L*) and Turkey red (*Rubia cordifolia*) have been applied on cotton fabric through pad-steam dyeing procedure. To evaluate the possibility of increasing their colour fastness, various dyeing auxiliaries (mordants, UV absorbers, cationizing agents, crosslinkers, etc.) have been applied by pre-treatment and post-treatment techniques. Metallic mordants included aluminium sulphate, copper sulphate, ferric chloride, potassium dichromate and hydrated potassium aluminium sulphate or alum.

Better fastness (wash, light, crocking), colour coordinates (lightness, chroma, hue and colour strength) as well as improvement in tensile strength was achieved with post-mordanting of copper sulphate on most of these dyes. Pre-mordanting of potassium dichromate brutally damaged the tensile strength of the alkanet dyed sample. Cationization of cotton with quaternary ammonium compound (Albafix WFF) has improved the fastness properties, tensile strength as well as relative colour strength (K/S) of cotton dyed with alkanet, cutch and marigold flower dyes. Post-padding of reactive UV absorber based on oxalanilide (UV-SUN) and UV absorber Rayosan C (heterocyclic compound) greatly increased the light fastness of cotton fabric, dyed with these dyes. Similarly, post-treatment of soft polyurethane emulsion (Dicrylan) has enhanced the light and wash fastness as well as retained the tensile strength of natural dyed cotton. The use of crosslinkers could not bring further enhancement in the K/S value of cotton dyed with alkanet and generally, they yielded lighter shade.

Cutch root extract yielded variety of beautiful brown shades with different mordants. It made an excellent demonstration of the colour fastness and tensile strength of cotton. Improved fastness properties and tensile strength have resulted from the post-padding of crosslinkers i. e., Knittex (modified dihydroxyethylene urea) and Fixapret F ECO (modified dimethyloldihydroxyethylene urea) on cutch dyed cotton. Pre-treatments of most of the metallic mordants have decreased the tensile strength of Turkey red dyed cotton to a great extent. Madder was the least successful dye in terms of fastness and tensile properties. The post-padding of crosslinkers glyoxalmonourein (Fixapret CPF) on marigold flower dyed sample imparted good fastness properties in addition to improving the tensile strength of the fabric. However, the shade of sample was lighter (pale yellow) than the other dye formulations. Among the two types of treatments, post padding proved significantly better in most of the dyeing recipes.

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CHAPTER-I

INTRODUCTION AND LITERATURE REVIEW

1.1 INTRODUCTION TO DYEING

Dyes are organic compounds possessing colour due to the presence of radicals called chromophores and auxochromes. Chromophores are believed to be the colour bearing group of the dye molecules. These are unsaturated organic radicals due to which they can absorb or reflect incident electromagnetic radiation even within very narrow band of visible light. They have a conjugated system with a structure of alternating single and double bonds. These molecules display resonance of electron which provides stabilizing force to the organic compounds. Auxochromes such as carboxylic acid, amino, sulfonic acid and hydroxyl groups etc. are the colour helpers. Their presence is equally important in dye molecules. They intensify the hue of colour and influence the solubility of dye due to their polarity.

Dyeing involves an interaction between a textile, a dye, water and some sort of auxiliary agent. Whether anionic or cationic, dye molecules are applied to textile from aqueous solution. Auxiliaries are the chemicals/compounds which assist the process of dyeing. These may include leveling agents, wetting agents, swelling agents, antifoaming agents, detergents and dispersing agents etc. Dyestuffs and dyeing are as old as textiles themselves. Today, colouration of textiles is a complex and specialized science which involves continuous research and advancement.

1.2 HISTORICAL BACKGROUND OF TEXTILE COLOURATION

Until the 20th century, natural dyes were widely used and traded (Ke et al., 2006). These were the only available source for colouring. However, modern dyeing rarely uses them and their application is limited to craft dyers and specialist companies. Most of the dyes used in textile colouration are nowadays synthetic. Research has initiated to find renewable resource of colouring matter from natural products. The current move for the interest in dyes from natural sources also expedited since many countries imposed

stringent environmental standards in response to the allergic and standard reactions exposed by synthetic dyes.

Textile dyeing has been in practice since ancient times. People used natural dyes for colouring rugs, carpets and clothing by using various parts of plants (Gulrajani, 1992). Textile dyeing in today's developed stages has undergone through many changes (Bhatti et al., 2010). In the early age, plants and animals resources were used to dye textiles. However, with the advent of synthetic dyes, their use became limited. The reason was obviously, the variety of colours and shades yielded by synthetic dyes in comparison to these available natural dyes (Deo & Desai, 1999).

1.3 REVIVAL OF NATURAL DYES FOR TEXTILE

Natural dyes are known from prehistoric times for colouring food items, leather and textile fibres like cotton, wool and silk etc. However, they have not attained wide acceptability due to minimal accessibility of standard procedures of dyeing, difficulty in reproducibility and matching as well as lack of sufficient scientific knowledge of chemistry on mechanism of dyes and technology of dyeing. Almost any organic material will produce a colour when boiled in a dye-bath, but only certain plants yield colour that can act as a textile dye. Colouration procedures are aimed not only to add value to the textile articles but also to make them attractive and desirable for customers. Nowadays, many of the textile exporters and commercial dyers are re-looking into the possible usage of natural colourants for the dyeing and printing of textiles.

The word "natural dye or colourant" is used for all such dyes which are obtained from sources such as vegetables, animals and minerals. Most of these dyes have no affinity for fibres and are usually applied with the help of mordants. These can be called the bridging material as they make natural dyes substantive towards textiles. Most of the mordants are usually metallic salts which can make insoluble precipitates so that the dye is fixed in the material and it becomes colourfast. Bringing little variation in the dyeing procedures and using various products as mordants, the same dye can provide a wide range of totally different colours and shades. This vista is not possible in case of synthetic dyes. In addition, through a mix and match system a wide range of new colours and

shades can be created. While some of the natural dyes show enhancement with ageing process, synthetic dyes show fading as the article becomes aged.

Natural dyes are derived from animal (mostly insects) and vegetable sources without any chemical processing. It was in 1856, when new colouration techniques were introduced by William Henry Perkin with the discovery of so called basic dye (synthetic) from coal tar (Corbman, 1985; Bechtold & Mussak, 2009; Ratnapandian et al., 2012). These dyes were different in many respects from the already established natural colourants and were low cost, brilliant and independent of vagaries of agriculture (Trotman, 1984). Under all these circumstances, natural dyes at the industrial level have nearly become obsolete but amongst craftsmen and hobbyists their popularity still exists.

The revival interest of these dyes has led to the scientific investigations and publications of new knowledge and research. In this connection research findings related to various sources of dyes, (Ratnapandian, 2013; Shahid et al., 2013), chemistry of dyes (Sequin-Frey, 1981; Vankar, 2000), extraction and method of application (Gulrajani et al., 2001; Mongkhlorattanasit, 2010), fastness performance of these dyes (Gupta, 1999 a; Gupta, 1999 b) and antibacterial/antifungal treatments (Gupta et al., 2004 a; Gupta et al., 2005; Gupta & Bhaumik, 2007) of natural dyes are now available. Pertaining to the revitalization of natural dyes, there is sufficient development but the current accrued knowledge is yet insufficient for the natural dyes to use them on industrial scale. There is also a need to thoroughly investigate the environmental impact on the increased use and production of natural dyes. The current trend of renewed interest in natural dyes for textiles have also provided opportunity to offer further scope for the development of other areas such as environmental science, biotechnology and textile technology etc. (Hill, 1997; McCarthy, 1997).

For commercialization of natural dyes for textile colouration, the use of modern application techniques need evaluation (Ratnapandian, 2013). Despite their inferior fastness properties and other characteristics such as low colour yield, limited availability and poor reproducibility, they are more acceptable to the people around the world who are environmentally conscious (Nakpathom et al., 2012). These dyes are becoming more of interest because of environmental issues and concern over synthetic dyes.

Until the invention and commercialization of synthetic dyes, the target of textile colouration was mainly achieved by the utilization of natural colours. Synthetic dyes are produced from petrochemical sources through hazardous chemical operations and are supposed to be the cause of many harmful effects on human body such as skin allergies etc. They produce/release toxic and unsafe chemicals during their synthesis which are undesirable. They pose threat of being eco-destructive. In comparison, natural dyes are environment friendly and shades produced by them are soft, uncommon and soothing. Today, consumer has more awareness of these issues due to the availability of greater number of products with green or organic label (Patel et al., 2002 a) which has expedited a resurgent interest in utilizing colours obtained from natural sources (Samanta et al., 2009 a).

In addition to eco friendly textile colouration, some of the colouring matters from natural sources may possess medicinal properties also. These dyes have nowadays attracted the attention of the entire world due to their non-toxic and non-hazardous nature (Goodarzian & Ekrami, 2010). In a study on such colourants (Lokhande & Dorugade, 1999), nylon fabric was coloured with turmeric (*Curcuma longa*), onion (*Allium cepa*) and lac (*Laccifer laeca*), although, it is usually dyed with disperse and acid classes of synthetic dyes. This is all due to the increasing awareness about the chemicals and intermediates required for synthetic dyes being risky and toxic to human and environment. These dyes have also been receiving increasing interest of the researchers as they have been reported for not causing waste water problems (Wang et al., 2012). Common drawbacks of natural dyes are their non-reproducible and non-uniform shades as well as poor to moderate colour fastness (Kumaresan et al, 2013). Their inferior fastness compared with synthetic dyes and the difficulty in extracting and storing the colourant is an obstacle to their use.

Majority of the plants contain coloured material in one or more of their parts. They have natural potential for dye in their root, stem, leaves, flower, berries etc. They have been used since ancient times for many purposes. However, all of these cannot be utilized in textile colouration due to required amount of colour and fastness properties. Plants having dyes with high to moderate fastness properties and colour stability are used

for textile dyeing (Nateri, 2011). Conventional knowledge about natural dyes leads to the conviction that such colourants are environmentally friendlier as compared to their synthetic counterparts. They have many advantages over synthetic dyes as they are generally considered as environmentally responsible (Deo & Paul, 2003). They exhibit better biodegradability and are generally highly compatible with the environment. These dyes contain natural colouring matter which are non-allergic, non-toxic, non-carcinogenic, non-hazardous to environment, warm, appealing and soothing to eyes colours, earth friendly and help in maintaining ecological balance (Mahatma & Tamari, 2005; Moiz et al., 2010). In the present context of eco-friendliness and eco-preservation, their use in the colouration of textile and food has been revived (Mac Dougall, 2002).

The greater part of the natural dyes belongs to the group of mordant dyes. Some other known classes of natural dyes comprise acid, direct, vat and pigment types. While producing or applying synthetic dyes to textiles, some hazardous chemicals are released into the environment (Dutta, 1996). Serious environmental problems result from large quantities of salts/electrolytic used with synthetic dyes on cotton such as direct and reactive for increasing their levelness and dye uptake (Kamel et al., 2009). A typical cotton dye plant discharge large volumes of waste water, loaded with significant amounts of chemicals and dyes (Hauser & Tabb, 2001). Cationizing of cotton is one method of avoiding this problem for the improvement of wash fastness, colour strength and other dyeing properties.

Although synthetic dyes have been cited as the potential cause of skin diseases, respiratory sensitivity and other health and environmental issues, natural colourants are not without some level of toxicity, no matter how the level is (Hill, 1997). Some of the natural dyes such as elderberry colour and yellow safflower have detectable mutagenic effects which represent a concern for food industry. Similarly, some traditional mordants applied with natural dyeing are also objectionable on environmental grounds. These generally include certain tin salts and chrome. It is therefore, desirable to regard no substance (whether natural or synthetic) as being totally harmless. In the recent past, considerable research work has been carried out and published around the globe in the context of revival of traditional dyeing of textile.

1.4 EXPLORING SOURCES OF NATURAL DYES

There are numerous plants that provide natural dyes utilized in the textile industry. Some examples of plants used for producing natural dyes are: alkanet, balsam, bougainvillea, canna, tulsi, arjuna (*Terminalia arjuna*), etc. (Vankar, 2013). *Alkanna tinctoria* (boraginaceae) is obtained from the roots of the alkanet plant. It is used as pharmaceutical and textile colourant. Specie, *Acacia catechu* (mimosaceae) with a common name cutch tree, gives brown colour and its part used for colouring is heartwood. Its colour application has a place in textile (ship sails, mailbags) and calico printing etc.

Marigold flower is grown as a cut flower and a garden flower, in addition to being grown for its medicinal values. These flowers are yellow to orange-red in colour. They have a strong pleasant odor and also a great value in cosmetics treatment. The two genera are tagetes and celandula. Tagetes further includes African marigolds and French marigold. African marigold (*Tagetes erecta* L) is a major source of lutein, which is a popular ingredient used in textile and food industry for colouration (Jothi, 2008). It is nowadays becoming significant due to its excellent colour value. The extracts of marigold flower have also been used in veterinary feeds. Due to the lack of information, this pigment has not fully acquired a potential of being used as natural dye for textile colourations. Studies have been carried out which reveals that this natural extract can dye 100 per cent cotton, wool and silk fabrics. Its pigments are extracted for use in the colouration of food and textiles.

Alkanet (*Alkanna tinctoria*) is a perennial herb which belongs to borage family. It grows as wild weed and has small-sized bright blue flowers with grey-green leaves. It is also known as dyer's alkanet. Its dye, alkannin is obtained from the extracts of dried roots that contain several naphthoquinone derivatives but most of them are alkannin esters. It poses satisfactory antioxidant activity. It is mostly used in the colouration of textiles, food, soap and cosmetics. It can also act as an indicator due to its varying shades in different pH values. For example, it is blue at pH 10; purple at pH 8.8; and red at pH 6.8. Its root extract also changes to blue by treatment with alkali hydroxides (Rekaby et al., 2009).

Madder is a perennial herbaceous climbing plant, the roots of which are utilized as a natural orange to red dye. It belongs to Rubiaceae family. It is also known as manjista or majth. Its roots are very long, cylindrical and flexuous with a thin red bark. Plants belonging to this family are well known for notable quantities of anthraquinone, particularly in the roots. With the help of a mordant, it is suitable to colour both plant and animal based textile fibres with this dye. The principal constituents in Indian madder (*Rubia cordifolia*) are purpurin, munjistin, xanthopurpurin or purpuroxanthin (Chandravanshi & Upadhyay, 2012). The colouring component of madder is located only in its thin red barks of the outer layers of root. Hence dyeing of dark shades will require large quantities of madder roots powder. The extract of madder root is exposed to have brilliant dyeing characteristics. When the extract is applied to woolen yarn it yields dazzling orange to scarlet shades (Bhatt & Kushwah, 2013; Yusuf et al., 2012).

The use of madder root has been found since ancient times for textile dyeing in many parts of the world. The Turkish red dye procedure was introduced in Europe in 17th and 18th Century (Derksen, 2001). Cotton cloth was printed with natural dye extracts from madder, weld, and coreopsis with two mordanting agents, aluminium acetate, and aluminium potassium sulphate in three concentrations viz., 5, 10, and 20 percent. The printed fabric was evaluated for fastness to light and washing. Colourfastness to laundering was greatly influenced by the type of aluminium mordant, whereas, the type of dye had a greater control in light fastness. However, aluminium acetate as mordant did not improve fastness of coreopsis (Haar et al., 2013). Dyeing behavior of cotton fabric with two natural dyes weld and madder with metal mordants alum, copper sulphate and ferrous sulphate was studied by Haji and Barani (2009) to observe the improvement in dye absorption and fastness properties of the samples. Increased dye absorption was related to increasing dyeing time and temperature. A study has been carried out to reconstruct and optimize the methodology of extraction, mordanting and dyeing of saffron, turmeric, weld, safflower, Persian berries, henna, dyer's bugloss, Brazil wood, scale insect and madder. Variety of mordants such as SnCl_2 , ZnCl_2 , FeCl_3 , $\text{K}_2\text{C}_2\text{O}_7$, CuSO_4 and $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (Mikropoulou et al., 2009) have been applied for the revival of traditional yellow and red colourants used in the European dyeing techniques.

Scientific interpretation and analysis of natural dyeing processes is essential in order to reveal the economic feasibility of dyeing cellulosic (flax) and other natural fibres with environmentally benign natural dyes. In a study, natural colourants extracted from plant and animal sources cochineal, madder root, red sandalwood and osage orange were used on linen fabrics to check the influence of mordanting on the colour strength of dyed fabrics. Samples were analysed for perspiration, washing and crocking fastness also (Sarkar, 2003). A different study was carried out to investigate the application of extracts of madder root and walloon oak together in the same dye-bath (Deveglu et al., 2012) and weld and walloon oak (Deveglu et al., 2011) on silk fabric. Good wash and rubbing fastness silk fabrics was reported from these findings. This combination of dyes could prove suitable option for eco friendly dyeing of fibres. Gupta et al. (2004 a) have applied purpurin and munjistin on nylon fabrics to evaluate the light fastness of natural anthraquinone dyes. Post-mordanting with ferrous or copper sulphate produced good to excellent light stability. It is worth mentioning that not only the type of mordant but the method of mordanting is also critical in the determination of light fastness of natural dyes on nylon.

Another important plant-based dye has been obtained from eucalyptus leaves. The dye is yellowish-brown in colour. It contains a colouring substance having plentiful natural tannins and polyphenols (Mongkhlorattanasit et al., 2011 a) which varies from 10-12% (Ali et al., 2007). It gives out a dark grayish-brown shade with ferrous sulphate mordant on silk fabric. Its wash fastness has been found good, whereas, the light fastness is only fair. Studies on this natural dye have shown that by the help of metal mordants, it has potential application in the fabric colouring and UV protection. It has also been reported by Mongkhlorattanasit et al. (2011b) that the UPF value (Ultra-violet protection factor) of silk fabrics dyed by this colourant ranges between good to excellent with increasing the concentration of dye. Moreover, better UPF as well as darker shades have been observed while using ferrous sulphate as mordant.

Eucalyptus leaves contain colouring components described as tannins and flavonoids (yellow compounds) in literature. About 90 per cent of the yellow dyes are flavonoids. Generally, they produce pale shade with quicker fading. Wash fastness rating

of natural yellow dyes ranges from fair to excellent (Samanta & Konar, 2011). Yellow synthetic dyes can possibly be substituted by a natural dye from turmeric (*Curcuma longa*) or curcumin (Adeel et al., 2011). A fabric treated through radiation and dyed with extracts of turmeric has shown improved fastness properties along with increased colour strength and requirement of lesser concentration of mordant. The use of curcumin is very common both in food and textiles. It is a non-toxic dye which also has an anti-microbial ability on wool (Han & Yang, 2005).

A natural dye carthamin has been examined for its light fastness. It was extracted from safflower (*Carthamus tintorius L*) or dyer's saffron. Carthamin is obtained from fresh or dried flowers and is responsible for the red constituent. It is used in food, cosmetic and textile dyeing. Historically, this dye was used as red dye stuff for colouring cotton and silk fabrics. However, due to its inherent poor light fastness, its use is limited in modern-day application (Oda, 2001a). The yellow colourant and tannin reacting with the salt of complex forming metals enhance absorption of light in the visible region of spectrum (Mongkholrattanasit et al., 2009). Ali (2007) conducted a comprehensive investigation on the dyeing of cotton with reactive dyes and alkaline extracts of some natural colourants from indigenous plants namely acacia bark, henna leaves, turmeric rhizome and eucalyptus leaves. Mordants have been found useful in improving wash fastness of acacia bark. This has been attributed to the formation of insoluble colour complex on fabric which might remain as an aggregate of molecules. The best possible relative colour strength from alkaline extracts of acacia bark was hypothesized due to mordant and dye affinity and the blessing of the negative zeta potential which play a vital role in the electrical characterization of fabrics in wet processing. Likewise, better light fastness was available from the post-mordanting of iron. Acacia extract contains tannin/polyphenols which are utilized as mordanting agent as well. The rubbing fastness of samples dyed without mordants was better than the mordanted samples. The dyed cotton fabric postmordanting with FeSO_4 was almost completely matched with sample dyed with reactive dyes. The colour coordinate values of samples dyed with natural and synthetic dyes were comparable regarding their intensity, shades and tones etc. It was deduced that all these natural dyes except turmeric, have admirable potential to proceed as co-partner with synthetic dyes.

Natural dye has also been obtained from a shrub or small tree called *Lawsonia inermis* (mehandi or henna). It is frequently cultivated in Pakistan, India, Afghanistan, Iran, Egypt and Yemen etc. Its ancient use is evidenced from henna dyed nails of Egyptian mummies found in the tombs (Yusuf et al., 2012). In many Asian countries its aqueous paste is used to dye hair and decorate hands in marriage and religious festivals etc. Antibacterial properties of wool fabrics dyed with henna have also been reported (Dev et al., 2009). This dye has a stable crystalline structure; exhibits better mechanical properties and protect cotton fabric more than Remazol reactive dye (El-Nagar et al., 2005). Iqbal et al., (2007) worked on the dyeing of cotton with henna and studied the effect of UV radiation on the dyed samples. They reported that the colour fastness properties were improved from moderate to good by the UV radiation.

Indigo carmine (an indigo derivative) is a source of blue dye which is mostly obtained from *Indigofera tinctoria*, the primary commercial specie in Asia. The dyeing of Indigo carmine requires 40-60 °C temperature and 4-5 pH for substantial absorption. An interesting concept of hybrid dyeing with a combination of indigo carmine and other natural colourants in one bath emerged as a result of the earlier investigation by Komboonchoo and Bechtold (2009) which demonstrated advantages in the form of energy, chemical consumptions and water. A natural dye, based on naphthoquinone molecule with red colourant has been isolated from *Arnebia nobilis* roots (Ratanjot in India). It has a wide traditional application in the fields of medicine, pharmacy, food and cosmetics due to its anti-inflammatory, anti-fungal, anti-viral and anti-tumor properties. The dye components in *Arnebia* are hydrophobic. Therefore, they are not anticipated to have an affinity for cotton. Arora et al. (2012) applied the dye on different fibres and found it excellent for its wash, rub and perspiration fastness. However, its light fastness was found to be poor. Its colour yield was different on each fibre, most likely due to the dye fibre interactions. Natural dyes from flavonoid and anthocyanin groups were tested by Bechtold et al. (2006) and their light fastness as well as shades have been found dependant on the mordant type. Wang et al., (2012) efficiently extracted dye from *Alpinia blepharocalyx* K. Schum in the presence of NaOH and 20 minutes ultrasound procedure. The dye exhibited good colour fastness when applied on silk fabric with the help of potassium aluminium sulphate through pre-mordant method. Some of their common

shortcomings are non-uniform and non-reproducible shades (Kumaresan et al., 2013), poor to moderate colour fastness and scarcity of scientific information related to the chemistry of dyeing as well as standardized methods of dyeing (Gulrajani & Gupta, 1992).

Dyes have also been extracted from the leaves of deciduous plants namely flame of forest (*Spathodea campanulata*), silver oak (*Grevillea robusta*), tanner's senna (*Cassia auriculata*), serviceberry (*Amelanchier arborea*) and wattle (*Acacia decurrens*). These were experimented for their fastness properties and K/S values on wool fabrics. Samples dyed with these vegetation exhibited good wash and light fastness properties with the aid of mordants (Raja & Thilagavathi, 2008). Shade and reproducibility of wool fabric was also studied by Bechtold et al. (2007) using aqueous extracts from the bark of ash tree (*Fraxinus excelsior L*) through meta- mordanting ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ as mordant). The type of mordant and textile material, both were found dependable for the shade of dyeing. Natural dye was successfully extracted from *Acaicia nilotica* and good colour fastness properties were reported on cotton through pre-mordanting procedures. Improvement in colour depth and brightness in some cases were achieved without mordanting. While, enhancement in colour fastness properties from mordanting was reported with ferrous sulphate. Overall best results of fastness properties and colour depth were available from double mordanting with ferrous sulphate and tannic acid (Ali et al., 2010).

Natural dyes including cochineal, madder, weld, walnut husks, pomegranate shells and red and white onion skins were applied on wool, mordanted with alum and post- treated with various concentrations of ammonia (Montazer et al., 2004 a). This treatment was reported for: obtaining better colour yield (decrease the lightness value), dullness in the shade and shifting the shade of dyed samples. The yellow- orange shade yielded by white onion skins became bright- orange yellow. Similarly, the shade of madder dyed sample was also altered due to ammonia after treatment. Silk and wool fabrics have been dyed with a herb, dolu (*Rheum emodi*) found in Himalaya (from Kashmir to Sikkim) through exhaust method. All the fastness properties of both the fabrics were found good which were further improved by the use of aluminium sulphate

and ferrous sulphate (Das et al., 2008). Pre-mordanting and post-mordanting were reported as dependable for the improvement of depth of shade. A study was conducted on cotton and silk dyeing in which *Spathodea campanulata* flowers were used to obtain natural dye through various solvent extracts using natural and metallic mordants. The dyed samples were found with excellent crocking and washing fastness and fairly good light fastness performance (Kumerasan et al., 2012; Lokesh & Kumara, 2013).

Natural dyes have been isolated from the leaves, shell dice and coat of hazelnut by aqueous extraction and applied to cotton wool and viscose fabrics by exhaust method through mordants. The waste parts of the hazelnut were found suitable to dye these fibres (Tutak & Benli, 2012). With the intention of achieving the greatest absorbency in the ultraviolet region and finding out ultraviolet protective properties, vegetable dyes extracted by means of optimum extraction conditions from Sophora flower (*Flos sophorae*) were used on silk fabrics. This aqueous solution of vegetable dye was found to have excellent thermal stability in addition to stability in acid environment (Wang et al., 2009). In an investigation on natural colourants on cotton fabric, Gupta et al. (2004 a) applied eleven natural dyes namely acacia, lac, pomegranate, cutch, Himalayan rhubarb, golden dock, indigo, kamala, gall nuts, myrobolan and Indian madder on cotton fabric. The anti-microbial properties against three types of Gram-negative bacteria were checked. Among all these, five of the natural dyes demonstrated activity against one or more types of these bacteria. In addition, kamala, pomegranate and gall nuts also presented good wash fastness properties. These dyes could therefore, be important for the dyeing of gowns and sheets used in hospitals and in items which are less appropriate for laundering such as upholstery, mattresses etc. This study has opened up a new avenue of investigations in the field of natural dyes for textile application.

Besides plants and vegetables, natural dyes such as carmine can also be isolated from dried bodies of insects named cochineal. It was used to be the main red colour in Central America before the Spanish conquest (Kamel et al., 2009). In Peru and India these insects are accumulated for purple colour which is due to the compound called carminic acid (Willmott et al., 1998).

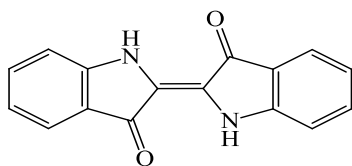
1.5 CLASSIFICATION OF NATURAL DYES

There are number of ways to classify natural dyes/colourants. In the beginning, classification of these dyes was made on the basis of botanical names arranged in alphabetical order. Then its mode of classification was changed, sometimes according to hue or chemical composition or on the method of application. On the basis of hues, natural dyes may be yellow, red, blue and black in colour. Depending on origin, natural dyes are generally classified into vegetable, animal and mineral sources. Examples of vegetable dyes are turmeric, madder, sappan wood, henna, marigold, pomegranate rind etc. Animal (insects) sources of natural dyes include cochineal, kermes and lac. Colourants from mineral origin are the derivative of particular mineral source created from purified inorganic compounds. Some important examples are chrome-yellow, manganese brown, prussian-blue, red lead (sindoor) and zinc white etc. (Kuhad & Singh, 2013). On the basis of method of application, natural dyes may belong to acid, basic or cationic, direct, disperse, mordant and vat classes of dyes (Gulrajani & Gupta, 1992; Kumar & Sinha, 2010). In classification based on structure, the most commonly available natural dyes comprised indigoids, anthraquinones, alpha naphthoquinones, flavones, dihydropyrans, anthocyanidin and carotenoids (Prabhu and Bhute, 2012).

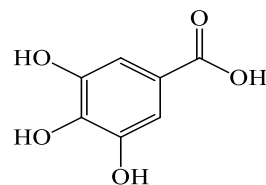
Chemical structure is the basis on which herbal dyes are classified. Within each structure class, grouping is carried out in accordance with hue. These classes are broadly described as: iso- quinoline (yellow), naphthoquinones (brown and purple grey), chromene (orange- yellow), flavones (yellow and brown), anthraquinones (red), indigoids (blue), benzophrones (purple and black) and neutrals, vegetable tannins (Gokhale et al., 2004).

1.6 CHEMISTRY/CHEMICAL STRUCTURES OF NATURAL DYES

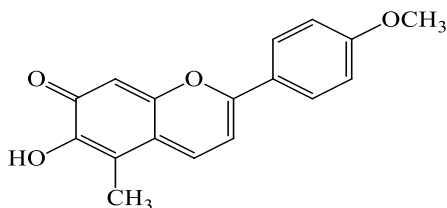
Natural dyes have their own distinct chemical structure and chemical properties. Structures of some of the groups of natural dyes are presented below which show their versatility.



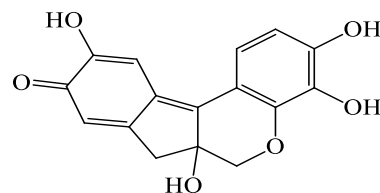
Indigo



Gallic acid



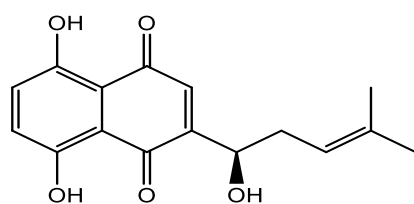
Anthocyanidin



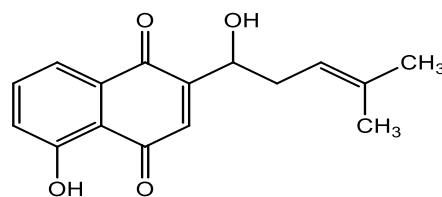
Hematein

Figure 1.1 Chemical structures of some natural dyes as reviewed by Ratnapandian et al. (2011).

The colouring component of Alkanet or *Alkana tinctoria* is alkanin which is believed to have deep red colour in oily or greasy media and violet in alkaline media. The dye is also used as food and cosmetic colouring (Zarkogianni et al., 2010; Margareta, 1981). Its molecular formula $C_{16}H_{16}O_5$ and its chemical structure as naphthoquinone was first determined in 1936. It is presented in Figure 1.2 as below:



(a)



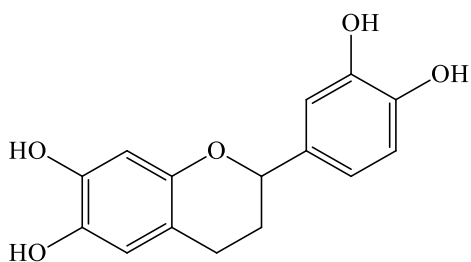
(b)

Alkannin

Figure 1.2 Alkannin (a). Form Zarkogianni et al. (2010) (b). From Sequin-Frey (1981)

The chemistry of *Acacia catechu* has caught the attention of chemists from quite some time back but still the views and conclusions are somewhat conflicting. The ether

extracts of cutch has been found to have catechin or catechuic acid. In addition to catechin, cutch also possesses mimotannic acid which is present in about equal proportion to catechuic acid. Minotannic acid is however, cold water soluble and can be removed from cutch by simple maceration (Watt, 2014). Chemical structure of cutch with colour Index CI Natural Brown 3 is presented in Figure 1.3 as below:



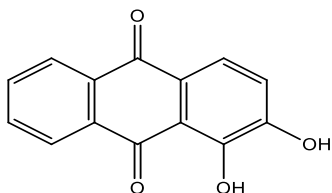
Cutch (CI Natural brown 3)

Figure 1.3: Chemical structure of cutch as presented by Bhattacharya and Shah (2000).

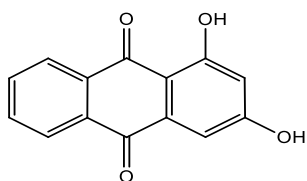
Anthraquinone is aromatic organic compound with molecular formula $C_{14}H_8O_2$. Its structural formula contains 3 rings and the keto group is located in the central ring. It is the building block of many dyes. Synthetic dyes are often derived from 9, 10 anthraquinone such as alizarin. Historically, alizarin was derived from the roots of plants belonging to genus madder. For dye production, the roots are harvested in the first year. By drying, fermenting or treatment with acids, this is changed to sugar i.e., alizarin and purpurin. It is the first natural pigment to be duplicated synthetically. Alizarin is dihydroxyanthraquinone, whereas, purpurin is trihydroxyanthraquinone. Apart from being important medically, manjistha is also used as a natural dye and food colourant. Purpurin and munjistin are the two colouring pigments found abundantly in the roots of manjistha (Bhatt & Kushwah, 2013).

The chemical structures of various colour components found in madder root are depicted in Figure 1.4. The colour developed by madder on textile is the sum of many components. The European variety (*Rubia tinctorum*) contains alizarin while the major colour components of *Rubia cordifolia* are purpurin, munjistin and xanthopurpurin or

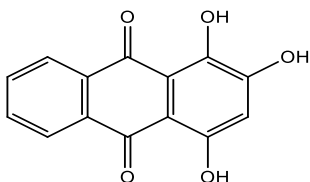
purpuroxanthin (Samanta et al., 2003; Gupta et al., 2004). The structure of alizarin was suggested as 1, 2- dihydroxyanthraquinone in 1868 (Derksen, 2001).



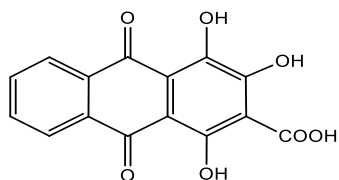
Alizarin



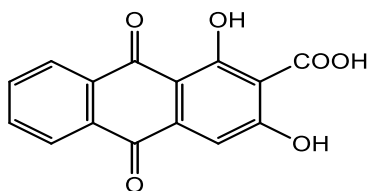
Xanthopurpurin



Purpurin



Pseudopurpurin



Munjistin

Figure 1.4: Chemical structures of colourants from madder root extracts (Kasiri and Safapour, 2013).

The main colour components in a *Tagetes erecta* dye are quectrol and xanthophylls esters. They belong to carotene group. The colour of this dye is caused due to the long alternating single and double bonds. Other examples of this group are annatto and Saffron (Vankar, 2000). Carotenoids are bright coloured pigments. Different colours like orange, red and yellow are awarded by their highly conjugated electron system. Basically, the name carotene is taken from carrots having orange pigment. Carotenoids present in nature are of two types. One is carotene or β -carotene from *Daucus carota*

(carrot) and another one is xanthophylls or lutein from marigold flower (Piccaglia, 1998) as in Figure1.5 below:

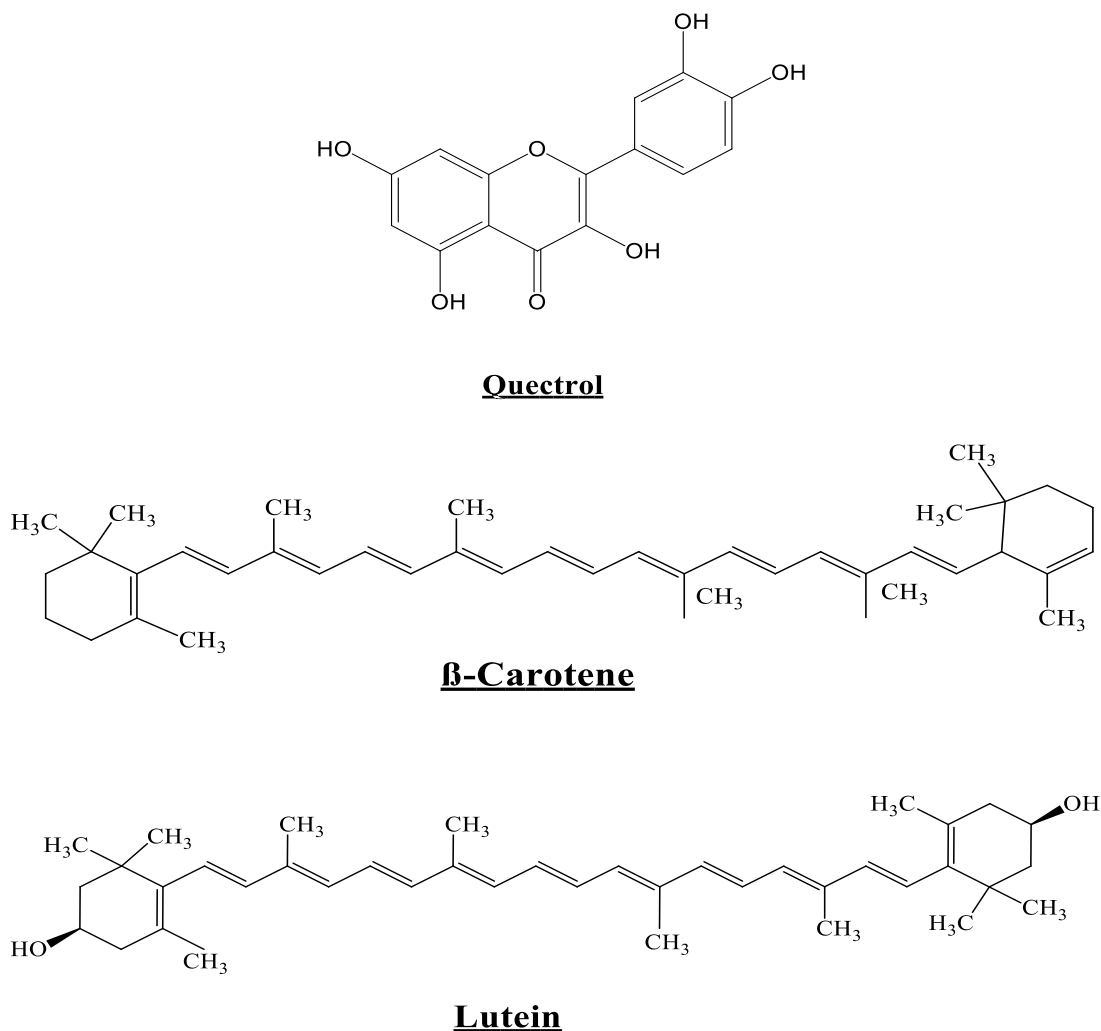


Figure 1.5: Structures of carotenoids

1.7 EXTRACTION OF NATURAL COLOURANTS

For achieving the desired dyeing characteristics, extraction of colourants from sources available in nature could prove one of the most important steps to treat textiles (Kasiri & Safapour, 2013). It is also important to find and optimize the standard extraction process and their variables for particular natural sources which should be cost effective for the price of end product. Different methods for extracting dyes from these materials are aqueous extraction, enzyme assisted extraction and alcoholic or organic solvent extractions. Natural dyes are extracted from various parts of plants and majority

of them have inherent antibacterial/anti-microbial properties. They therefore, possess high medicinal values too. Several micro-organisms have the ability to produce pigments known as biopigments. These include carotenoids, flavins, quinones, indigo etc. (Khanafari et al., 2006; Shinyoung & Yiqi, 2005). One such important and commercially produced, natural antibacterial agent is chitosan which is a linear polysaccharide. It has been used by researchers on cotton, wool, silk and some synthetic fibres for imparting anti-microbial properties as well as anti-felting and good wash fastness to wool fabrics (Ranjbar-Mohamadi et al., 2010).

In aqueous extractions, water is used with or without adding salts, acids, alkalis or alcohols in the extracting bath along with chelating with mordant as well as acid precipitation. Aqueous extraction of natural dyes normally takes boiling water (Ahmad et al., 2011). Solvent method is also used to extract colours. As there are different colour compounds in every plant, therefore, different solvents are employed for extraction regarding the polarity and chemical nature of these compounds.

The most common procedures of colour extraction include the use of hydrochloric acid and methanol (Shrivastava & Dedhia, 2006). A liquor ratio of 1:20 (material in grams: methanol in ml) is used to soak the crushed root/wood with the addition of 0.1% HCl for acidification of methanol. Soaking period includes 48 hours at room temperature in dark place. The mixture is then filtered for extract which is afterward evaporated (though rotary evaporator) for crude production in the form of paste. For conversion to powder form, the crude is dried inside desiccators for another 24 hours. The dried crude is mixed in 1:1 ratio with beta cyclodextrin and is then ground manually. In a research study (Win & Swe, 2008), various dyeing methods were used to extract purified dye stuff from mango bark. It was applied on wool and silk yarns for assessing its fastness properties. Determination of compounds present in the mango bark was carried out by phytochemical tests. Conditions optimized for dye purification include types, solvent, ratio of solvent to solid, time and temperature of the process. Acetone, 95% alcohol and petroleum ether were used to extract the colourant from mango bark. The phytochemical test indicates colour compounds of glycoside, flavonoid, tannin and phenolic compounds from the purified dye stuff of mango bark.

Natural dye can be analysed by absorbance spectra with the aid of UV- Vis photometer (Nateri, 2011). For this purpose raw madder natural dye is initially made into powder. After that the temperature of the dye solution is raised to boil and is kept on boiling for 1 hour. Next, the solution is left to attain room/environmental temperature and it is kept at this temperature for 24 hours. Now the solution of extracted dye is filtered and diluted by water. Colour can also be extracted from plant sources by exhaustion method. In a study, commercially available tea powder was used to prepare aqueous extract. A mixture of tea and water at a ratio of 2-5:100 g/l was heated, stirred and held at the boil for half an hour. It was then allowed to stand for 15 minutes before filtration (Moiz et al., 2010). For the tea natural dye to be applied on wool, it is required first to boil wool with a mordant. This chemical will attach itself to the fibre. After the dye application, it will stick to the chemical/mordant. Beside this pre- mordanted method of wool, the dye can also be used in a mordant solution at the same time. After wards the dyed wool is thoroughly rinsed, hot washed in soap or detergent for the removal of any unattached dye to the fabric.

Better colour yield can be achieved by alkaline extraction of dye from henna leaves as compared to aqueous extraction (Ali et al., 2009). Measured quantities of powdered henna leaves were added to sodium carbonate (Na_2CO_3) solution at pH 8.5-9 with a liquor ratio of 1:20 and heat applied to bring 80-85 °C temperature for 1 hour with occasional stirring, then cooling and filtrations through clean cotton cloth (Shahid et al., 2012). However, this alkaline extract is shifted back to pH 7 with the additions of HCl before using for dyeing wool. The K/S values also vary due to the method of extraction of dyes. The researchers found the ultrasound technique an effective way for the extraction of cochineal dye, enhancing the dyeability in terms of K/S value as compared to the conventional dyeing procedures (Kamel, et al., 2009).

In some plants such as beet root, the colouring matter is strongly held up with the membrane of plant cell and extraction of colour needs some improved method such as the use of power ultrasound (Sivakumar et al., 2009). Earlier to the use of this method, extraction was made by gamma ray irradiation technique and the use of electric pulse etc. to improve the extraction efficiency of natural dyes. Keeping the environmental pollution

and health issues in focus, development of suitable techniques for more effective and efficient dye extraction from plant materials is greatly required. Similarly, the health sensitive applications such as colouration of children textiles, toys, leather garments and food need special attention towards non toxic methods as well as suitable colouring material from natural sources of vegetation.

1.8 METHODS OF APPLYING NATURAL DYES ON TEXTILES

Rubbing of crushed pigments into a cloth or sticking plants to fabric are some of the primitive techniques of natural dyeing (Win & Swe, 2008). These methods and other processes have gradually been improved with the passage of time and new techniques such as obtaining and using natural dyes from plants and crushed fruits and then boiling them onto fabric, came into play. The methods of dye extraction of natural colourants and dyeing procedures that have been explained by the traditional dyers do not present/ offer a complete picture. Therefore, a need of developing and standardizing new methods of extraction and purification of natural dyes arises. In order to have the final dye powder containing maximum dyeing colours, methods of drying of colours as well as extraction and purification of dyes have now been developed.

Traditionally, exhaust dyeing is practiced with natural dyes. A great degree of simplification is brought to the complicated recipes; huge amounts of water and energy are still used by the dyeing processes with few exceptions, like cold dyeing with indigo. With the use of natural dyes, unconventional methods like ultrasonic, sonicator and microwave dyeing have been reported.

Modern methods of low liquor ratio, like high temperature high pressure (HTHP) and jet dyeing have also been practiced. Fastness properties and shades of comparable depth are attributed to the modifications and variety in application methods for natural dyes as compared to those obtained by traditional methods (Ratnapandian et al., 2012). Large amount of water is used in various wet processes by the textile industry, as a result of which great volumes of textile waste water is produced, which gets changed by chemicals and unconsumed dyes.

The type of procedure to be used depends on several things including type of fibre, yarn, fabric and end use etc. Textile dyeing processes consist of batch, continuous or semi-continuous process. Batch dyeing process is also called an exhaust dyeing. In this dyeing process, temperature is the most important parameter. It is usually maintained up to 100 °C for a good quality fabric. Pad-batch is a kind of semi-continuous dyeing process, which is primarily used for dyeing natural and manmade cellulosic fabrics like cotton or viscose with reactive dyes (Jadhav et al., 2013).

Three natural dyes *Punica granatum*, *Terminalia arjuna* and *Rheum emodi* have been employed on silk and cotton fabrics using ultrasonic technique along with the pre-treatment of enzyme and tannic acid. The aim of the study was the investigation of effectiveness of enzymes. The process has been found analogous to one step simultaneous dyeing (Vankar et al., 2007). The dyeing Kinetics of rapid and higher dye adsorption as compared to untreated samples coloured with these three natural dyes on cotton and silk was obvious from their findings.

In order to obtain shades with acceptable light, wash and rubbing fastness, cotton fabrics can be padded with low concentration of mordant and natural dyes (Ratnapandian et al., 2012). Taking into consideration the depth of shade, post-mordanting precedes meta-mordanting and pre-mordanting. Using the same natural dye obtained from Acacia plant family, grey and beige shades were obtained with ferrous sulphate and copper sulphate. Every mordant-dye combination presents a unique feature on account of the optimum mordant amount needed for the same amount of dye. It was found that for the 10 g/l dye, the optimal concentration of mordant was 5 g/l ferrous sulphate and 15 g/l copper sulphate. It can be inferred from this research work that using the process of padding, certain natural dyes can be readily applied (Perkins, 1991).

1.8.1 Continuous dyeing process

Commonly used continuous dyeing method include: pad-steam, pad-pad-steam (wet-on-wet), pad-dry-pad-steam and pad-dry-cure. Among all these, pad-dry-pad-steam is conventionally used for 100% cotton fabrics where dye is applied on the first pad and then the fabric is dried (Aspland, 1997).

Pad dyeing usually gives good dye penetration and leveling, low tailing risk and excellent washing off as well as wet fastness. The advantages of pad-dye pad-steam process includes high colour yield, cost-effectiveness for large production runs, neat attractive appearance of the dyed fabric, better reproducibility and no detrimental influence on chlorine and light fastness (Hussain, 2012 a). Tailing is minimized at low temperature of the formulation in padder, while at high temperature wetting is promoted within a short span of time till the fabric is in the pad formation. For dyeing long runs of a particular shade, continuous dye range provides the most efficient and economical process.

Padding technologies are particularly beneficial for dye application with products exhibiting low affinity. In case of padding process, the dye's affinity to fibre is unnecessary in the phase of dye deposition on fabric (Mongkhlorattanasit et al., 2009). Numerous methods of dye fixation are known in the semi continuous technology. Two important principles in this case are: cold batching and hot batching. Fixation by hot batching is a proven rapid process, but for this process, a reliable functional dyeing device is needed. A brilliant even-drying effect, both cross ways and breadth ways is essential in the fabric, otherwise unevenness and colour depreciation may result. The second one is cold batch method i.e. fixation by batching at room or slightly higher temperature of the padded goods. An air tight plastic sheet is used for wrapping the padded and rolled goods, to avoid the occurrence of selvedge drying during storage, which lasts for about 8 to 24 hours. Water rinsing is repeatedly followed after both the dyeing fixation procedures.

1.9 TYPES OF MORDANTS AND NATURAL DYEING

The process of mordanting has been known for many centuries. It is used to improve dye adsorption on the fibre and its wash fastness because the mordant has substantivity for both the colourant and the fibre and in bonding with the dye on the fibre, forming an insoluble precipitate. Mordants are often polyvalent metallic ions which form a complex with the fibre and the pigment. The most generally used mordant is supposed to be alum (aluminium potassium sulphate). Other fairly common mordants are potassium dichromate, tin chloride, copper sulphate, iron (II) sulphate or iron (III)

chloride (Zarkogianni et al., 2010). Surfactants are also needed in dyeing bath. They are used as leveling, dispersing and wetting agents in the dyeing process (Chandravanshi & Upadhyay, 2012). They play useful role in textile processing by wetting the fibre surface quickly and uniformly.

In the dyeing of cotton fabrics with natural colourants, metal mordants are essential as they influence the shade/colour produced from the process. The intensity of shade and relative colour strength (expressed as K/S values) available from natural dyeing depend on the type of mordant and the nature of the complex formed by mordant and dye (Wanyama et al., 2010; Saravanan et al., 2013 a). Mordant is a term derived from Latin word “*mordere*” which means to bite. Actually, these are the chemicals which bind dye molecules with fibre molecule. Basically these substances are used to fix a dye to fibres, however, they also help in improving some dyeing properties such as dye uptake wash and light fastness (Moiz et al., 2010). Natural dyes are also considered as mordant dyes due to the requirement of one or more metallic mordants such as salts of aluminiums, copper, iron, zinc and some others in order to ensure reasonable wash and light fastness.

In recent past, Guesmia (2012) used potassium aluminium sulphate, manganese sulphate and cobalt sulphate and found them best for enhancement of colour strength (K/S) and light fastness. In addition, several other metallic mordants salts and bio mordants have been researched upon. In a study by Vankar et al. (2007) tannins were employed with cationic dyes for increasing the dye uptake of cotton and importing adequate fastness properties. However some of the frequently used metals are Al, Cu, Fe, Pb, Sn etc. The type of mordant employed, affect the colour yield by the natural dyestuff which results in a variety of shades from a single dye. In addition, the degree of light fastness is also influenced by the choice of mordants. Copper should always be used with dilute acetic acid. Iron and tannin present no threat to the environment. However, two other chemical mordants tin and chrome should be avoided as they have the potential to pollute the environment (Jenny, 2001).

The use of various mordants causes different colour hues (H), significant changes in K/S values as well as differences in lightness (L). The strength and stability as well as

shade of dye on cotton fabrics largely depend on the choice of mordant selected and the nature of the textile fibre. Ferrous sulphate can provide dark shade when used as mordant with natural dyes. Considering the depth of shade, Ratnapandian et al. (2012) consider post-mordanting procedure as a better option as compared to meta-mordanting or pre-mordanting. They obtained beige shade on fabric from copper sulphate and grey from ferrous sulphate while using a natural dye from acacia plant family.

Beside the type of mordant, the amount or ratio of mordant with dye is also peculiar. The same amount of dye can take various optimum amount of mordant to produce dark shade. Most of the available natural dyes generally need metallic mordants to enhance the dye affinity for particular fibre, thereby resulting higher colour yield, better fastness properties and variable shades. Examples of such metallic mordants are alum, copper sulphate and iron sulphate etc. (Nakpathom, 2012). However, their excessive use is harmful to consumer's health as well as environment because majority of these mordants are toxic in nature and therefore they should not be commercially employed.

1.9.1 Dyeing with mordants

Mordants are used by three methods namely pre-mordanting, meta-mordanting and post-mordanting. In the pre-mordanting process, the fabric is first immersed (exhaust dyeing method) in an aqueous solution of metallic salt usually at 30°C for 45 min. In the meta- mordanting the fabric is immersed in a dyeing bath consisting of both the dye extract and the mordants and is treated at 85°C for 30-35 minutes. In the post-mordanting procedure the fabric is first dyed in the absence of a mordant and then mordant is applied in separate bath usually at 30°C for 45 minutes. The fabric is then rinsed/washed with nonionic soap at 60°C, and then with water and then squeezed and dried. The three dyeing methods of mordanting have also been studied by Moiz et al. (2010) while using aqueous extracts of tea on wool yielding brown shades. Superior wash and light fastness and better depth of shade is the result of post-mordanting method. Among mordants, copper salts have been proved dominant in achieving best results on tea dyed wool.

Wanyama et al. (2010) investigated five plants namely *Morinda lucida*, *Vitellaria paradoxa*, *Albizia coriaria*, *syzgium cordatum* and *justicia betonica* which could yield

dyes. An important role of different mordants was identified in the development of colours from these plants. Natural dyes have been derived from the plant family of Acacia and applied to cotton fabric by padding at an amount of 10g/l (Ratnapandian et al., 2012). All the three techniques of mordanting were researched upon. However, the most even shade was available from post-mordanting with copper sulphate and ferrous sulphate. Beige shade was produced by copper sulphate at 15g/l and yellow grey shade was the best performance of ferrous sulphate at 5g/l. Moreover, the sequence of the process was dye padding, dyeing, steaming and this was followed by mordant padding. Rubia is a genus of flowering plants of Rubiaceae family. *Rubia tinctorum* can grow up to 1.5 meters in height. The roots can be over a meter long, up to 12 mm thick and the source of red dyes known as rose madder and Turkey red.

1.9.2 Mechanism of mordant-dye-fibre interactions

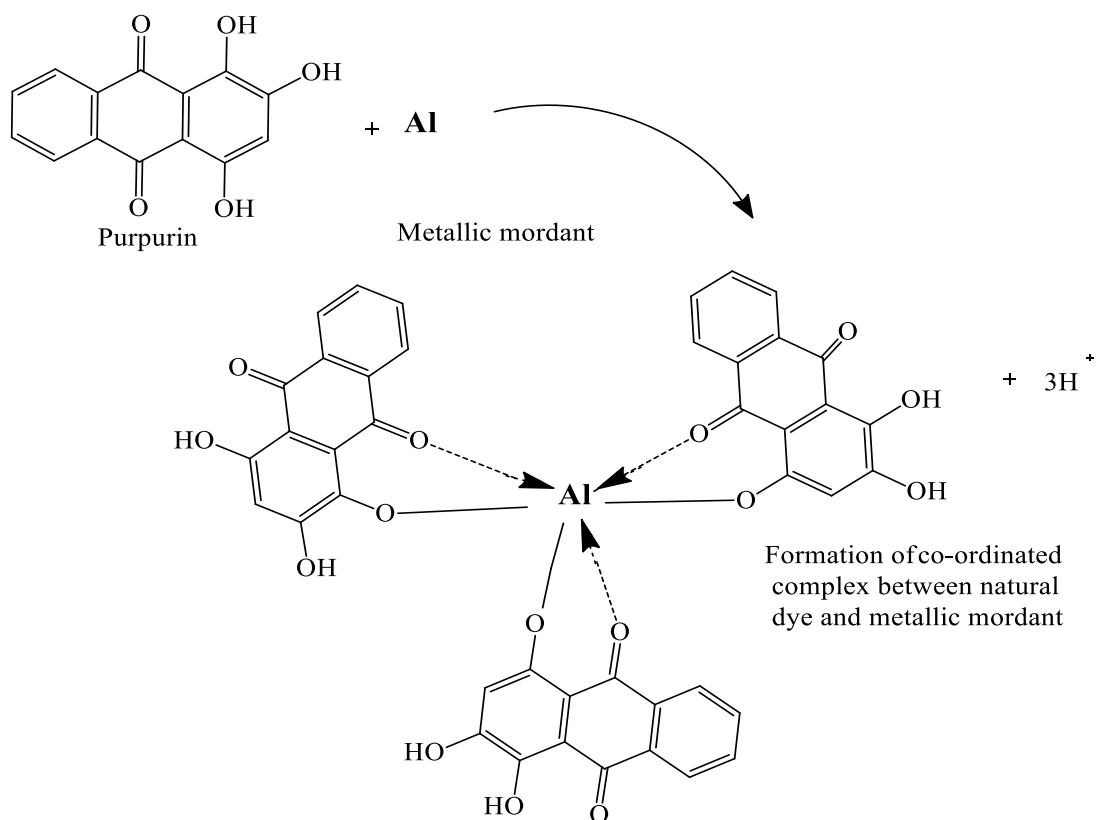


Figure 1.6: Fixation of natural dye through mordant as presented by (Samanta & Konar, 2011).

Most of the natural dyes are not substantive to cellulosic fibres and need a mordanting chemical which is usually known as metallic mordant capable of forming coordinating complex between dye and fibre so as to create the affinity of fibre for that dye. After their application, these metal salt attaches to the fibres and attracts the organic natural pigment or dye molecules to fasten them to the fibres and in this way creates a link or bridge between the dye and fibre molecules. One possible coordination is presented in Figure 1.7 as below:

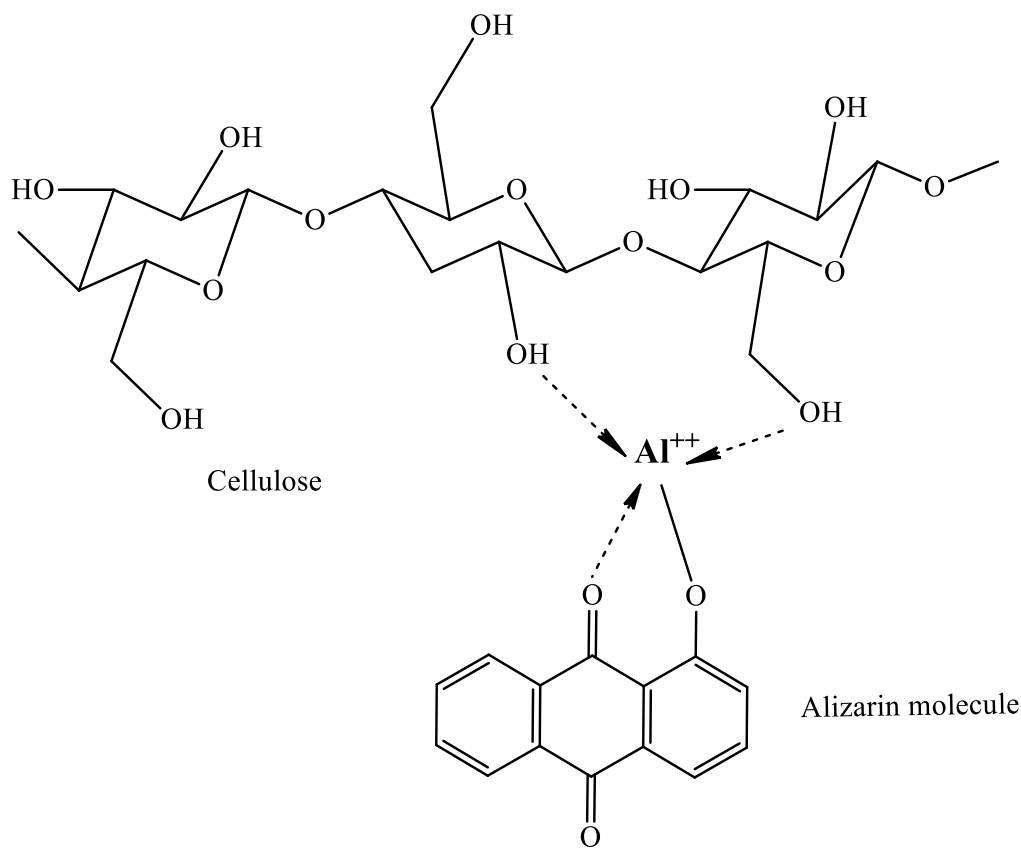


Figure 1.7: Fixation of natural dye to cellulose through metallic mordant

The chemistry of fibres to dye bonding is a complex phenomena which involve not only direct bonding but are also held through hydrogen bonding and hydrophobic interactions. Mordants are capable of making insoluble compounds within fibre polymer system from the dye applied on the fibre. The coordination of dye with mordant or metal ion takes place due to the presence of certain functional groups in the dye molecule in suitable positions.

Binding of natural dyes through mordants have also been explained by Vankar, (2000) with by taking chromium salt as an example. In the formation of alizarin-chromium complex, the chromium ion combines by covalent coordinate bond with three molecules alizarin forming 'Lake'. Protein molecules retain the dye molecules with the help of hydrogen bonding (Vankar, 2000). Most of the natural dyes are applied on cotton as mordant dyes. The reaction chromium is presented in Figure 1.8 as follows:

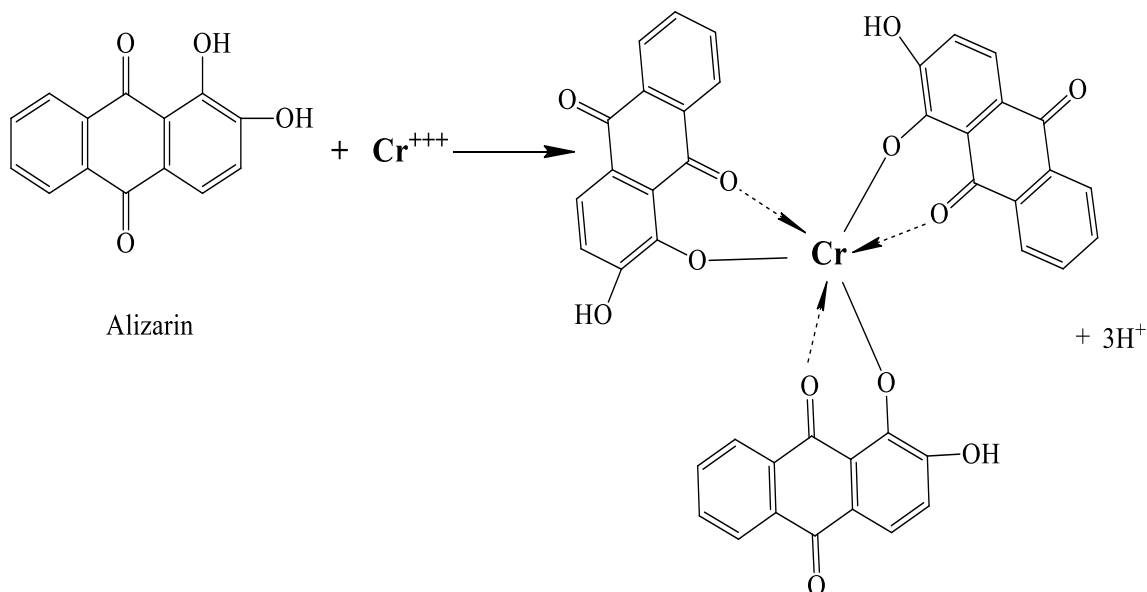


Figure 1.8: Formation of chromium complexes a proposed by Vankar, (2000).

1.10 CATIONIZATION OF COTTON FABRIC AND NATURAL DYEING

Numbers of methods has been developed for the modification of cotton. Most of the techniques are either too complicated or not economically feasible. Surface modification may lead to ring dyeing, resulting in a marked difference in hue and brightness compared to conventional dyeing. Lewis and McIlory (1997) reviewed numerous chemicals that can be used to improve the dyeability of cotton fibre. Like most other textile fibres, cotton has negative zeta potential (negatively charged) in neutral and aqueous alkaline mediums. Adsorption processes are difficult as dyestuffs and finishing agents have the same electrical charge as cotton in aqueous solution, due to which repulsive forces takes place. One way to overcome by these forces is the addition of

large amounts of salts/electrolytes. However, this is unfavorable both economically and ecologically. Fabrics modified through cationization have encouraging influence on dyeing, as cationized cotton have more positive zeta potential as compared to untreated fabrics. Cationic dye fixers also play important role in the fixation of dye molecules as well as improvement of wash fastness. In case of mordanting a complex formation takes place between dye fibre mordant. If cation dye fixers are used along with mordanting, then a complex is also formed between dye fixer. One such example has been depicted by Samanta et al., (2009 a) which is shown below:

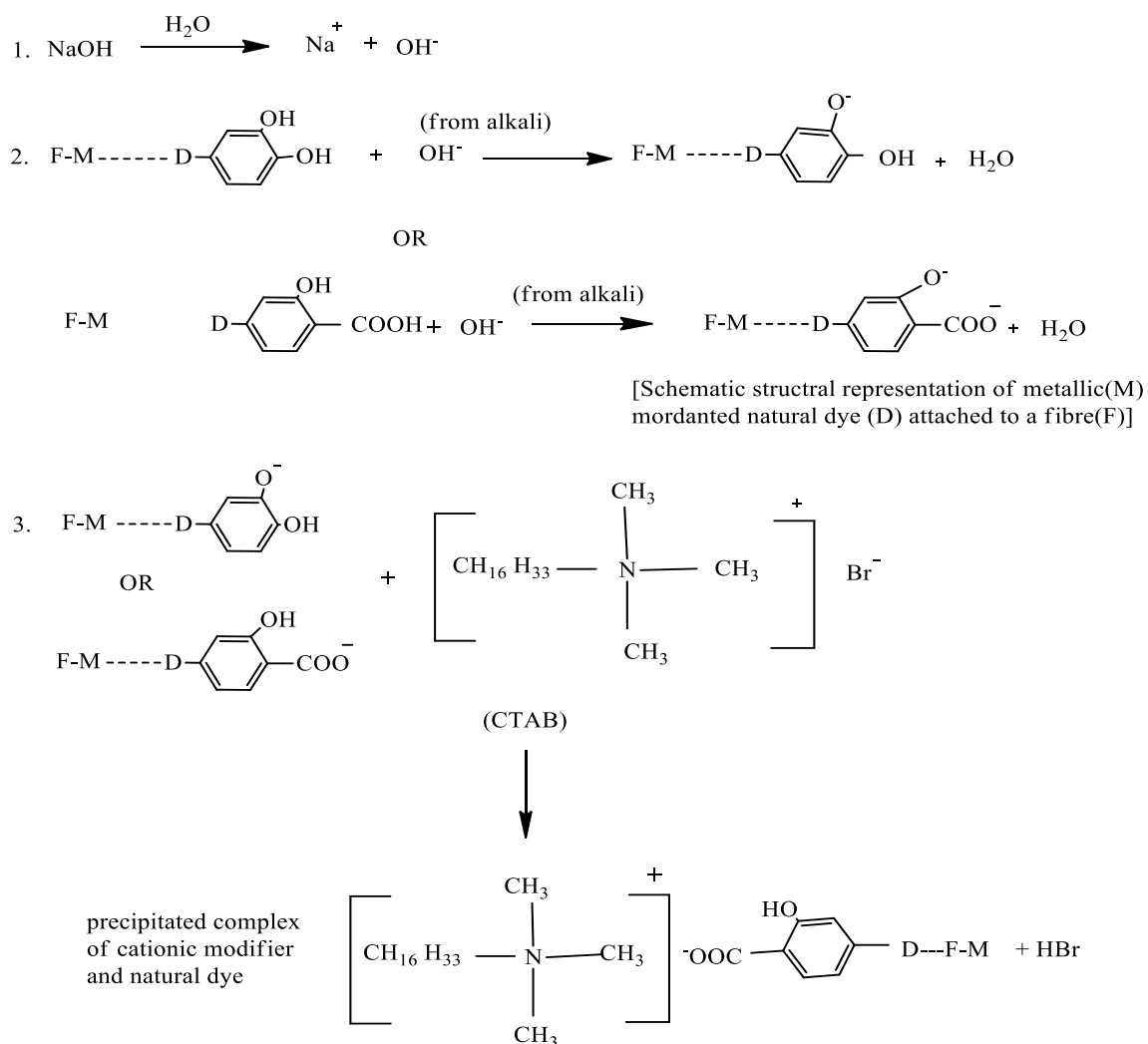


Figure 1.9: Complex formation between mordant –fibre- dye system and cationic dye fixers (Samanta et al., 2009)

The first two steps reveal the schematic structural representation of natural dye (D) with metallic mordant (M) fastened to a fibre (F). In the third step the production of fibre mordanted dye anions of natural dyes has been elucidated in the presence of alkali. Cotton fabric was treated with poly aminochlorohydrin quaternary ammonium polymer with epoxide functionality (Solfix E by Ciba Geigy-Co., Germany) which was supposed to react with cellulose in the presence of alkali (15 g/l). The cationization was carried out by padding at 100% wet pick up, drying at 80 °C for 3 minutes and curing at 115 °C for 4 minutes. The study reveals increased colour strength as the concentration of cationizing agent was increased (Kamel et al., 2009).

1.11 THE ROLE OF UV ABSORBERS IN NATURAL DYEING

Day light reach the earth's surface from sun through the atmosphere and is distinguished as visible light, ultra violet rays (UV rays) and infrared rays. Ultra violet rays are in the form of UVA, UVB and UVC. The wave length of UVA is from 320-420 nm (nanometers), UVB are 290-320 nm in length, whereas, the wavelengths of UVC are less than 290 nm. Among these, UVA and UVB can reach the earth's surface. UVB rays are the main cause of sunburn and development of skin cancer. UVA plays a drastic role in skin aging and wrinkling and is also of the causes of skin cancer. They more deeply penetrate in the skin as compared to UVB rays. It is important that human skin should be protected from the harmful effects of UV rays. Focus is also required to be made on the research related to textile surfaces and UV radiation (Akgun et al., 2010).

The relation between the physical structure and properties of fabrics and ultraviolet light is important to be investigated. Various studies are available in the subject relating to the factors affecting the transmission of UV radiation of undyed fabrics. Crews et al. (1999) concluded fabric porosity as the best factor responsible for blocking properties of undyed woven fabrics from UV rays. Some of the earlier studies have focused on the application of available commercial UV absorbers for the improvement of UV protection properties of fabrics. The surface of cotton is modified with sol-gel method (Xin et al., 2005) to impart UVR (Ultra violet radiation) scattering property to the light weight 100% cotton.

Textile dyes are also selective absorbers of visible light. Most of these absorb light in the visible region i.e. from 400 nm to 700 nm (Akgun, 2010). Dyes often impart good blocking action to fabrics from the transmittance of ultraviolet light which is otherwise, not available in undyed and untreated knitted or woven cotton fabrics due to their high UV transmission (Gorensek & Sluga, 2004). Therefore, coloured fabrics provide better protection against UV rays than undyed fabrics, although many factors such as the type and amount of dye as well as the type of fibre and fabric construction have their natural due share. The best ways for increasing the ultraviolet protection factor (UPF) appears to be the use of chemical crosslinking agents in the form of UV absorbers (Abidi et al., 2001).

Shade of the fabric is also very important in having excellent UV protection. With the same fabric and same dyestuff, darker shades provide high protection against UV rays. Colours such as black, dark green and navy blues etc. significantly improve the ultraviolet protection as compared to pastel shades (Akgun et al., 2010). UV protection also depends upon the type of fabric and construction type. Cellulosic fibres such as cotton, linen and rayon present little protection (Hussain, 2012 b) which can be significantly improved by colouring. UV protection also depends on the absorbing properties of dye. Highly penetrated dyes, producing dark shade fabric give better protection. However, this can better be predicted by the transmission or absorption behaviour of colourants in the UV region as compared to the colour or shade of the fabric.

According to Mongkholrattanasit (2011), UV-C, the highest energy region is absorbed in the upper atmosphere by oxygen and ozone layer. The total solar UV radiations approaching the surface of earth are 6% in the region of UV-B and 94% in the region of UV-A. Conservation experts have hypothesized on the effectiveness of UV absorbers as an alternative method of reduction in dye fading. Interest and emphasis should therefore, be made to investigate various types of UV absorbers for improving the light fastness of natural dyes. Various kinds of UV absorbers are available in the market having absorbing functions but only four classes have attained commercial significance (Oda, 2001 b) which includes the derivations of 2-hydroxy benzophenone, cinnamic acid,

2-(2H-benzotriazol-2-yl) phenols and phenyl esters. UV absorbers are added to textiles and other materials to manufacture articles that reflect or absorb or sunscreen the damaging UV light.

UV absorbers provide protection to fabrics in two ways. Solids such as zinc oxide and titanium oxide reduce UV light by reflecting it away. Organic chemicals provide UV protection by absorbing UV light and creating heat. According to Cristea and Vilarem (2006), the following characteristics must be present in the UV absorbers. They must be highly absorptive for the radiation having length between 290-400 nm. They must be stable to long exposure to light and should be chemically inert to other additives. The general mechanism of light fastness improving finishes is that they absorb high ultraviolet energy, convert it to vibration energy and then transform it to heat energy without any destruction or photo degradation. Disadvantages of these UV light absorbers include their high price as well as requirement of high concentration (Hussain, 2012 b).

1.12 INFLUENCE OF CROSSLINKING AGENTS AND OTHER FINISHES IN NATURAL DYEING

Fabrics intended for the manufacture of apparel/clothing requires possessing certain specifications. Therefore, the composition of chemicals/resins such as crosslinking is important for producing cotton fabrics for clothing. To achieve some physical properties in cotton fabrics, crosslinking agents (DMDHEU, Fixapret CPN from the BASF Company) was used by Mortazavi and Boukany (2004). It is the most common low-formaldehyde crosslinking agent. Majority of crosslinking agents used today is DMDHEU based with low formaldehyde level. It is a bi-functional compound that can react with cotton (cellulose) by forming ether linkage under the influence of catalyst. DMDHEU can react with free hydroxyl groups of cellulose polymer chains and can convert the weaker hydrogen bonds between cellulose chains to strong covalent bonds.

In order to enhance the action of *Azadirachta indica* (natural antibacterial agent) on cotton/ polyester, blend fabrics, glyoxal a crosslinking chemical agent was used in a study (Joshi et al., 2007). Similarly in the antibacterial finishing of cotton with the extracts of green tea leaves for enhancing the durability against washing, the crosslinking

agent used in this case was citric acid (Syamili et al., 2012). The low efficiency of the process of extraction (a few grams of pigment per kilogram) limits their application only to natural coloured garments that are high value added (De Santis et al., 2005). The effect of different crosslinking agents on natural dyed cotton has been studied by Sheth et al. (2003) with the help of alum, stannous chloride or tartaric acid and dimethyloldihydroxyethyleneurea of Clariant Ltd. The colour depth, tear strength and tensile strength of DMDHEU treated fabrics depends on the type of mordant employed with natural dyes. DMDHEU was applied to Jute dyed fabrics through simultaneous dyeing and finishing (Kamaluddin et al., 2007) to study its physical properties. A direct relationship was found in the dyed fabrics, between the improvement in dye fixation and concentration of resin.

1.13 COLOUR STRENGTH (K/S VALUE) OF DYED FABRICS

Colour is defined by its attributes of intensity (saturation, chroma), value (brightness) and hue (the name of a colour: red, blue, green, etc.). A computer may require the amount of red, green and blue phosphor emissions to match a colour. CIEL*a*b* and CIEL*C*h° colour spaces are directly based on the measurement of the parameters or coordinates to specify the colour. The term CIE is the abbreviation from its French title *Commission Internationale de l'Eclairage* which relates to International Commission on Illumination. It has been recognized by ISO for representing the best authority on the subject.

CIEL*a*b* is extensively used in textile industry for colour specification. This colour space has been a general utility for illustrating the relationship among colours since its inception in 1976 (McDonald & Smith, 1995; Ibrahim et al., 2011). The L* axis denote lightness which ranges from 0-100 whereas, a* and b* (which are at right angle to each other) represent the horizontal of the axis. They meet in the centre representing neutral colours (gray, black or white). The axis a* is red at one extreme (positive) and green at the other (negative). Similarly, b* axis has yellow (+b) at one end and blue (-b) at the other. The colour space CIEL*C*h° contains three axes that is L*, C* and h°. The axis C* ranges from 0 at the centre of the circle (neutral colours: gray, black or white) to 100 or greater at the edge of the circle (very high chroma or colour purity). Likewise, the

axis h° represents hue. Every possible saturated colour (hue) can be seen around the edge of the circle. The units of h° are in the form of degrees which range from 0° (red colour) to 270° (blue colour). This has been illustrated through Figure 1.9 (a) and (b) given below:

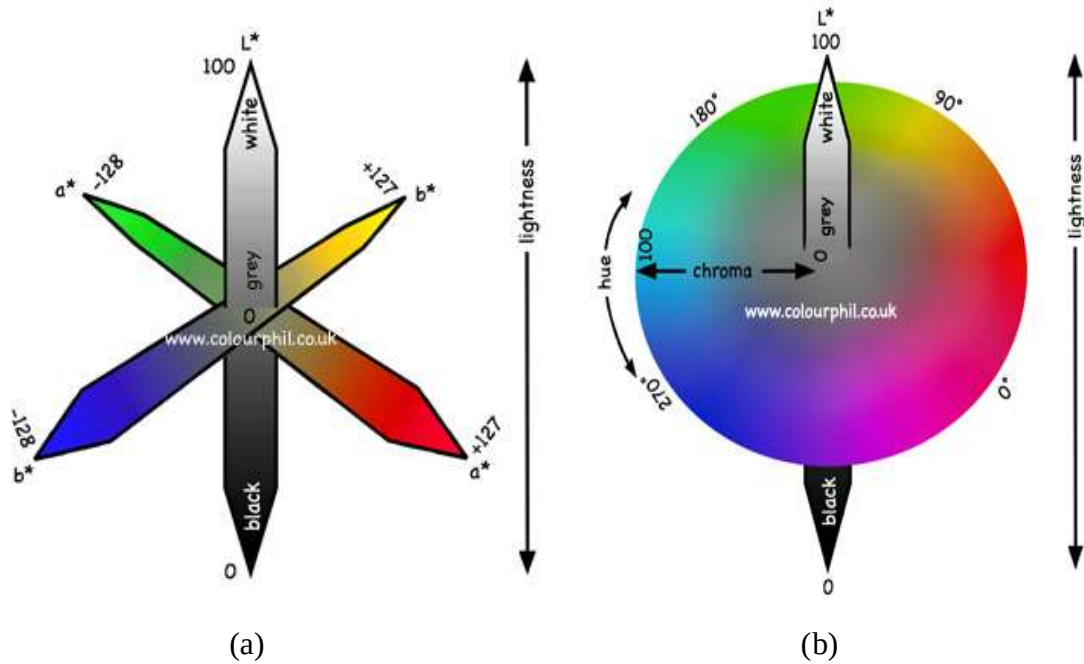


Figure 1.10: (a). The CIEL*a*b* colour space, (b). CIEL*C*h° colour space as presented by Graphic Quality Consultancy.

The ability of a pigment or dye to change the colour of otherwise colourless material is known as colour strength. Its calculations are made on the basis of numerical value related to the amount of light-absorbing material (colourant) contained in a sample (Zarkogianni et al., 2010). This colour value is calculated as the sum of K/S values for the sample. It is proportional to the dye concentration on the fibre. According to the Kubelka–Munk equation, $(K/S = (1-R)^2/2R)$.

For all colour matching software, Kubelka-Munk series of equations are mathematical basic. The ratios of total absorbed and scattered light by the dyes are separately measured. Absorption is defined as “K” and scattering is defined as “S”. Datacolor SF 600 is equipped with computer added software which provides the computed values of K/S rather than the reflectance etc.

For many years transmittance absorption system has been used in the dyeing industry. The absorptivity of the dye, the shape of the absorption spectrum of the dye and the maximum absorbance wavelength is determined from the spectroscopic studies of dyes in solution. The use of organic synthetic dyes during dye production in the standardization procedures is a result of the bent towards the usage of spectrophotometers (Nateri, 2011). Using the values of absorbance spectra, the final colour of the sample is calculated. Ke et al., (2006) used Datacolor SF 600 computer colour matching system (Data Color International) and illuminant D65 and 10° standard observer for the measurement of colour coordinates such as L*, a* C*, h° and K/S values for a dyed fabric. The colour strength (K/S value) has been measured at $\lambda_{\max}$ values of 400-410 nm for garcinia bark and marigold dyes; 520-530 nm for lac dye; and 470 nm for dye from annatto seed. It was found that for marigold dye, an exceptionally high K/S value was obtained in comparison to others (Nakpathom et al., 2012).

In order to determine the colourant mixtures, a derivative spectrophotometry method has been developed in recent times to decrease the effects of interference from scattering and to enhance differences between spectra or other absorbing compounds in quantitative analysis (Nateri & Ekrami, 2008). A graph between the dye concentration and shade presented by Yusuf et al. (2012) reveals inverse proportion between the dye concentration and lightness (L*) values. Lightness of shades is also significantly affected by mordanting. From the above mentioned study, the values of colour coordinates, a* and b* specify the shade of madder dyed samples in red yellow zone and the K/S values of mordanted samples dyed with madder are also sufficiently greater as compared to their corresponding un-mordanted dyed samples. It seems that mordants are capable of increasing the fixation of colour. Generally, madder yields dark shades. However, the difference in darkness of shades due to various mordants etc. can be better judged visually rather than numerically. The lightness values etc. show little difference in spite of the considerable increase in colour (Yusuf et al., 2012).

1.14 CREATION OF SHADES FROM NATURAL DYES

Various shades are obtained from natural dyes. An extract of famous natural dye henna leaves yields from beautiful orange brown to shades of light yellowish- green

(Yusuf et al., 2012). The extracts of madder root dye results in orange- red to shades of scarlet. Deep shades can also be produced in some kind of multiple dyeing. Large number of shades can be created by using mixtures of dyes such as yellow, red, blue and black. However, practically, this is not possible as various natural dyes require different auxiliaries (mordants) and procedures. In a study by Gulrajani et al. (2001), a number of shades were attempted on cotton to produce yarns in different colours by fibre dyeing process in various shades and then blending them for creating compound shades.

The renewed interest in natural dyes has revived scientific enquiry, and new literature in various areas has been published. Research findings related to many aspects of natural dye are now available. However in recent years, an increase interest in natural dyes has been visible by researches such as reconstruction of ancient and traditional dyeing technology, conservation and restoration of old textiles and museum textiles, replacement of synthetic dyes by natural dyes for food, textiles, etc. (Zarkogianni et al., 2010).

1.15 TENSILE PROPERTIES OF COTTON INFLUENCED BY DYEING

The development in cotton fabric's dyeing properties without altering or degrading the inherent natural tensile strength is of great importance. Whether used for apparel, home furnishing, recreational or industrial purposes, cotton fabric has to experience tensile loads. Mechanical properties of cotton fabrics such as tensile strength, tear strength and elongation etc. are among the important components in contributing durability and serviceability of the article. Tensile strength is generally expressed in terms of the amount of load or maximum stress which the fabric can withstand before getting ruptured. It is therefore, expressed in the unit of force. In a comparative study on dyeing polyester/cotton fabric, the pad-steam process has been found more effective than the conventional exhaustion process. The pad-steam process has the benefit of less strength loss of the fibers and a reduced amount of water and chemical consumption. This process is therefore, less dangerous to the environment. The dyeability and handle were improved by both processes (Haji et al., 2011).

Every fabric undergoes some increase in length under tensile loading while resisting rupture during the stress. The increase in length, usually expressed as percentage

is known as elongation. The most popular method of determination of tensile strength and elongation is supposed to be the strip method which requires a prepared standardized strip of fabric.

The tensile strength of gray fabrics consequently relates to the inherent properties of fibre, yarn count, yarn twist fabric construction and other technological parameters. However, for the final end use, these fabrics need to be treated (dyeing, printing, finishing) for adding the required functional properties. In many cases, various thermal and chemical treatments are carried out during these post-treatments. This can worsen some of the important mechanical properties of fabrics such as strength and elongation.

1.16 ROLE OF VARIOUS TREATMENTS IN FASTNESS PROPERTIES OF NATURAL DYES

Colourfastness of a textile is one of the important factors in determining the serviceability of an article. It is an outstandingly important property of a dyed material which refers to the resistance of colour to fade/change in any of its colour characteristics or extent of transfer of its colourants to adjacent white material in touch or both for different environmental and use conditions or treatments like washing, dry cleaning etc. or exposure to different heat, light etc. (Samanta & Konar, 2011). Factors affecting the colourfastness include the chemical nature of the fibre, molecular structure of dye, the manner of bonding of dye to the fibre, the amount of dye present in the fibre i.e. depth of shade, the presence of other chemicals/auxiliaries in the bath and the actual conditions prevailing during use. Light fastness is influenced by internal factors: the chemical and the physical state of dye, the dye concentration, the nature of the fibres, the mordant type etc. (Cristea & Vilarem, 2006).

Good fastness to rubbing, washing and light are desirable properties in dyed textiles (Ratnapandian et al., 2012). The whole question of determination of colourfastness to light specially at elevated temperatures and humidity is very complicated and the matter has been made more complicated due to the fact that ISO and SAE (The society of Auto motive Engineers) both have their own test methods. This has made the act of light fastness testing a maze of both technology and politics. The two test methods do not correspond exactly. Poor to moderate light and wash fastness of natural

dyes extracted from flowers have been reported which is the result of photo-oxidation of chromophores. However, such photo-oxidation is better prevented by metallic mordanting by forming their complexes. Further improvement can also be made by treating dyed cotton fabrics with cationic dye fixing agents and UV absorbers (Grover & Patni, 2011; Hussain, 2012 c). UV-protection properties of fabrics are related to the composition, structure including weight, thickness, porosity, wave pattern, presence of pigments or dyes, dyeing auxiliaries etc. All these factors are able to decrease or prevent the transmission of UV-radiation. A study has been conducted on natural dyed Knitted cotton to increase the UV-protection and antibacterial activities (Ibrahim et al., 2010). The pre-mordanting step was found very promising for the development of protection properties against micro organisms and harmful UV-radiation.

A comprehensive review on different attempts taken for improving colourfastness properties of dyes on different textile fibres by different means has been reported which also includes after-treatments for improving the wash fastness and light fastness of mordantable dyes on cotton). With the exception of indigo and logwood, most natural dyes have poor light stability (Lee et al., 2001; Samanta & Konar, 2011). Recently, there has been a growing interest in the use of natural dyes in textile applications. Extensive research work is being undertaken around the world on the application of natural dyes. Most of the natural dyes have poor light stability (as compared to that of the best synthetic dyes), and hence the colours in museum textile are often different from their original colours.

Application of natural dyes and its fastness testing indicate some change of the colours of the dyed samples which involve several factors. This may be due to the decomposition of dye (Jothi, 2008) which leads to its conversion into differently coloured or colourless compound. It may also be takes place because of the detachment of dye from substrate due to wear and rupture of dye-fibre bond and ionization of the natural dye due to the alkalinity of the soap. Cotton fibre as well as most of the natural dyes has hydroxyl groups in their structure. It is the characteristic of these groups that they ionize under alkaline conditions. The use of mild and non ionic soaps are therefore suggested to use for washing of natural dyed articles so as to avoid change of colour. Although the

utilization of natural dyes have been linked with “poor fastness” properties in the literature on the subject, Bechtold et al. (2003) have suggested the establishment of one bath dyeing process for various natural dyes which can lead to the achievement of acceptable fastness properties both on natural proteinic and natural cellulosic fibres. The application of dyestuff and mordant in the same bath can also help in adjusting the colour depth as well as shade of the dyed article due to the reelection of amount and composition of dye. Reproducibility of the dyeing as compared to pre or post-mordanting (two-bath methods) is also hoped to be improved. Along with treatments with UV absorbers and other additives, the increase in concentration of dye itself also plays a role in producing high level of light fastness.

1.17 WHY ECO-FRIENDLY TEXTILE DYEING

Having a safe finished product in hand is no longer an adequate requirement nowadays. Rather, an environmentally safe product during the entire service life is the need of the day as the excessive use of chemicals has created a polluted environment and soil deterioration. Some elements of concepts about eco-friendliness of textile production has been reviewed by Deo (2001), including processes such as preparatory steps; dyeing, printing, finishing effluent treatment; recycle and reuse practices; recycling machinery and other miscellaneous aspects etc. “German ban” includes 118 azo dyes. The class of disperse dyes (synthetic dyes) could be a big casualty in future. For the past two centuries, science and technology has been the buzzword and for the new millennium the eco-friendly revolution will be the new buzzword for the entire global village.

For successful commercial use of natural dyes, the suitable and standardized procedures of dyeing for particular fibre-dye (natural) system needs to be adopted. Therefore, to obtain novel shades with acceptable colour fastness and reproducibility, appropriate scientific dyeing techniques/procedures have to be derived. Thus, relevant scientific studies and their output on standardization of dyeing methods, dyeing process variables, dyeing kinetics and test of compatibility of selective natural dyes have become very important. However, the information on them is insufficient (Samanta and Agarwal, 2009).

1.18 AIMS AND OBJECTIVES

The present study is aimed to examine the possibility of dyeing cotton fabric with various natural dyes using different dyeing auxiliaries (mordants, crosslinkers, UV absorbers, cationizing agents and some finishing agents). The research work also focuses on investigating the dyeing behavior and fastness characteristics of natural dyes on cotton fabric in terms of comparison between dye application with and without the above mentioned auxiliaries as well as their pre-dyeing and post-dyeing treatments.

Main objectives of the current research work are to:

- Study the application of selected natural dyes by pad-steam dyeing technique.
- Examine the role of various mordants on the shades, colourfastness, colour strength and tensile strength of cotton fabric dyed with various natural dyes.
- Investigate the role of UV absorbers in improving the lightfastness of cotton fabric dyed with natural dyes.
- Assess the role of crosslinking agents and some other finishes on the colourfastness and strength of cotton fabric dyed with natural dyes.
- Formulate the best possible recipe for the selected natural dyes on cotton (by attempting various auxiliaries) in terms of shade, colourfastness, colour strength and minimum or no loss in tensile strength of dyed fabric.

CHAPTER-II

MATERIAL AND METHODS

The current research project “appraisal of fastness and tensile properties of cotton fabric dyed with natural colourants by pad-steam method” was carried out in the College of Home Economics, University of Peshawar in the period of 2011-2014. Dyes from natural resources compatible with textiles were extracted and applied on samples of pure cotton fabric by traditional dyeing recipes as well as by those which were planned for the present research project. The study comprised the following phases.

- i. Collection of samples
- ii. Extraction of dyes
- iii. Preparation of fabric for dyeing
- iv. Application of dyeing recipes on fabric samples using mordants
- v. Dyeing with the aid of crosslinking agents
- vi. Use of UV absorbers and finishes in dyeing
- vii. Physical testing of dyed cotton samples
- viii. Analysis of data

Extraction of dyes was carried out partially at Centre of Biotechnology and Microbiology, University of Peshawar and partly in the PCSIR laboratories, Peshawar, while, dyeing was accomplished in the processing laboratory of National Textile University, Faisalabad. Testing of the performance characteristics of dyed samples was completed partly in the textile testing laboratory of National Textile University, Faisalabad and partly in the experimental textile laboratory of College of Home Economics, University of Peshawar.

2.1 COLLECTION OF SAMPLES

In order to design the best possible dyeing recipe of natural dyes for the colouration of cotton in terms of shade, colourfastness, relative colour strength and

minimum or no loss in tensile strength, dye formulations were prepared by using various dyeing auxiliaries such as mordants, crosslinking agents, UV absorbers, cationizing agents, and some fixative type of finishes.

2.1.1 Fabric

Light-weight, plain woven, 100 % cotton fabric in gray form (20 meters) was purchased from Koh- e- Noor textile mills limited, Faisalabad. Before any dyeing process, the sample was subjected to preliminary testing according to available standard procedures, such as count of yarn, both in warp and weft direction (ASTM D1059-01); twist or turns per inch in both directions (Booth, 1996); threads per inch (ends and picks) or thread count of fabric (ISO 7211-2-1984); weight per unit area or GSM (ASTM D3776/ D3776M - 09a (2013)); colour coordinates (Datacolor, 2007; Color iQC & Color iMatch, 2012) ; and tensile strength and elongation (ASTM D5035-06, 2006).

2.1.2 Natural dyes

Natural dyes selected for this project were alkanet, cutch, madder, marigold flower and Turkey red. Dyes of alkanet, cutch and madder were extracted from the roots of their respective plants. Dry roots of these plants were obtained from Pride International, Karachi, Pakistan. Colourants of Indian madder (Turkey red) and marigold flower (Sun yellow) were acquired from Sam vegetable colours, Muradabad, India in powder form.

2.1.3 Dyeing auxiliaries

Laboratory grade, commercial chemicals namely aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3$), copper sulphate (CuSO_4), ferric chloride (FeCl_3), Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and hydrated potassium aluminium sulphate or alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) were utilized as mordants. Other products used as dyeing auxiliaries included crosslinking agents, UV absorbers, cationizing agent and other washfastness improving finishes. These were obtained from their companies of origin. Detail of different auxiliaries used with natural dyes on cotton fabric is given in Table 2.1.

Table 2.1: Dyeing auxiliaries used in this study for the colouration of cotton.

Commercial Name	Function	Chemical constitution	Supplier
Thermacol MP	Migration Inhibitor	Aqueous solution of a poly-acrylic acid derivatives	Huntsman, Textile Effects
Albaflow Conti	Penetration Accelerant	Preparation based on fatty alcohol ethoxylate and alkyl phosphoric acid	Huntsman, Textile Effects
Albafix WFF	Cationizing Agent	Fixative, cationizing agent/ aqueous preparation of a polymeric, quaternary ammonium compound	Huntsman, Textile Effects
Dicrylan	Finishing Agent	Multipurpose polymer/polyurethane emulsion	Huntsman, Textile Effects
UV- SUN	UV Absorbers	Reactive UV absorber based on an oxalanilide	Huntsman, Textile Effects
Rayosan C		Fibre-reactive UV absorbers/ heterocyclic compound	Clariant International Ltd.
Fixapret CPF	Crosslinking Agents	Crosslinking agent/ methylolation product based on glyoxalmonourein	BASF chemical company
Fixapret F-ECO		Crosslinker/ modified dimethyloldihydroxyethylene urea	BASF chemical company
Knittex RCT		Crosslinking agent/modified dihydroxy ethylene urea	Huntsman, Textile Effects

2.2. MACHINERY FOR DYEING

Samples were coloured by continuous dyeing method which required the relevant machinery of pad-steam dyeing. The details of machinery utilized for the applications of various dyeing recipes and fabric testing equipments are as below:

2.2.1 Dyeing paddler

Dye formulations were padded in padding mangles of the thermosol machine. In order to apply the dye, the machine was switched on and the air hose (1/4 inches in aperture) connected between the compressor and the hose nipple of the air regulator and a pipe or hose was arranged to the exhaust port under the sink of mangle. In order to wash the rollers of mangle, a running water pipe was arranged near the mangle rollers. The air pressure was increased up to 7 kg/cm² for the air compressor and the motor stopped automatically when the desired air pressure was reached. Likewise, it re-started automatically when it came down to 5.5 kg/cm².

For handling the padding mangle, the air regulator handle was turned clockwise and the air pressure for the mangle roller was increased as was indicated on the gauge. Then the turning of air regulator handle was stopped, the lever of the manual valve was closed and mangle roller was loaded with pressure. In the same way, if the pressure previously increased was desired to be reduced, the air regulator handle was turned anti clock wise and the lever of the manual valve was pushed outwards i.e. on pressure reduction side. To utilize the mangle of the thermosol machine the operation order for the test was as follows:

The test fabric was joined with the guide cloth on the machine. One set of guide rollers on the fluid beck was removed and dyeing liquor was supplied in the fluid beck and the beck was then fixed at the determined place. The cloth speed was set to the desired value. As the length of the moved cloth came back and returned to the original state, the take-up roller was removed and was pulled out from the guide cloth under the mangle roller. Now one dip- one nip step was over. The same was repeated for more number of dip and nip. When the mangles were not in use then nip was always kept open.



Figure 2.1: A front view of thermosol machine

2.2.2 Pre/post-treatment pad mangle

This machine was used for padding various pre and post-treatments (dyeing auxiliaries) required in the dyeing formulas for the present project. To operate the machine, pressure was applied to the right and left shaft separately for the rubber roll pressure. The pressure of each rubber roll was set to the specified value with air regulator, while observing pressure gauge. Then the pressure switch was pushed on the front and the rubber rolls were pressurized. (In case of pressure of rubber rolls below 1.5 kg/cm², they were not pressurized sufficiently).

The rubber rolls used to rotate when the motor switch on the front was switched on. The rotating speed of the rubber roll ranged from 2 to 8 m/min. The speed could be changed by turning the handle of the variable speed changer while the rubber rolls were rotating. To treat the fabric, liquor (dyeing auxiliary) was put in the fluid back and the fabric sample was inserted. The sample was then put through the nips of the mangle. After squeezing process of the fabric sample was finished, it was pulled horizontally at the back side. This was the completion of one dip-one nip procedure. The process was repeated according to the pre-planned number of dip-nip for the current project. Pickup rate was determined by adjusting the nib pressure. Pickup was set at 80%.

Finally, the motor was switched off, the breaker switch was pressed down and roll pressure switch was switched off and the rubber rolls were thoroughly cleaned (with water only) from the back side of the machine to avoid any danger of hands being caught in the rubber rolls. Figure 2.2 presents a view of the heavy duty mangle machine used for the application of various pre and post-treatments with mordants or other auxiliaries.

2.2.3 Over feed pin tenter

This machine is designed for heat treatment of a test fabric. It was used to dry the dyed fabric samples according to the standard recommended temperature and time required for each dyeing auxiliaries. The machine can take 200-450 mm wide test fabric with an adjustable device. Its maximum temperature capacity is 230° C. It is provided with automatic temperature controller. Its fabric processing speed is 30 seconds to 6 minutes with variable speed changer. For preparatory operations, all the breaker switches in the

switch box were switched on. A pilot lamp on control panel was lighted up. To drive a change, motor switches located on the front and the on the end of the machine were operated. The required temperature was set and the fan motor was switched on. For the current research project, the appropriate heater switches (according to the required temperature for various dye formulation) were as below:

- i. In order to get 80-120 °C: 9 KW heater was activated.
- ii. For 120-160 °C: 9 KW and 3.5 KW heaters were switched on.

The machine's width was adjusted to the width of fabric sample. The engagement of the clutches of tentering handle to each other was checked. Subsequently, the adjustment of the tentering ratio of the cloth was required. It ranges from 0-12% on this machine. Finally, after adjusting the duration of heat treatment on timer, the fabric sample was fixed onto and over feed mechanism. The end of the fabric sample was guided to the end of over feed roller passing through a swivel tension and delivery rollers. The end of fabric was pinned slightly and the nip of delivery rollers was opened by lever. After the fabric sample was set, it was pulled out so as to be slightly tightened. Now the nip was closed by a lever and the preparation of over feed was completed. Afterwards, the motor was switched on and the test was performed. Fabric was automatically taken out by a cloth remover with a caterpillar system. In dye formulation where lowered temperature lines were required, only a motor fan was switched on. The doors were opened thoroughly to lower the temperature to the required level. A view of the Over feed tenter utilized for drying fabric samples is displayed in Figure 2.3 (a) and 2.3 (b).

2.2.4 Laboratory steamer

The laboratory steamer type DHe is provided with the functionality of (i) steaming with saturated steam (ii) high temperature steaming and (iii) drying, curing or setting. To proceed for the pad-steam dyeing, steaming was predetermined at 100 °C for which the very first function of the steam box was workable. For steaming with saturated steam of approximately 102 °C, fan and heating were switched on after turning on the main switch (for pre heating the steamer up to 100 °C, as was required for the experiment).



Figure2.2: Padding mangle machine



Figure 2.3(a) Front view of Tenter frame (feeding fabric for drying).



Figure 2.3(b): Back view of Tenter frame (fabric received after drying).



Figure 2.4: A picture of Rotawash utilized for wash fastness testing.

The fan and heating were closed as soon as the steamer was warmed up to acquire an air free system. Subsequently, the switch for saturated steam was turned on. Afterwards, the steam regulating valve was completely opened and it stayed in that mode during the steaming process, for the purpose of avoiding a pressure in the steam generator while water was let in. Next, water supply valve was opened completely and it also stayed like that during the steaming process. Now the exhaust air channel at the beck was closed and was put in the psychomotor. After reaching the set temperature, the required dwell time was pre selected. Eventually, the frame was placed in the holding device; the push button operated and the frame was transported into the steamer. As soon as the adjusted dwell time was over, the frame came out again automatically.

2.3 EQUIPMENT AND STANDARDS FOR FABRIC TESTING

For the purpose of investigating the role of various dyeing auxiliaries utilized in the application of natural colourant, fabric samples were examined for wash fastness, light fastness, rubbing fastness, tensile strength and relative colour strength. Fabrics were tested according to ISO 105-C06; ISO 105-X12; ISO 105-B02; ASTM, D5035-06; and Color iQC (2012), for wash, crocking, light, Tensile strength and colour coordinates, respectively. The specific tests were applied using the following instruments:

2.3.1 Washfastness

Washfastness of the dyed samples was tested according to the standard procedure described by International Organization for Standardization (ISO 105-C10:2006) using Rotawash by SDL (Shirley Development Limited). For this purpose, a solution of 5g/l of soap (as per requirements of ISO recommendations) along with 2g/l of Na_2CO_3 were used at a liquor ratio of 1:50. Washing was carried out at 60°C for 30 minutes. Both change in shade and staining on the adjacent white fabric was analyzed by Grey-Scale. The Rotawash (Figure 2.4) has been designed to operate at temperatures of up to boiling fresh water. To load the samples for testing, the lid was lifted; “Mains” push button was pressed, followed by pressing “Rotor drive” push button and tubes were placed in rotor rack. The tubes were afterwards secured with bayonet and spring action. Now the final bath temperature was set through the temperature controller. The control knob on the time was rotated for required soak time and “Mains” push button was pressed. Time

switch was on. The bath began heating up and tubes started rotating. After the desired temperature was reached, the timer got initiated and made it to maintain the set temperature for the desired time. The heater automatically switched off and the “Time Elapsed” light illuminated at the end of the time period. Eventually, the samples were removed from the tubes, rinsed with clear water and kept for drying.

Results of various tests were evaluated by Grey-scale. It consisted of five sets of squares in which one set was white and 4 pairs were of grey and white colour chips, each signifying a contrast of visual difference. The white chips on the Grey-scale represented to fastness rating of 5. Rating of 4 to 1 was corresponded to a reference white chip material with those which were used for rating 5, paired with similar but neutral grey chips. The visual difference was compared between the original piece and the stained piece with the difference represented by the Grey-scale. The fastness rating of the tested sample was that the number of Grey-scale which corresponded to the contrast between the original and the stained samples. A rub fastness rating of 5 GS could be assigned only when there was no difference between the original white material and the stained cloth. Likewise, 1 GS was supposed to be allocated to that tested sample in which the stained sample was similar to the dyed sample (representing very poor wash fastness). In case the number was indicated between two of the contrasts of the scale, the sample was allocated an intermediate assessment e.g. 4-5 GS.

As far as staining on the fabric is concerned, the transfer of colour from the test sample to the adjacent white specimen is evaluated in the same manner as was done for change in shade on Grey-scale. There are five standard pairs in which one half of each standard is white and the other half ranges from white (meaning no staining) to the similar gray (meaning great deal of staining). No staining is represented by a value of 5 GS, whereas, 1 GS indicates maximum staining i.e. poor colour fastness.

2.3.2 Crockmeter

For determining the colour fastness to rubbing, experiments were carried out for dry as well as wet rubbing using Shirley crock meter model number 225 (Figure 2.5). Rubbing fastness of dyed samples was tested according to ISO 105 X-12:2001 and the results were assessed by Grey-scale for change in shade. Crocking fastness test

determines the extent of colour which may be transferred from the surface of dyed textile object to another surface by crocking or rubbing. Two pieces of fabric samples were required to accomplish dry and wet rubbing fastness test. In the present study, white crocking samples were prepared from the fabric that was previously desized, scoured and bleached for dyeing. Principle of testing involved fastening of the dyed test specimen to the base of the crockmeter and rubbing it under controlled conditions with white crocking cloth. Change in shade both for dry and wet rubbing was assessed by Grey- scale.

2.3.2.1 Test for dry rubbing

In order to investigate the dry rubbing fastness of the samples dyed with the aid of various dyeing formulations, the crocking cloth (white piece) measuring 50x50 mm square was mounted on to the rubbing finger of the machine in dry state and was secured with spring clip. Next, to fix the testing sample to the machine, the clamps were removed from the instrument, the sample was laid down in flat and tight position and the clamps were replaced for clamping the dyed sample for testing. Eventually, the machine was switched on and reading was adjusted on digital readout for the number of rubs or strokes. The finger covered with crocking cloth was lowered automatically and started to and fro motion on the dyed (clamped) sample. It slid 10 times to complete the predetermined (10 turns) number of rubs at a speed of one stroke per second. The distance for crocking was adjusted as 10 cm for the rubbing finger.

2.3.2.2 Wet crocking test

For the accomplishment of wet crocking fastness, the procedure adopted earlier for dry rubbing test was followed with a fresh sample. The test sample was clamped in the instrument in dry state. The crocking (white) cloth was previously wetted out with water, squeezed and was on to the crockmeter's finger. The instrument was switched on to complete the predetermined number of rubs.

2.3.2.3 Light booth - visual color control

Under different lighting conditions, colours appear in a different way. To simulate different lighting conditions, light booth was used to obtain colour assessments (wash and crocking) with highest confidence.



Figure 2.5: Electronic crockmeter/ rubbing fastness tester at work.



Figure 2.7: Tensile strength tester used in this study.



Figure 2.6: Glimpses of light fastness tester used in this study.



It provided better opportunity for comparison of standard and sample in a colour-neutral environment and the risk of biasness due to subjective assessment was minimized.

2.3.3 Light fastness tester

Light fastness was tested according to the standard procedure described by ISO (ISO 105-B02) using digital light fastness tester, SDL 237 (Figure 2.6). The tester utilizes mercury ballast tungsten filament tungsten lamp and internally phosphor coated with controlled condition of light, temperature and humidity with the apparatus. The units consist of a hollow cylinder of metal with a fading lamp mounted centrally so that the light distribution is constant around the circumference. An hour meter totalizer is mounted on the base. 50 test tube holders are installed at equidistance in the inner circumference of cylinder. As temperature may touch 80 °C, constant cooling arrangement with water flow is provided. Temperature is maintained by two plastic tubes connected to tap water and drained in the exterior. Humidity inside the tubes was controlled by adding 2ml of 73% sodium nitrate solution to each cell.

Table 2.2: Hours and standard specification of light fastness tester

Number of hours required for testing	Blue Wool Standard No.	Light Fastness Rating	Degree/extent of fading
5	1	Very poor	Very extensive fading
10	2	Poor	Extensive fading
20	3	Fair	Significant fading
40	4	Moderate	Appreciable fading
80	5	Good	Moderate fading
160	6	Very good	Slight fading
320	7	Excellent	Very slight fading
640	8	Outstanding	No fading

2.3.4 Colour coordinates

Colour strength and other colour coordinates of dyed specimens were evaluated by computer-aided, Datacolor SF 600 reflectance spectrophotometer with software for colour measurement. Colour characteristics were measured as L^* , a^* , b^* , C^* , h° and K/S values of the coloured fabric samples.

2.3.5 Tensile strength tester

Since the third main objective of the present work was to study the effect of natural dyes on the tensile properties of cotton fabric, the tensile strength and elongation of cotton fabric samples were determined before and after the application of various dyeing formulas. The procedure was adopted according to the standard method prescribed by American society for testing and materials (ASTM D5035-06). An electronic tensile strength tester (Testometric 220 D) was used for the purpose (Figure 2.7). After adjusting the instrument with the required jaws-separation for fabric strength, the strain speed was set to 90 inches per minute.

The counter was calibrated to 334.4 ± 0.2 by pressing, “reset” and “cal” buttons, while rotating the span knob. Next “reset” was pressed and “zero” button was rotated to bring the counter at zero reading. A fabric strip $2^{1/2}$ inches wide and 10 inches long was cut initially from the specimen. The width of the sample was reduced to 2 inches by removing threads from edges. The tested length was taken 8 inches between the jaws, allowing 1 inch extra fabric on each side, for gripping.

After inserting the specimen in the jaws, the strain button was pressed to put load on samples. The machine used to stop automatically when the specimen broke. Finally, the “return” button was pressed to bring the crosshead back to its original position. The number of pounds required for breaking the sample (tensile strength) and extensions (inches) was recorded from the digital readout.

2.4 EXTRACTION OF DYES

Solvent extraction procedure of natural colourants was performed with soxhlet apparatus, using ethanol as an organic solvent. For the solvent to evaporate, rotary evaporator was used. The total amount of extracted dye was more than 25 % after

weighing the dry extracts. To isolate the colourant from the plants of alkanet, cutch and madder, their roots were chopped manually. The dried and chopped root material of plant was refluxed with 1:1 of water: ethanol (2.5 g in 100ml solution). After 3-4 hours, the suspension was filtered and the filtrate was evaporated. All operations were carried out at room temperature. The extract was suspended in 2 % H_2SO_4 and was refluxed for 2 days. Greenish extracts from alkanet, brown from cutch and reddish-brown semi solid natural dye extract was obtained from madder.

2.5 METHODOLOGY OF DYEING

Fabric treatment involved various stages including: desizing, scouring and bleaching of fabric to prepare fabric for dyeing; preparation of dyeing formulas; pre-treatment procedure of pad-steam dyeing and post-treatment of pad-steam dyeing procedure.

2.5.1 Preparation of fabric for dyeing

As the fabric was purchased in unfinished grey form, it was desized, scoured and bleached in the processing laboratory of department of textile chemistry, National Textile University, Faisalabad. Desizing is the process of removing starch or size usually from the warp yarns of woven fabrics. Sizing agents are selected on the bases of type of material, ease of removal, environmental friendliness, efficient treatment etc. To prepare the cotton fabric samples for dye uptake, it was processed through enzymatic desizing, as it is the most widely practiced approach for the removal of starch size.

Formulation for desizing involved 2 g/l of Bactosol MTN (bacterial amylase, provided by Clariant Ltd) treated under pH 6-6.5 at 60 °C for 1 hour. Scouring was done to remove impurities which cotton may contain (4-12 % by weight in the form of waxes, ash, proteins and other substances such as reducing sugars etc). For good scouring the proper choices of auxiliaries in alkaline bath is essential. Recipe for scouring comprised 15 g/l of NaOH; 1 g/l of wetting agent, 2g/l of sequestering agent (Polyron by Clariant Ltd) and 1 g/l of detergent. All the ingredients were processed at 80-90 °C for 1 hour. Bleaching was carried out by adding 10 g/l of hydrogen peroxide (H_2O_2) in the formulation. Other substances were: 2 g/l of NaOH (pH 10-10.5), 2 g/l of stabilizer

(Pentex GP, by Clariant Ltd., which contains anionic detergent and wetting agent with built-in peroxide stabilizer) and 1 g/l sequestering agent all managed at 80-90 °C for 1 hour. Eventually, the desized, scoured and bleached fabric was cut into small pieces of 10×18 inches each for the application of various dyeing recipes.

2.5.2 Preparation of dyeing liquors.

All the five natural dyes were tested with the help of various dye formulation including pre and post-mordanting and pre and post-treatment of crosslinker, UV absorbers and other finishing agents. Dye bath for control sample (untreated sample) was prepared by adding 30 g/l of dye together with 1 g/l of wetting agent, Albaflow Conti (penetration accelerant by Huntsman, Textile Effects) and 1 g/l of migration inhibitor, Thermacol MP (by Huntsman, Textile Effects). Dye formulation of pre-mordanting and post-mordanting included 20 g/l of a specific mordant either before or after the padding of dye formula. Likewise, UV absorber, Dicrylan and Fixative finishes were used in the quantity of 30 g/l and crosslinkers in the amount of 50 g/l were also part of pre and post-treatment of dyeing recipes for natural dyes on cotton.

2.5.3 Procedure for dyeing

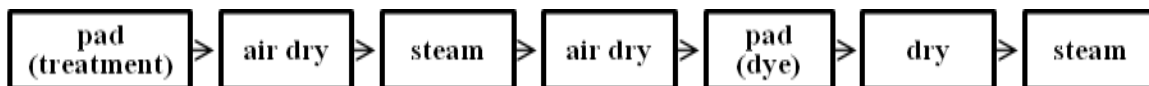
Dyeing was accomplished through continuous method. A two bath-two stage, pad steam dyeing process was carried out for the application of all the selected natural dyes. Dyeing auxiliaries were applied both as pre-treatment as well as post-treatment. However, the control sample (untreated sample) was coloured with a dyeing recipe having no mordant, crosslinker, UV absorber or any finishing agent. Dyeing bath for this reference sample was prepared by only a natural dye and required dyeing auxiliaries such as wetting agent and migration inhibitor.

Pad-steam dyeing is a type of continuous dyeing process which is primarily used for the dyeing of cellulosic fibres such as cotton or viscose rayon as well as their blends. This dyeing process offers some exceptional advantages in the form of simplicity, versatility and flexibility. The process is an economical and efficient way of colouring long runs in particular shades. The method has greater tolerance of colour variation in comparison with other methods such as batch dyeing etc. In the present study, this

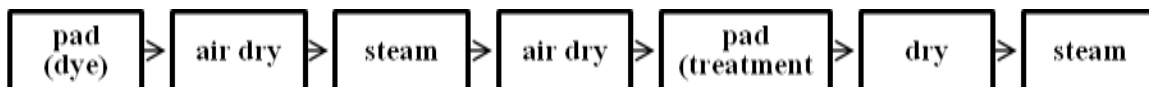
method was adopted to colour cotton fabric samples. Already cut out/prepared samples were introduced to the dye range (dye recipe). The process was carried out in open width so as to acquire uniformity of dye application. Dye formulations were applied through the padding mangle at liquor ratio, sufficient enough to acquire 80 % wet pick up. The samples were dried in the air.

2.5.3.1 Pre-treatment and post-treatment procedures

The application dye through mordanting process consisted of padding the sample with 20 g/l of every mordant on heavy duty mangle machine by 2 dip-2 nip process. The sample was dried in the air at room temperature and it was subsequently shifted to steamer. Steaming was carried out at 100 °C for 10 minutes. The dried sample was padded with dyeing recipe in the padder by 3 dip-3 nip process. The sample was again dried at room temperature and was taken once again in a steam box (at 100 °C for 10 minutes). The sequence of the entire operation of pre-padding is as below:



In the post- treatment process, the sample was padded first with the dye formula. In the second stage, the specific mordant/auxiliary was applied through padding. The order of experimentation can be stated as:



The same procedure was adopted for the dyeing of cotton with natural dyes using crosslinkers, UV absorbers and other fabric finishes. Auxiliaries such as Albafix WFF and UV-SUN were dried/cured at 30 °C; all the mordants and Dicrylan at 120 °C and the crosslinkers were processed in the over feed tenter from 120- 130 °C for drying or curing.

2.6 ANALYSIS OF DATA

Data was analyzed statistically by simple percentages as well as t-test using SPSS (Statistical Package for Social Sciences) to check the significance of difference between

pre and post-treatments (paired sample t-test); between control and pre-treated sample; and between control and post-treatments (one sample t test) of the cumulative colour fastness and tensile strength of dyed samples. Findings are presented through Tables, graphs and charts wherever necessary.

CHAPTER 3

RESULTS

Dyeing auxiliaries including mordants, finishes, UV absorbers and crosslinkers were employed to assist various plant-based natural colourants applied on pure cotton fabric samples by pad-steam method. To know the fabric construction, variety of laboratory tests were performed on the fabric sample before it was put to dyeing operations. These comprised count of yarn (56 Ne in warp and 46 Ne in weft direction); twist in yarn removed from fabric (36 and 25 turns per inch in warp and filling); thread count (62 ends and 60 picks per inch); fabric thickness (0.05 mm) and weight per unit area or GSM (70 g/m²) etc. After the application of dye formulations, the dyed cotton samples were subjected to wash fastness (change in shade, staining on fabric); crocking fastness (dry and wet rubbing); light fastness; colour coordinates (lightness, colour tone, chroma or purity of colour, hue or shade, relative colour strength or K/S); tensile strength and elongation testing in the warp direction.

3.1 DYEING COTTON WITH ALKANET (*ALKANA TINCTORIA*)

Data related to the colour fastness, colour strength and tensile properties of alkanet dyed cotton samples with various pre and post-padding of auxiliaries are included in Tables 3.1- 3.10 and displayed through Figures 3.1- 3.6.

3.1.1 Shades obtained with alkanet root extracts

Dyeing of cotton fabric with natural extracts of alkanet by twenty-five different dyeing formulas produced greenish (inclined towards grey) colour samples. On the basis of intensity and shades, samples were grouped as medium greenish- grey, greenish-brown and yellowish- brown. The most greenish, smooth, leveled, soft and attractive sample was yielded by the formulation of post-mordanting with potassium dichromate (Exhibit 3.1). This was followed by a coloured sample obtained from the post-mordanting of copper sulphate. Medium greyish- green samples were those which resulted from the pre-treatments of aluminium sulphate, Fixapret CPF, Knittex, and both pre and post-treatment of Rayosan C. These samples were exactly similar in shade to control sample.

Exhibit 3.1: Shades produced by cotton samples dyed with natural extracts of alkanet under different conditions.

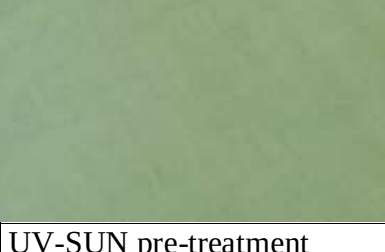
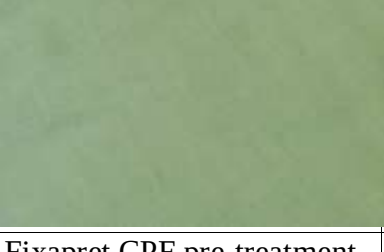
		
Control sample	K ₂ Cr ₂ O ₇ post- mordanting	K ₂ Cr ₂ O ₇ pre- mordanting
		
CuSO ₄ pre-mordanting	CuSO ₄ post-mordanting	Albafix pre-treatment
		
Alum pre-mordanting	Alum post-mordanting	Albafix post-treatment
		
UV-SUN pre-treatment	FeCl ₃ pre -mordanting	FeCl ₃ post-mordanting
		
Al ₂ (SO ₄) ₃ pre-treatment	Fixapret CPF pre-treatment	Knittex pre-treatment

Table 3.1: Fastness and tensile properties of cotton fabric dyed with root extracts of *Alkana tinctoria* using various mordants.

Method	Mordant	Wash Fastness		Crocking Fastness		Light Fastness	Tensile strength (lb)	Elongation (%)
		Change in shade	Staining on fabric	Dry rubbing	Wet rubbing			
Pre-mordanting	Al ₂ (SO ₄) ₃	3-4	4-5	4	3	4	48.4	5.25
	CuSO ₄	3-4	4	3-4	2-3	4	47.4	4.50
	FeCl ₃	4	4-5	2	3	4	43.0	2.88
	K ₂ Cr ₂ O ₇	3	4-5	3	3	5	41.4	4.63
	KAl(SO ₄) ₂ ·12H ₂ O	3	4	3-4	2-3	4	59.5	5.50
Post-mordanting	Al ₂ (SO ₄) ₃	4	4	4-5	3	4	51.6	5.00
	CuSO ₄	2-3*	4-5	4-5	2-3	4	55.2	5.38
	FeCl ₃	3-4	3	4-5	4-5	5	47.6	4.88
	K ₂ Cr ₂ O ₇	4	4	4-5	3	4	66.6	6.30
	KAl (SO ₄) ₂ ·12H ₂ O	2*	3-4	4	3-4	4	61.2	5.75
No mordanting	Control sample	2-3	4	4-5	3-4	3	57.5	5.38

* Became darker than original during testing

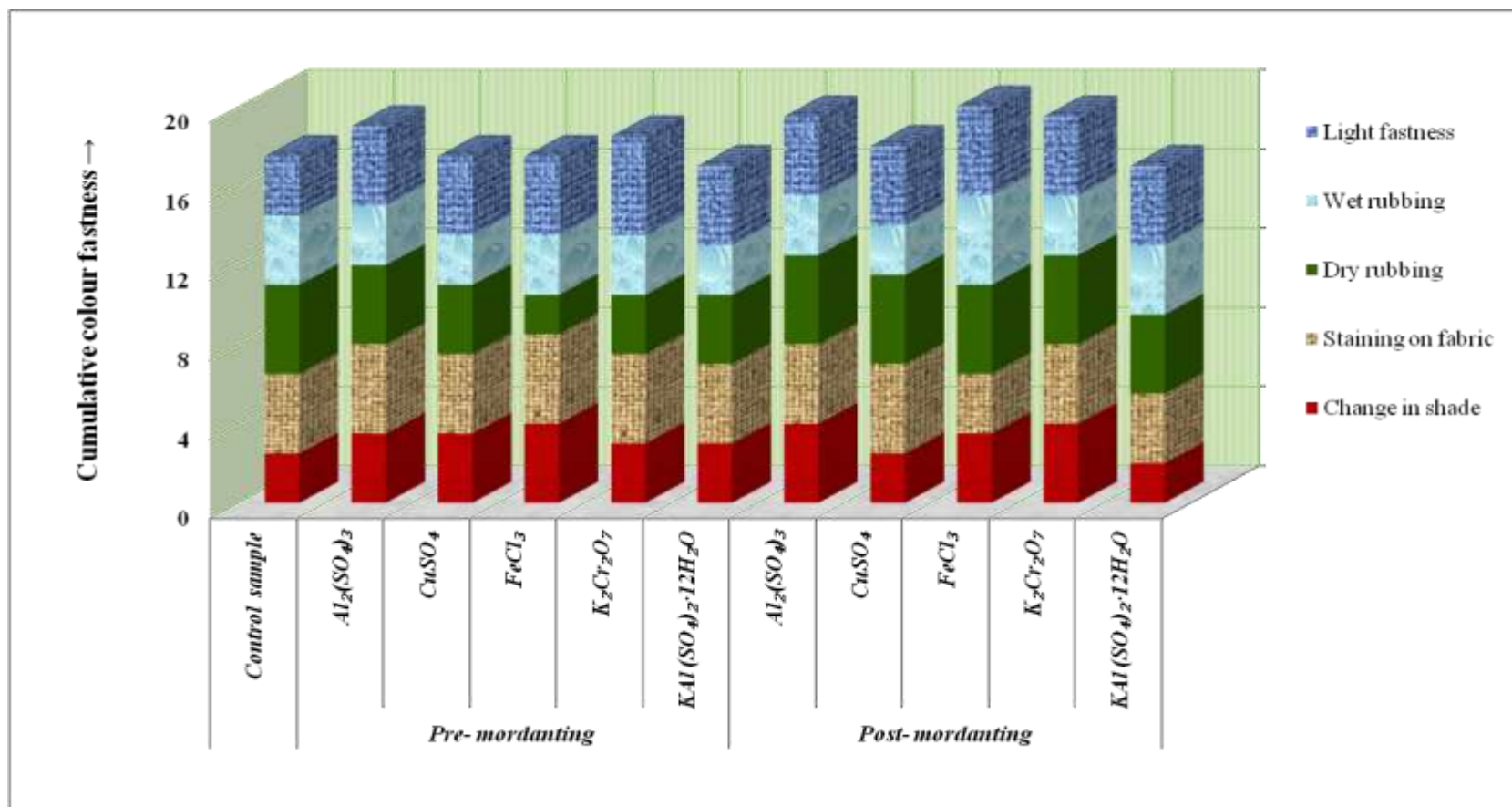


Figure 3.1: Cumulative colour fastness of cotton samples dyed with root extracts of *Alkanna tinctoria* using various mordants.

Table: 3.2 Fastness and tensile properties of cotton fabric dyed with root extracts of *Alkana tinctoria* using various finishes and UV absorbers.

Product	Method	Wash Fastness		Crocking Fastness		Light Fastness	Tensile strength (lb)	Elongation (%)
		Change in shade	Staining on fabric	Dry rubbing	Wet rubbing			
Albafix WFF	Pre cationizing	3	3	4	4-5	4	59.5	5.63
	Post cationizing	3	4-5	4	3	5	60.9	6.13
Dicrylan	Pre finishing	3	4	4	3	4	53.9	5.00
	Post finishing	4	2-3	3-4	4	5	59.9	5.75
UV –SUN	Pre-treatment	3	4	3-4	2-3	4	57.1	5.63
	Post-treatment	3	4	3-4	2-3	5	64.1	5.75
Rayosan C	Pre-treatment	3-4	4	4-5	3-4	4	49.9	4.25
	Post-treatment	2-3	4	4-5	3	5	55.9	5.50
Control sample	Untreated	2-3	4	4-5	3-4	3	57.5	5.38

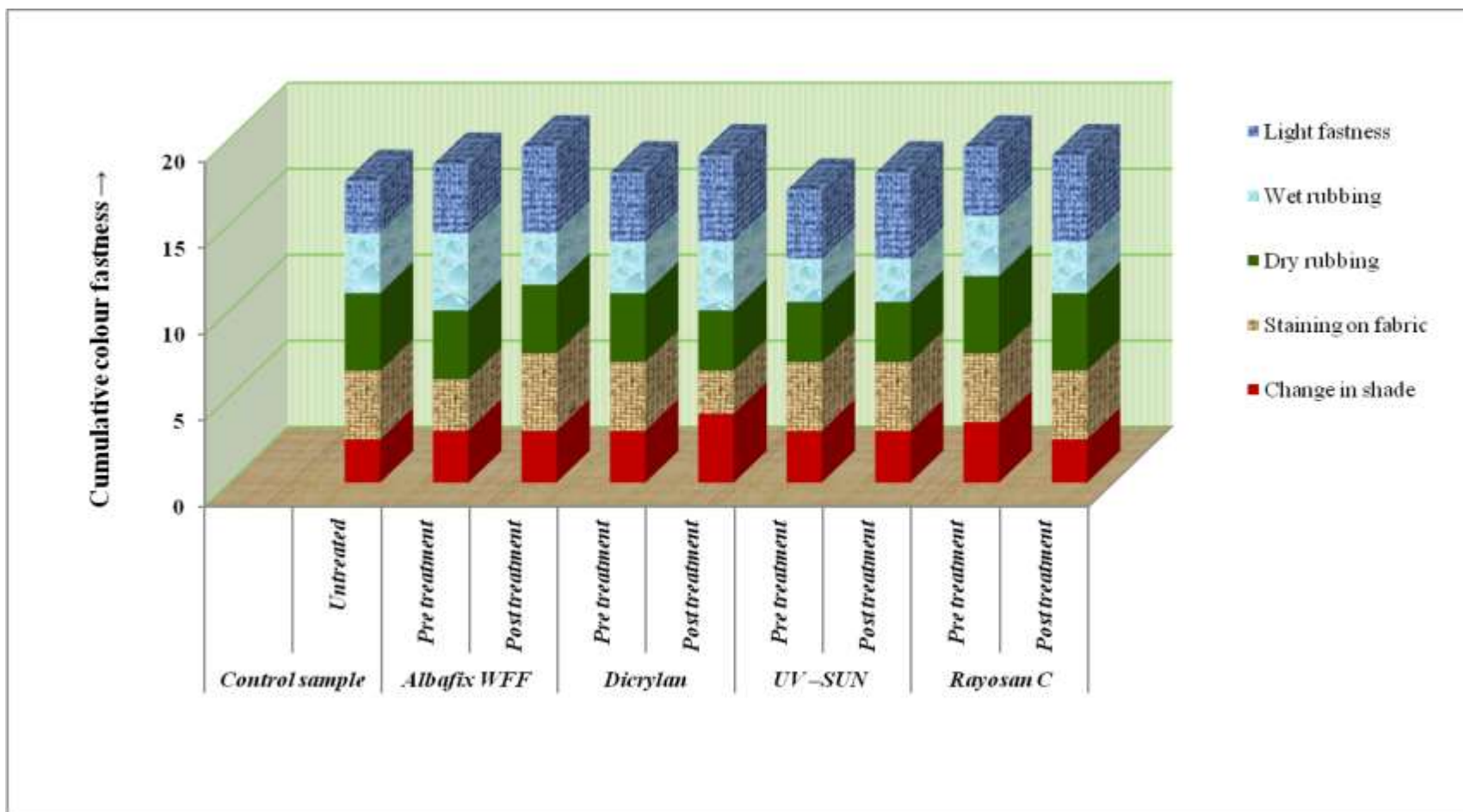


Figure 3.2: Cumulative colour fastness of cotton samples dyed with root extracts of *Alkana tinctoria* using various finishing agents and UV absorbers.

Table: 3.3 Fastness and tensile properties of cotton dyed with root extracts of *Alkana tinctoria* using various crosslinking agents.

Product	Method	Wash fastness		Crocking fastness		Light fastness	Tensile strength (lb)	Elongation (%)
		Change in shade	Staining on fabric	Dry rubbing	Wet rubbing			
Fixapret CPF	Pre-treatment	3	4	4-5	3	4	54.9	6.38
	Post-treatment	3	4-5	4	3	5	61.0	6.25
Fixapret F-ECO	Pre-treatment	3	4	4-5	3	4	54.0	5.25
	Post-treatment	3	4	4-5	3	5	54.2	5.50
Knittex RCT	Pre-treatment	3	3-4	4-5	3-4	4	53.0	5.75
	Post-treatment	3	4-5	4-5	3	4	60.8	6.25
Control sample	Untreated	2-3	4	4-5	3-4	3	57.5	5.38

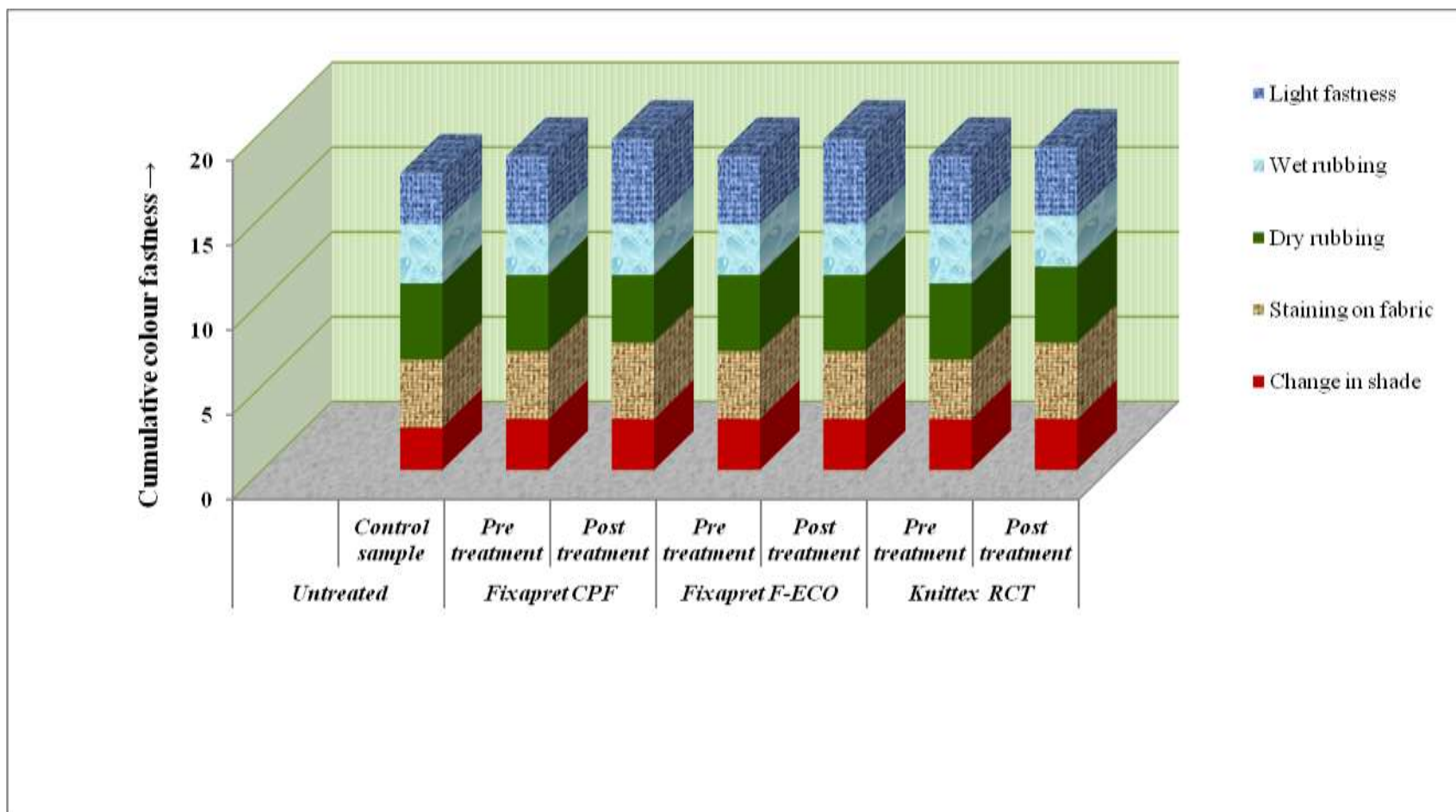


Figure 3.3: Cumulative colour fastness of cotton samples dyed with root extracts of *Alkana tinctoria* using various crosslinking agents

Table 3.4: Paired sample statistics for cumulative colour fastness of cotton dyed with *Alkana tinctoria* (alkanet).

Treatment	Mean	N	Std. Deviation	Std. Error Mean
T 1*	18.17	12	0.78	0.22
T 2	19.00	12	0.93	0.27

*T 1 = Pre-treatment; T 2= Post-treatment

Table 3.5: Significance testing of cumulative colour fastness of cotton fabric samples dyed with alkanet.

(a) Paired sample 2- tailed t- test for cumulative colour fastness: paired differences

Treatments	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
T 1 - T 2	-0.83	0.83	0.24	-1.36	-0.30	- 3.46	11	0.005

(b) One-Sample t-test: cumulative colour fastness

Cumulative colour fastness	Control sample = 17.5					
					95% Confidence Interval of the Difference	
	t	df	Sig. (2-tailed)	Mean Difference	Lower	Upper
T1	2.96	11	0.01	0.67	0.17	1.16
T2	5.59	11	0.00	1.50	0.91	2.09

Table 3.6: Paired sample statistics for tensile strength of cotton dyed with *Alkana tinctoria* (alkanet).

Treatment	Mean	N	Std. Deviation	Std. Error Mean
T 1	51.83	12	5.93	1.71
T 2	58.25	12	5.44	1.57

Table 3.7: Significance testing of tensile strength of cotton fabric samples dyed with alkanet.

(a) Paired sample 2- tailed t- test for tensile strength: paired differences

Treatments	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
T 1 - T 2	6.42	6.45	1.86	-10.51	-2.32	3.44	11	0.005

(b) One-Sample t-test: tensile strength

Tensile strength	Control sample = 57.5					
					95% Confidence Interval of the Difference	
	t	df	Sig. (2-tailed)	Mean Difference	Lower	Upper
T1	-3.31	11	.007	-5.67	-9.43	-1.89
T2	0.48	11	0.642	0.75	-2.70	4.20

Table 3.8: Colour coordinate values of *Alkana tinctoria* dyed cotton fabric samples using various mordants.

Method	Mordant	Colour coordinates					
		L*	a*	b*	C*	h°	K/S
Pre-mordanting	Al ₂ (SO ₄) ₃	54.06	0.04	5.13	5.13	89.56	2.83
	CuSO ₄	50.61	0.23	7.20	7.21	88.16	3.92
	FeCl ₃	46.59	2.48	12.02	12.27	78.33	7.80
	K ₂ Cr ₂ O ₇	51.12	-1.14	8.39	8.47	97.75	4.49
	KAl(SO ₄) ₂ ·12H ₂ O	49.31	-0.43	3.00	3.03	98.14	3.26
Post-mordanting	Al ₂ (SO ₄) ₃	59.74	1.85	5.25	5.56	70.58	1.28
	CuSO ₄	59.69	-2.89	12.78	13.10	102.73	7.94
	FeCl ₃	58.19	2.43	12.71	12.94	79.17	5.18
	K ₂ Cr ₂ O ₇	57.94	-1.81	4.26	4.63	113.02	2.30
	KAl (SO ₄) ₂ ·12H ₂ O	59.39	1.95	5.62	5.95	70.84	1.80
No mordanting	Control sample	58.77	0.41	4.32	4.34	84.55	1.92

Table 3.9: Colour coordinate values of *Alkana tinctoria* dyed cotton fabric samples using various UV absorbers.

Product	Method	Colour coordinates					
		L*	a*	b*	C*	h°	K/S
Albafix WFF	Pre cationizing	45.95	1.37	5.14	5.32	75.04	4.46
	Post cationizing	59.30	-0.17	2.44	2.45	94.01	1.28
Dicrylan	Pre finishing	56.56	-0.14	3.74	3.75	92.10	3.49
	Post finishing	57.92	-0.86	1.25	1.77	118.96	3.36
UV –SUN	Pre-treatment	56.25	-0.53	2.14	2.21	103.91	20.6
	Post-treatment	54.17	-0.29	2.83	2.84	95.81	2.42
Rayosan C	Pre-treatment	58.82	-0.37	1.30	1.36	105.79	1.27
	Post-treatment	59.90	0.67	1.85	1.97	70.09	1.38
Control sample	Untreated	58.77	0.41	4.32	4.34	84.55	1.92

Table 3.10: Colour coordinate values of *Alkana tinctoria* dyed cotton fabric samples using various crosslinkers.

Product	Method	Colour coordinates					
		L*	a*	b*	C*	h°	K/S
Fixapret CPF	Pre-treatment	58.22	0.02	3.24	3.24	89.60	1.82
	Post-treatment	58.30	-0.86	1.85	2.04	114.99	1.61
Fixapret F-ECO	Pre-treatment	58.78	-0.32	2.67	26.9	96.90	1.74
	Post-treatment	58.93	-0.72	1.93	2.06	110.56	1.24
Knittex RCT	Pre-treatment	57.94	0.40	4.30	4.32	84.63	2.04
	Post-treatment	59.75	-0.54	1.25	1.64	109.05	1.44
Control sample	Untreated	58.77	0.41	4.32	4.34	84.55	1.92

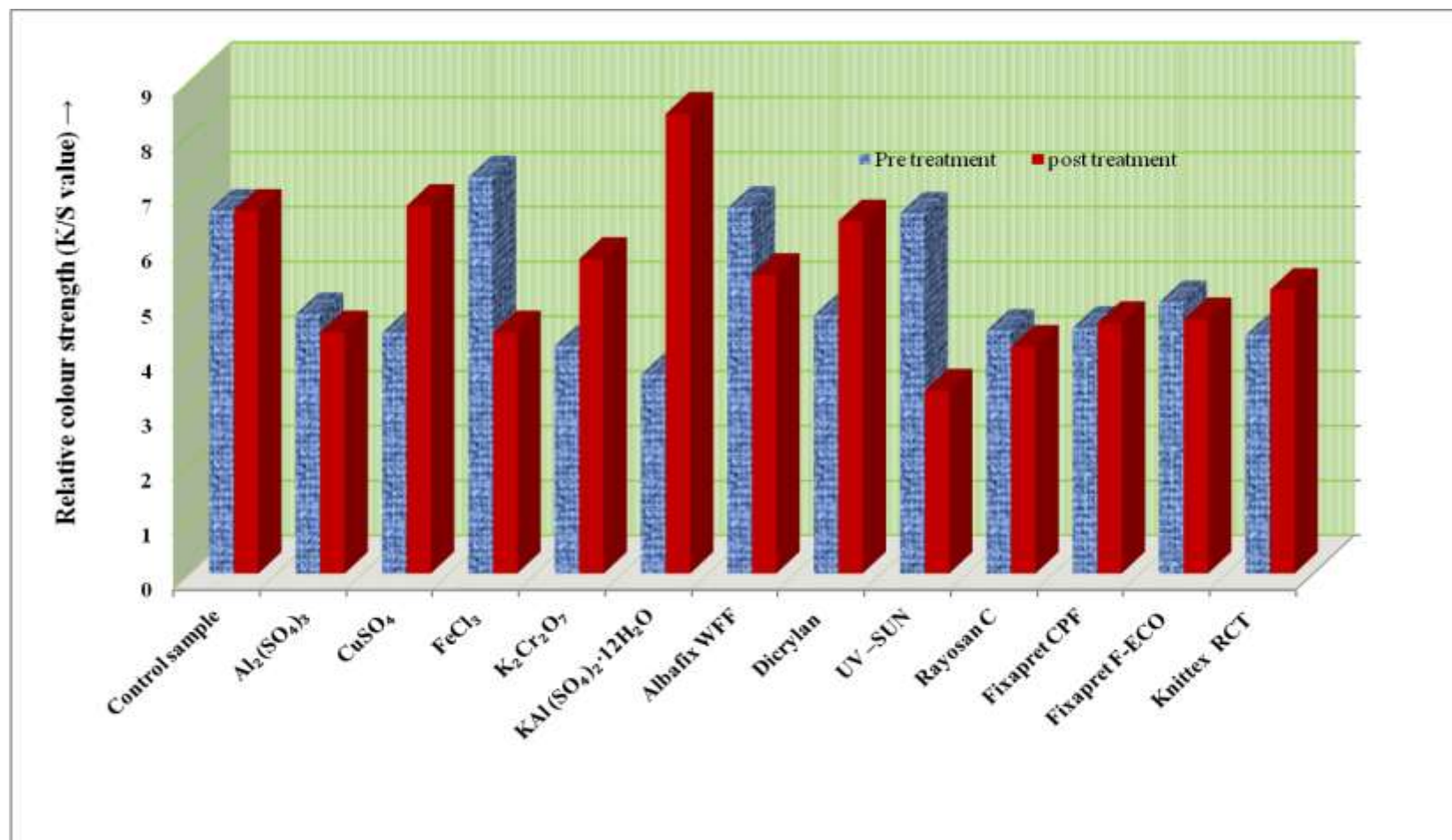


Figure 3.4: Effect of various dyeing auxiliaries on the colour strength of cotton samples dyed with root extracts of *Alkanna tinctoria*.

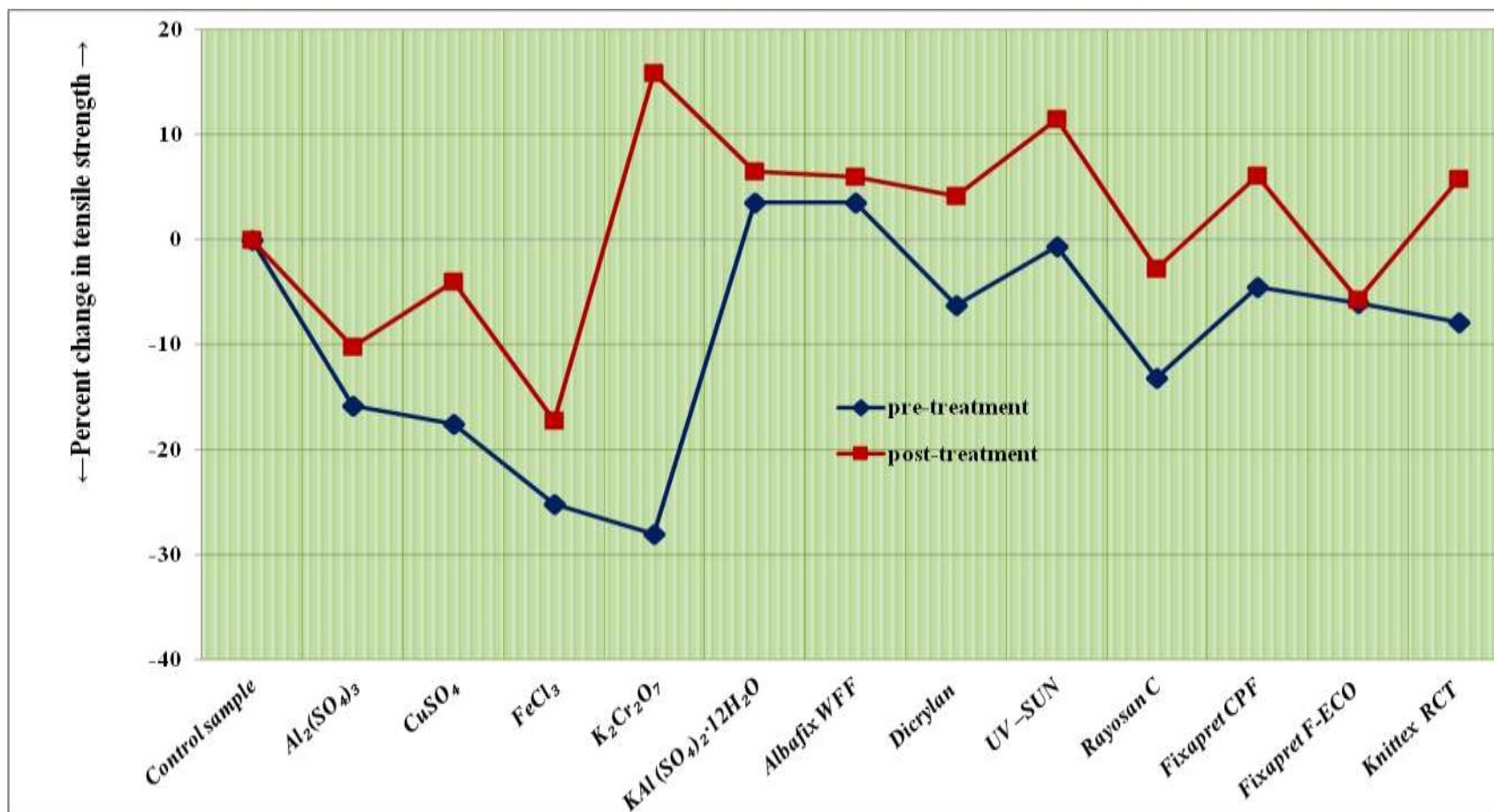


Figure 3.5: Effect of various dyeing auxiliaries on the tensile strength of cotton samples dyed with root extracts of *Alkana tinctoria*.

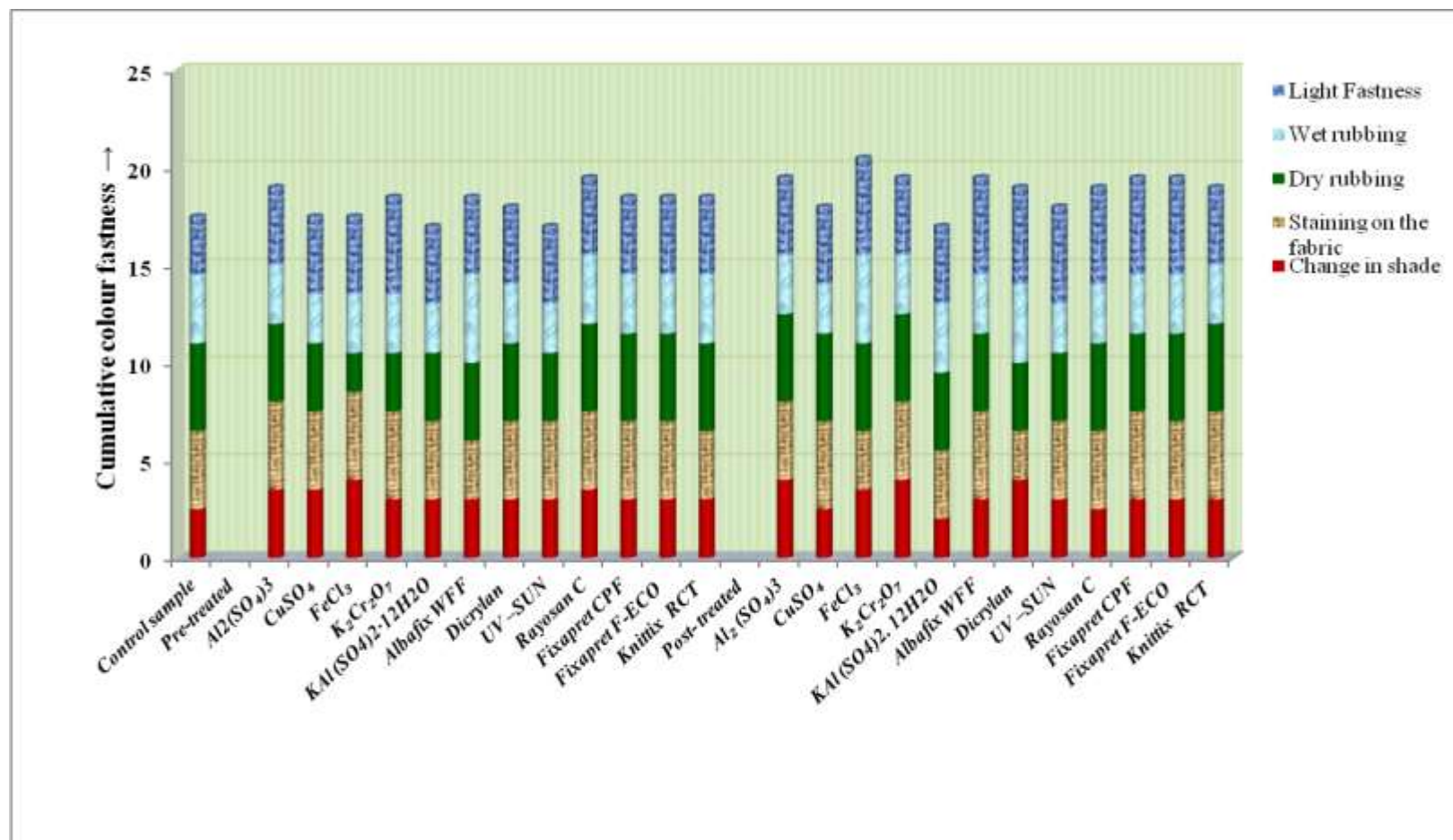


Figure 3.6: Comparative analysis of cumulative colour fastness of cotton dyed with various dye formulations of *Alkanna tinctoria*.

Samples similar to each other but having tone of green as compared to grey were obtained from the dye formulations of both pre and post- padding of UV-SUN, Fixapret F- ECO, Dicrylan as well as post- treatment of Albafix, Fixapret CPF and Knittex. Dyeing with mordants such as pre-treatment of copper sulphate, aluminium sulphate and hydrated potassium aluminium sulphate produced dark greenish-grey samples. Dye formulation with the mordanting of ferric chloride and alkanet dyed cotton produced yellowish- brown samples with the pre-mordanted sample having greater intensity (darker shade) than the post- mordanted fabric.

3.1.2 Wash fastness of sample coloured with alkanet

The reference or control sample which was dyed without any colour improving auxiliary, presented moderate wash fastness equal to 2-3 on Grey-scale (Table 3.1). Minimum change in shade due to washing resulted from the pre-mordanting of ferric chloride and post-mordanting of aluminium sulphate and potassium dichromate in the dye formulations. The rating measured from these recipes was equivalent to 4 Grey-scale (GS), representing good performance of wash fastness. This was followed by 3-4 GS ranking provided by pre-mordanting of cotton sample with aluminium sulphate, copper sulphate and post-mordanting with ferric chloride. A change in the shade of 3 GS was revealed by the cotton sample pre-mordanted by potassium dichromate and alum. In case of post-mordanting with CuSO_4 , the rating was similar to the wash fastness of control or untreated sample. The maximum change in the shade of 2 GS due to wash fastness test was resulted from the post-treatment of hydrated potassium aluminium sulphate (alum) on dyed cotton.

Post-treatment of alkanet dyed cotton with Dicrylan displayed the wash fastness rating of 4 GS (change in shade), which is considered to be good fastness (Table 3.2). Pre-mordanting of cotton sample with Rayosan and dyeing with alkanet exposed 3-4 GS rating due to washing. All other dyeing formulas among this group produced cotton samples with a fastness rating of 3 GS change in shade, thus allowing slight superiority to the wash fastness of the control sample. These included the pre and post-treatment of Albafix WFF, UV-SUN and pre-treatment of Dicrylan. The fastness due to washing caused by the post-treatment of Rayosan C was just similar to the rating assigned to the

control sample (2-3 GS). All the crosslinking products utilized in this study (irrespective of the method of application) offered 3 GS (satisfactory wash fastness) rating of change in shade due to washing (Table 3.3).

As far as staining on the adjacent white fabric is concerned due to wash test, best result (minimum staining) was displayed by samples dyed with formulas of pre-mordanting with $\text{Al}_2(\text{SO}_4)_3$, FeCl_3 , $\text{K}_2\text{Cr}_2\text{O}_7$ and post-mordanting with CuSO_4 , where the rating was 4-5 GS. This was followed by staining of 4 GS, available from control sample as well as samples pre-mordanted with CuSO_4 , $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and post-mordanted with $\text{Al}_2(\text{SO}_4)_3$ and $\text{K}_2\text{Cr}_2\text{O}_7$. Maximum staining of 3 GS among this group was shown by dyed samples, post-mordanted with ferric chloride.

Very little staining (equivalent to 4-5 on Grey-Scale) was noticeable from the tested samples, dyed with a combination of alkanet and post-cationizing of Albafix WFF. Good wash fastness performance related to 4 GS was offered by samples having pre-treatment of Dicrylan, pre and post-treatment of UV-SUN as well as Rayosan C. Pre-cationizing of cotton with Albafix WFF stained the adjacent white sample more than the control sample and was rated as 3 GS. Heavy staining of 2-3 GS was shown by the cotton sample dyed with a combination of alkanet and post-treatment of Dicrylan in the dyeing formula. Comparing the staining resulted from the treatments of various crosslinkers, it was observed that the dyed cotton resulted from the post-treatments of Fixapret CPF and Knittex RCT stained the adjacent white fabric very little (identical to 4-5 GS). Pre-treatments of Fixapret CPF and both pre and post-treatment of Fixapret F-ECO on cotton sample displayed 4 GS grading similar to the performance of the control sample. Maximum staining among crosslinkers was recorded from the sample which was pre-treated with Knittex RCT. It was rated as 3-4 on Grey-scale.

3.1.3 Crocking fastness of cotton dyed with alkanet

As regards the results of dry rubbing fastness of cotton samples dyed with alkanet and various mordants, it is evident from the tabulated data (Table 3.1) that the post-mordanting of a dyed cotton sample with $\text{Al}_2(\text{SO}_4)_3$, CuSO_4 , FeCl_3 and $\text{K}_2\text{Cr}_2\text{O}_7$ produced samples with dry rubbing equal to 4-5 on Grey scale, thereby, representing very good fastness performance of dyed articles. In the same group, the sample which faded the

most due to dry crocking was the one which had a treatment of pre-mordanting of ferric chloride in the dye formulation. The dry rubbing rating of this dyed sample was recorded as only 2 on Grey-scale. Fastness rating of cotton samples dyed with a combination of alkanet and pre-mordanted with aluminium sulphate; and dyed and post-mordanted with alum yielded dry rub fastness similar to 4 GS. Dry crock fastness rating equal to 3-4 GS was available from the pre-treatments of cotton sample with copper sulphate and alum as mordants.

As far as the dry rubbing fastness of cotton with treatments of UV absorbers and other finishes are concerned, 4-5 GS rating was exhibited by those cotton samples which were dyed with recipes having Rayosan C both as pre and post-treatments. This was followed by the pre and post-treatments of Albafix WFF and pre-treatments of Dicrylan. Lowest dry rubbing fastness in this group was 3-4 GS attained by samples having pre or post-treatments of UV-SUN and post-treatments of Dicrylan. The entire list of crosslinkers employed with alkanet dye displayed dry rubbing of 4-5 GS except the samples which was obtained from the post-treatments of Fixapret CPF. It scored a rating of 4 Grey -scale for dry crock fastness.

Regarding the wet rubbing fastness performance of cotton samples coloured with alkanet, the rating of 3-4 GS was assigned to the control sample. In comparison, only the dyed cotton sample resulted from the post-mordanting of ferric chloride was able to produce wet rubbing fastness greater than the fastness of that untreated sample (i.e. 4-5 GS). All other mordants in the dyeing formulas produce cotton with lesser wet rub fastness. The most faded sample due to wet rubbing was the one which was coloured with pre-mordanting and post-mordanting of CuSO_4 (2-3 GS) and pre-mordanting of alum. Post-mordanting of alum on dyed cotton sample with alkanet presented 3-4 GS grading, identical to the wet crocking of control sample. Wet rubbing fastness of 4-5 GS was exhibited by cotton pre-treatment of Albafix WFF and dyed with natural extracts of alkanet. This exhibition of best fastness of wet rubbing was followed by 4 GS, resulted from dyeing with post-finishing of Dicrylan. Lowest fastness due to wet rubbing of 2-3 GS among this group of dyeing auxiliaries was found in samples dyed with pre or post-treatment of UV-SUN. Among the auxiliaries of crosslinkers group, wet fastness was 3

GS with all the recipes except the one which was dyed with the formula of pre-treated Knittex RCT. It offered 3-4 GS grading, just equal to the scoring of the control sample.

3.1.4 Light fastness of cotton dyed with alkanet

Regarding light fastness performance, the results related to alkanet dyed cotton samples are presented in Table 3.1. Without any special dyeing auxiliaries, the control sample could achieve only 3 Blue Wool Standard light fastness. Highest light fastness was exhibited by the cotton sample dyed with a combination of natural extracts of alkanet and pre-mordanting potassium dichromate and dyed and post-mordanted with ferric chloride. Both these samples were rated as standard 5 which are matched with good light fastness property. Besides these, all other mordants employed with the application of alkanet posed light fastness of 4 Blue Wool Standard which is a fairly good performance.

Similarly, fastness rating of 5 Blue Wool Standard was displayed by cotton samples padded with alkanet and post-treated/padded with Albafix WFF, Dicrylan, UV-SUN and Rayosan C. Whereas, pre-treatments of all these products turned out alkanet dyed cotton fabric possessing light fastness equivalent to 4 Blue Wool Standard. The post-treatment of crosslinkers Fixapret CPF and Fixapret F- ECO on alkanet dyed cotton, yielded samples having good light fastness equal to standard 5. All other pre and post-treatments of crosslinkers utilized to assist dyeing moved the light fastness a little one step ahead of the control or reference sample and they were allotted standard 4 in favour of the fairly good fastness representation.

3.1.5 Analysis of cumulative colour fastness: t-test

Cumulative colour fastness (wash, crock and lightfastness) of cotton samples dyed with alkanet root extracts with the help of various dyeing auxiliaries has been displayed in Figure 3.6. A paired-sample t-test was conducted to compare the cumulative colour fastness of cotton samples dyed with alkanet in the presence of various dyeing auxiliaries employed before and after the padding of fabric with a dye formulation. There was a significant difference in the scores (rating) of pre and post-treatments of the dyeing auxiliaries (Table 3.4). For pre- treatments (mean= 18.17, standard deviation= 0.78); post-treatments (mean=19.0, standard deviation = 0.93); $t = - 3.458$ and $p = 0.005$ (Tables 3.4

and 3.5), these results propose that post-treatment procedure was a better option. Significance testing of the cumulative colour fastness of alkanet dyed cotton fabric samples was also carried out by applying t-test on control sample and pre-treated samples as well between control and post-treated samples (Table 3.5). Significant difference was found between the fastness of control and pre-treated samples as well as between the control and post-treated fabric samples.

3.1.6 Colour coordinate values of alkanet dyed cotton fabric

The effect of various treatments with natural extracts of alkanet roots applied on cotton samples with the assistance of various dyeing auxiliaries has been investigated through Datacolor SP 600 and the results are displayed through Tables 3.6-3.9. The values related to the colour yield or lightness (L^*) of cotton samples dyed with alkanet, ranged from 46.59 to 59.74. Greater colour yield was found in the sample which was pre-mordanted with ferric chloride. Lightness (L^*) values from other dyeing recipes were 49.31, 50.61, 51.12, 54.06, 57.94, 58.19, 59.39, 59.69 and 59.74 from pre-mordanting of alum, copper sulphate, potassium dichromate, aluminium sulphate and post-mordanting with potassium dichromate, ferric chloride, hydrated potassium aluminium sulphate (alum), copper sulphate and aluminium sulphate, respectively. The coordinate a^* which represent red- green tone, was negative (greener tone) from the dyeing recipe of post-mordanting CuSO_4 , pre and post-mordanting $\text{K}_2\text{Cr}_2\text{O}_7$ and pre-mordanting alum representing green tone of the dyed samples. Maximum redness was offered by pre-mordanting of FeCl_3 in case of the alkanet dyed sample. The values of b^* were all positive. Pre-mordanting with alum produced the lowest tone of yellow, whereas, the maximum yellowness resulted from the post-mordanting of CuSO_4 . Moreover, the chroma value (C^*) was also maximum from the same dyeing formula, i.e. post-mordanting with CuSO_4 and minimum from the pre-mordanting of alum. The hue (h°) or shade was more obvious (113.02) in case of treatment with post-mordanting $\text{K}_2\text{Cr}_2\text{O}_7$. As far as the relative colour strength (K/S) of dyed samples is concerned, the highest colour strength value was exposed by post-mordanting of CuSO_4 . This was followed by pre-treatment of FeCl_3 . Minimum K/S value (1.28) among this group was registered by post-mordanting of aluminium sulphate.

The colour coordinate values of alkanet dyed cotton with the aid of various finishes and UV absorbers are included in Table 3.7. The lightness (L^*) values ranged from 45.95 (pre-cationizing with Albafix WFF) to 59.90 (post-treatment with Rayosan). Most of the values of a^* were in the negative area showing green tone of the dyed samples. The highest value of -0.86 was introduced by the post-treatment of Dicrylan. However, the data related to b^* was all positive, representing yellowness of the *Alkana tinctoria* dyed samples.

The chroma (C^*) or purity of colour was maximum (5.32) from the treatment of pre-cationizing Albafix WFF. While, the smallest value of chroma was available from the pre-treatment of Rayosan. The highest value of hue was found to be 118.96 from the dyeing formula having post-treatment of Dicrylan, whereas, lowest h° was shown by alkanet dyed sample which was post-padded with Rayosan. Relative colour strength of samples dyed with this group of aides ranged from 1.27 to 4.46, with the maximum being available from pre-cationization of Albafix WFF. Lightness values of samples treated with crosslinkers was almost similar for all the dyed samples. It ranged between 57.9 and 59.7. The coordinate a^* was negative for samples achieved from pre and post- padding of Fixapret F-ECO, and the post-treatment of Fixapret CPF and Knittex RCT depicted a tone of green. Remaining samples of this group grabbed positive a^* value. However, the values were very small (ranging from 0.02-0.41). The data related to b^* was all in the positive region, describing yellowness in the tone. The chroma (C^*) values of crosslinkers treated alkanet dyed cotton samples ranged from 1.64 to 4.32. For control sample this value was 4.34. The hue or h° value was minimum for the untreated sample. The colour strength values of these dyed samples were in the range of 1.44 to 2.04. The maximum K/S value was conveyed by the pre-treatment of Knittex RCT.

3.1.7 Tensile strength of cotton dyed with alkanet

Most of the dyeing formulas in respect of natural extracts of *Alkana tinctoria* extracts were responsible for lowering the tensile strength of dyed cotton samples. Maximum decrease in strength of 28 percent was characterized by pre-mordanting of potassium dichromate and 25 percent loss in strength occurred due to the treatment of pre-mordanting ferric chloride. An increase in strength was also noticed from some of the

dye formulations having various auxiliaries. The most prominent among them were 16 and 12 percent from the post-mordanting of potassium dichromate and post-treatment of UV- SUN. Slight increase in strength was also yielded by the post-treatments of Albafix WFF, Fixapret CPF and alum. Paired sample statistics of tensile strength of dyed samples (Tables 3.6 and 3.7) showed significant result between pre-treated and post-treated samples at 5% level of significance. Furthermore, the mean strength value due to post-treatments was higher than the pre-treatments. Significance testing of the tensile strength of alkanet dyed cotton fabric samples was carried out by applying t-test on control sample and pre-treated samples as well between control and post-treated samples (Table 5.2). The result reveals significant difference between the strength of control and pre-treated samples. While the difference between the control and post-treated fabric samples were insignificant.

3.2 DYEING COTTON WITH CUTCH (*ACACIA CATECHU*)

The data related to the colour fastness, colour coordinates and tensile strength of cutch or Kath dyed samples by utilizing various pre and post-treated auxiliaries are included in Tables 3.11 to 3.20 and displayed through Figures 3.7- 3.10.

3.2.1 Shades obtained with cutch root extracts

Dyeing of cotton fabric with the extracts of cutch created brown shade samples, with the darkest one being available from the dye formulation of post-mordanting with FeCl_3 . It was the softest, most leveled, smoothest sample having attractive appearance (Exhibit 3.2). With the same intensity of brown shade but with slightly lower softness, a cotton dyed sample was available from the pre- treatment of ferric chloride. Among the reddish brown shade cotton samples the dye formulations consisting of pre-mordanting potassium dichromate and the post-mordanting copper sulphate produced samples with slightly stiffer hand, providing very neat and shiny appearance of the dyed samples.

The dyed fabric samples obtained from the recipe of pre- mordanting copper sulphate was slightly low in intensity of reddish brown shade available from the samples mentioned just above. Similarly, light reddish brown shade sample resulted from the dyeing of cutch dyed sample, post-padded with potassium dichromate.

Exhibit 3.2: Shades produced by cotton samples dyed with natural extracts of cutch under different conditions.

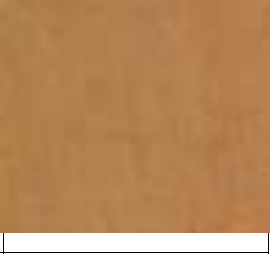
			
	Control sample	Pre-padded: $\text{Al}_2(\text{SO}_4)_3$	Post-padded: $\text{Al}_2(\text{SO}_4)_3$
			
	Pre-padded with FeCl_3	Post-padded with FeCl_3	Post-padded Albafix
			
	Pre-padded with alum	Post-padded with alum	Post-padded Knittex
			
	Post-padded with CuSO_4	Post-padded with $\text{K}_2\text{Cr}_2\text{O}_7$	Post-padded Fixapret CPF
	Various shades of cotton obtained from cutch dyeing		

Table 3.11: Fastness and tensile properties of cotton fabric dyed with root extracts of *Acacia catechu* using various mordants.

Method	Mordant	Wash Fastness		Crocking Fastness		Light Fastness	Tensile strength (lb)	Elongation (%)
		Change in shade	Staining on fabric	Dry rubbing	Wet rubbing			
Pre-mordanting	Al ₂ (SO ₄) ₃	3-4	4	3	2-3	5	55.4	4.00
	CuSO ₄	4	4	3	2	4	67.0	4.63
	FeCl ₃	3-4	4	3	2-3	4	45.6	2.30
	K ₂ Cr ₂ O ₇	3	3-4	3	2-3	4	52.0	3.30
	KAl(SO ₄) ₂ ·12H ₂ O	3	4-5	4	2	5	59.0	4.88
Post-mordanting	Al ₂ (SO ₄) ₃	4	3	4	2-3	4	47.4	3.75
	CuSO ₄	3	4-5	2-3	2	6	69.1	5.88
	FeCl ₃	3-4	3	4	2	4	56.0	4.63
	K ₂ Cr ₂ O ₇	3	4	3	3	6	60.1	4.75
	KAl (SO ₄) ₂ ·12H ₂ O	4	3-4	4-5	3-4	6	60.0	4.50
No mordanting	Control sample	3	3-4	4-5	3	3	58.5	4.12

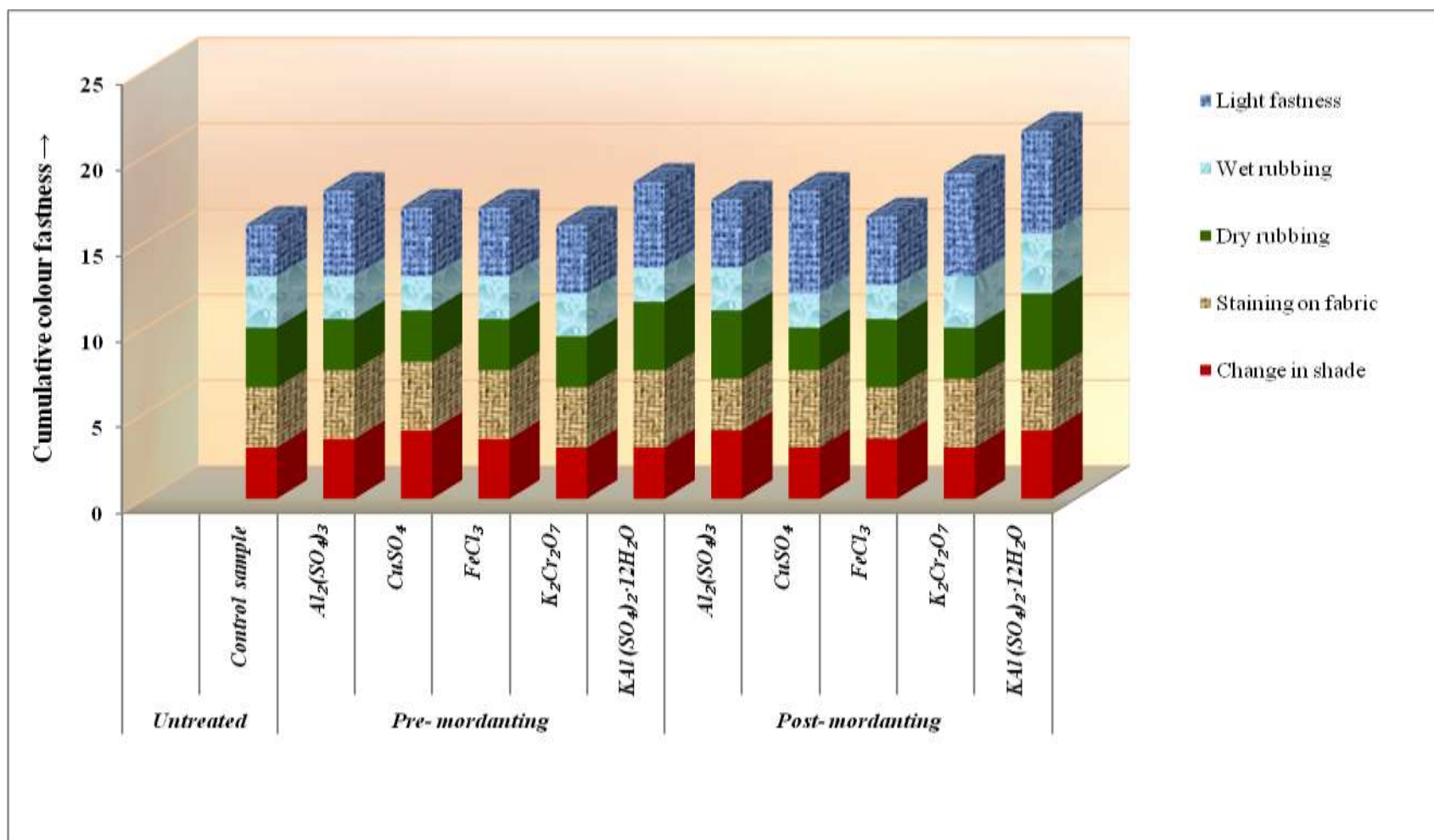


Figure 3.7: Cumulative colour fastness of cotton samples dyed with root extracts of *Acacia catechu* using various mordants

Table: 3.12 Fastness and tensile properties of cotton fabric dyed with root extracts of *Acacia catechu* using various finishes and UV absorbers.

Product	Method	Wash Fastness		Croaking Fastness		Light Fastness	Tensile strength (lb)	Elongation (%)
		Change in shade	Staining on fabric	Dry rubbing	Wet rubbing			
Albafix WFF	Pre cationizing	3-4	3-4	4	3	4	63.0	4.38
	Post cationizing	3-4	3	4	2-3	5	66.0	5.25
Dicrylan	Pre finishing	4	3-4	4-5	2-3	6	58.0	4.13
	Post finishing	3-4	4	3-4	3-4	5	69.8	4.88
UV –SUN	Pre-treatment	3	3-4	4-5	2-3	4*	59.0	4.13
	Post-treatment	4	3-4	3-4	3-4	5	56.2	3.75
Rayosan C	Pre-treatment	3	3-4	3	3	5	63.1	3.63
	Post-treatment	3-4	4	4	2	6	63.1	3.88
Control sample	Untreated	3	3-4	4-5	3	3	58.5	4.13

*** Became darker than original during testing**

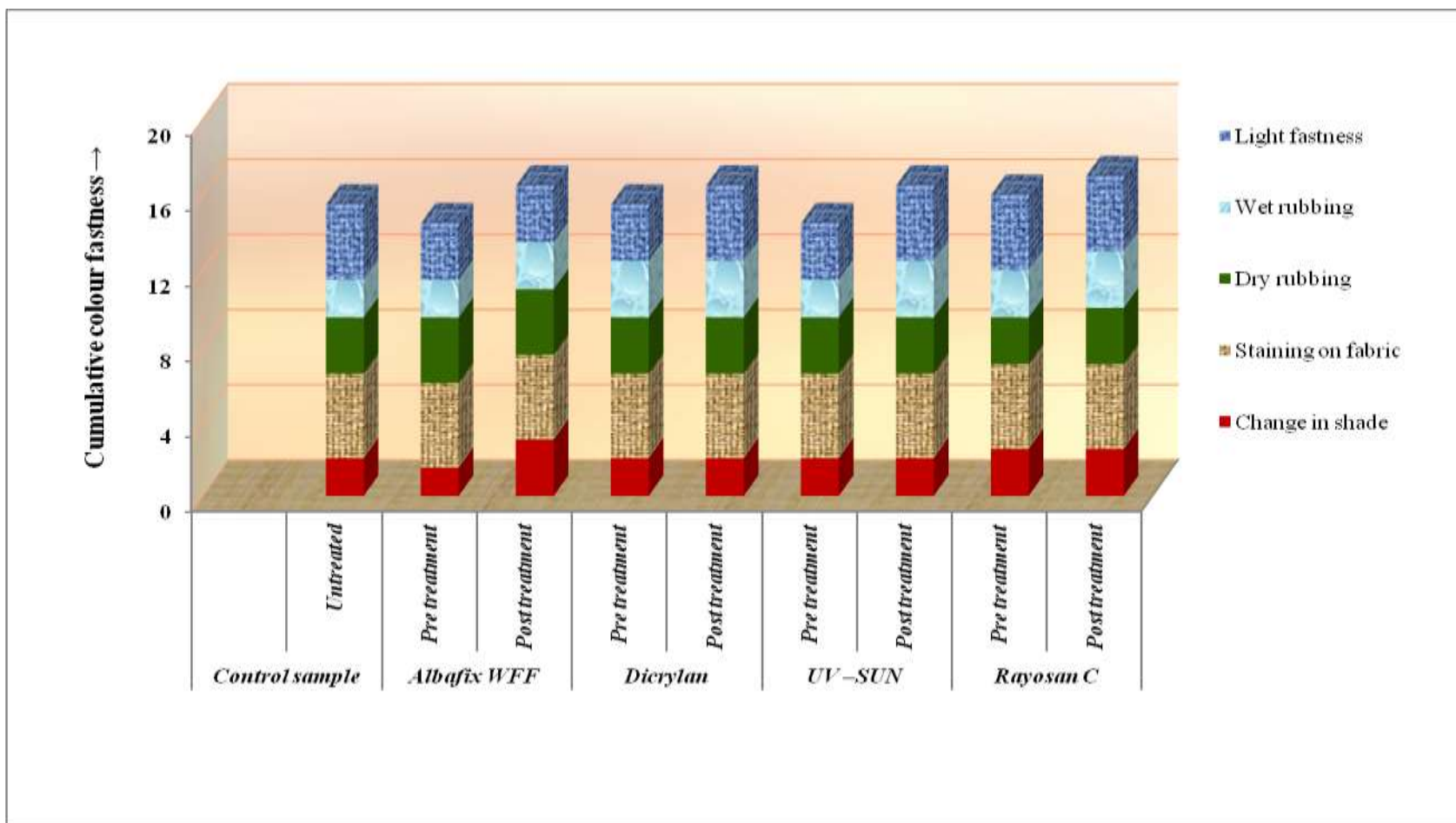


Figure 3.8: Cumulative colour fastness of cotton samples dyed with root extracts of *Acacia catechu* using various UV absorbers

Table: 3.13 Fastness and tensile properties of cotton dyed with root extracts of *Acacia catechu* using various crosslinking agents.

Product	Method	Wash fastness		Crocking fastness		Light fastness	Tensile strength (lb)	Elongation (%)
		Change in shade	Staining on fabric	Dry rubbing	Wet rubbing			
Fixapret CPF	Pre-treatment	3	4	4-5	3	4*	57.9	4.63
	Post-treatment	3-4	4	3-4	2-3	5	45.1	3.38
Fixapret F-ECO	Pre-treatment	3	4	4-5	3	6	59.8	4.50
	Post-treatment	4	4-5	4	2-3	5	66.9	4.63
Knittex RCT	Pre-treatment	3	4	4-5	3-4	5	55.4	4.13
	Post-treatment	3-4	4-5	4-5	2-3	6	60.9	4.25
Control sample	Untreated	3	3-4	4-5	3	3	58.5	4.13

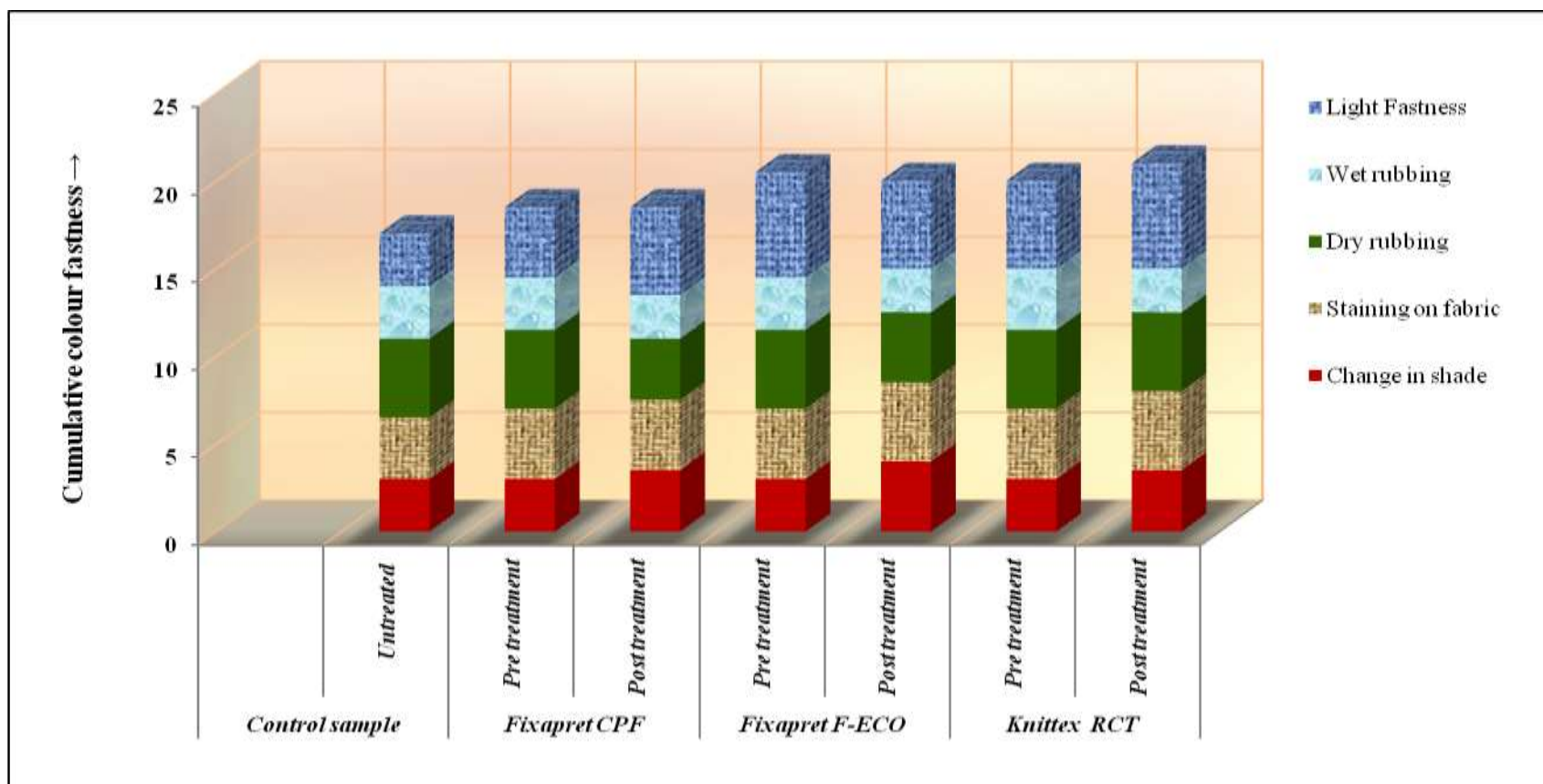


Figure 3.9: Cumulative colour fastness of cotton samples dyed with root extracts of *Acacia catechu* by pad-steam method using various cross linking agents

Table 3.14: Paired sample statistics for cumulative colour fastness of cotton dyed with *Acacia catechu* (cutch).

Treatment	Mean	N	Std. Deviation	Std. Error Mean
T 1*	18.25	12	1.44	0.42
T 2	19.04	12	1.43	0.41

*T 1 = Pre-treatment; T 2= Post-treatment

Table 3.15: Significance testing of cumulative colour fastness of cotton fabric samples dyed with cutch.

(a) Paired sample 2- tailed t- test for cumulative colour fastness: paired differences

Treatments	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
T 1 - T 2	- 0.79	1.42	0.41	-1.69	0.11	-1.93	11	0.08

(b). One-Sample t-test: cumulative colour fastness

Cumulative colour fastness	Control sample = 17					
					95% Confidence Interval of the Difference	
	t	df	Sig. (2-tailed)	Mean Difference	Lower	Upper
T1	3.01	11	0.01	1.25	0.34	2.16
T2	4.92	11	0.00	2.04	1.13	2.95

Table 3.16: Paired sample statistics for tensile strength of cotton dyed with *Acacia catechu* (cutch).

Treatment	Mean	N	Std. Deviation	Std. Error Mean
T 1	12	57.93	5.56	1.61
T 2	12	60.05	7.88	2.28

Table 3.17: Significance testing of tensile strength of cotton fabric samples dyed with cutch.

(a) Paired sample 2- tailed t- test for tensile strength: paired differences

Treatments	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
T 1 - T 2	-2.12	7.32	2.11	-6.77	2.54	-1.00	11	0.34

(b). One-Sample t-test: tensile strength of pre and post treated cutch.

Tensile strength	Control sample = 58.8					
					95% Confidence Interval of the Difference	
	t	df	Sig. (2-tailed)	Mean Difference	Lower	Upper
T1	-0.35	11	0.73	-0.57	-4.10	2.96
T2	0.68	11	0.51	1.55	-3.46	6.56

Table 3.18: Colour coordinate values of *Acacia catechu* dyed cotton fabric samples using various mordants.

Method	Mordant	Colour coordinates					
		L*	a*	b*	C*	h°	K/S
Pre-mordanting	Al ₂ (SO ₄) ₃	47.62	19.87	15.34	25.10	37.66	4.91
	CuSO ₄	46.78	18.61	9.27	20.79	26.48	4.34
	FeCl ₃	46.61	8.56	11.28	14.40	53.43	7.29
	K ₂ Cr ₂ O ₇	47.58	16.64	9.75	19.28	30.38	4.26
	KAl(SO ₄) ₂ ·12H ₂ O	50.39	20.27	15.40	25.46	37.22	3.92
Post-mordanting	Al ₂ (SO ₄) ₃	52.48	14.69	23.74	27.92	58.25	4.32
	CuSO ₄	42.66	18.81	11.80	22.21	32.10	6.81
	FeCl ₃	44.41	5.66	11.95	13.22	64.64	9.13
	K ₂ Cr ₂ O ₇	41.46	16.95	11.26	20.35	33.60	6.50
	KAl (SO ₄) ₂ ·12H ₂ O	57.86	18.22	25.79	31.28	54.76	3.22
No mordanting	Control sample	40.11	17.33	10.26	20.14	30.63	3.88

Table 3.19: Colour coordinate values of *Acacia catechu* dyed cotton fabric samples using various UV absorbers.

Product	Method	Colour coordinates					
		L*	a*	b*	C*	h°	K/S
Albafix WFF	Pre cationizing	41.11	16.47	11.16	19.90	34.13	6.74
	Post cationizing	42.21	15.87	9.10	18.30	29.83	5.42
Dicrylan	Pre finishing	46.82	15.95	10.18	18.92	32.36	4.63
	Post finishing	49.60	12.49	21.74	25.07	60.13	6.93
UV –SUN	Pre-treatment	48.66	15.92	11.75	19.79	36.43	6.62
	Post-treatment	53.42	13.69	12.17	18.31	41.36	3.29
Rayosan C	Pre-treatment	48.99	11.72	19.22	22-31	58.62	6.72
	Post-treatment	51.47	11.81	22.31	25.24	62.10	6.59
Control sample	Untreated	40.11	17.33	10.26	20.14	30.63	3.88

Table 3.20: Colour coordinate values of *Acacia catechu* dyed cotton fabric samples using various crosslinkers.

Product	Method	Colour coordinates					
		L*	a*	b*	C*	h°	K/S
Fixapret CPF	Pre-treatment	48.29	16.31	11.28	20.00	35.36	4.47
	Post-treatment	50.47	12.48	22.41	25.65	60.89	7.23
Fixapret F-ECO	Pre-treatment	46.93	16.58	11.18	20.00	34.00	4.67
	Post-treatment	55.34	11.26	22.15	24.84	63.06	6.24
Knittex RCT	Pre-treatment	46.89	16.48	11.48	20.09	34.87	4.74
	Post-treatment	47.80	13.12	21.19	24.92	58.24	7.65
Control sample	Untreated	40.11	17.33	10.26	20.14	30.63	3.88

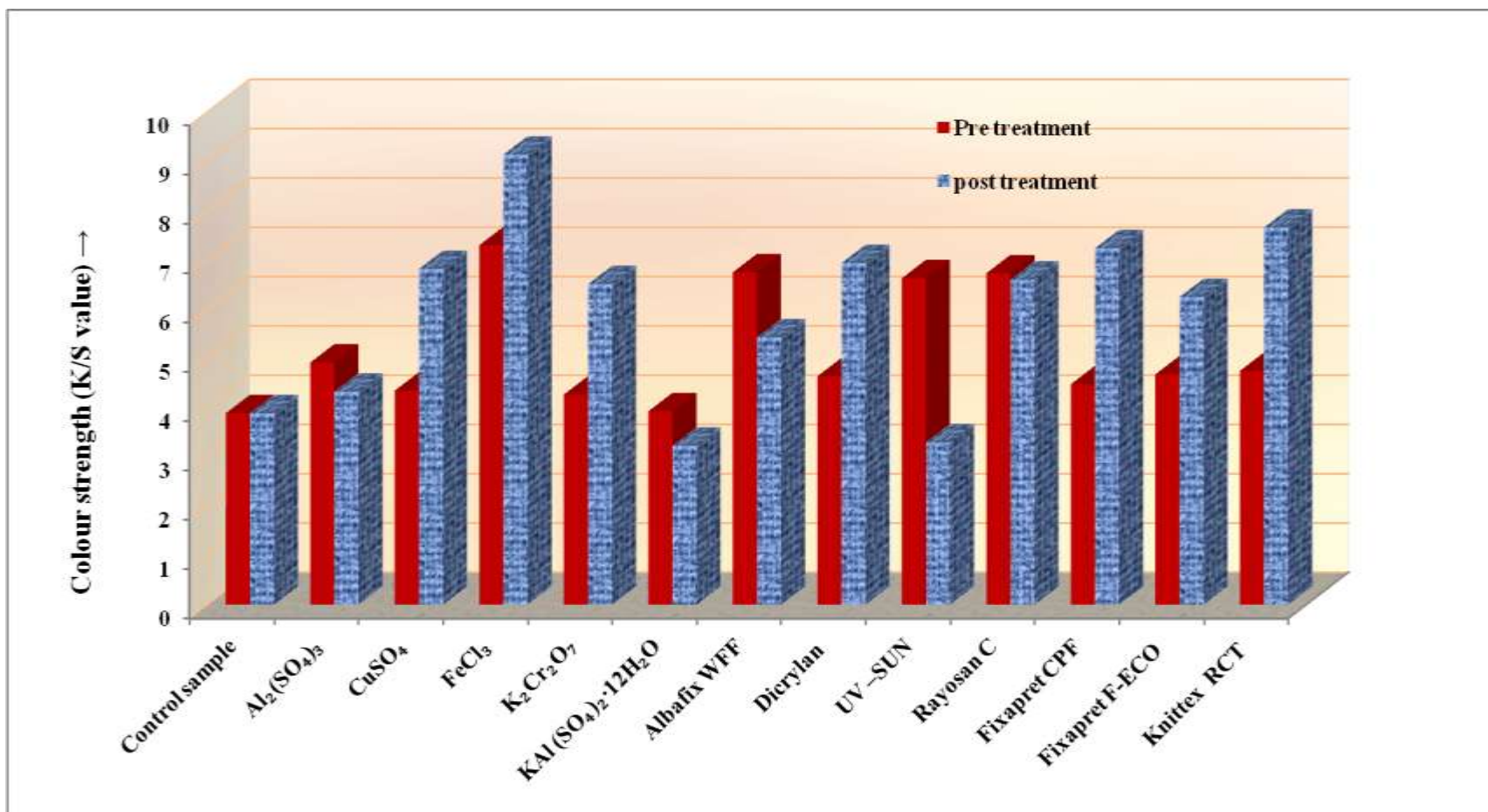


Figure 3.10: Effect of various dyeing auxiliaries on the colour strength of cotton dyed with root extracts of *Acacia catechu* by pad-steam method.

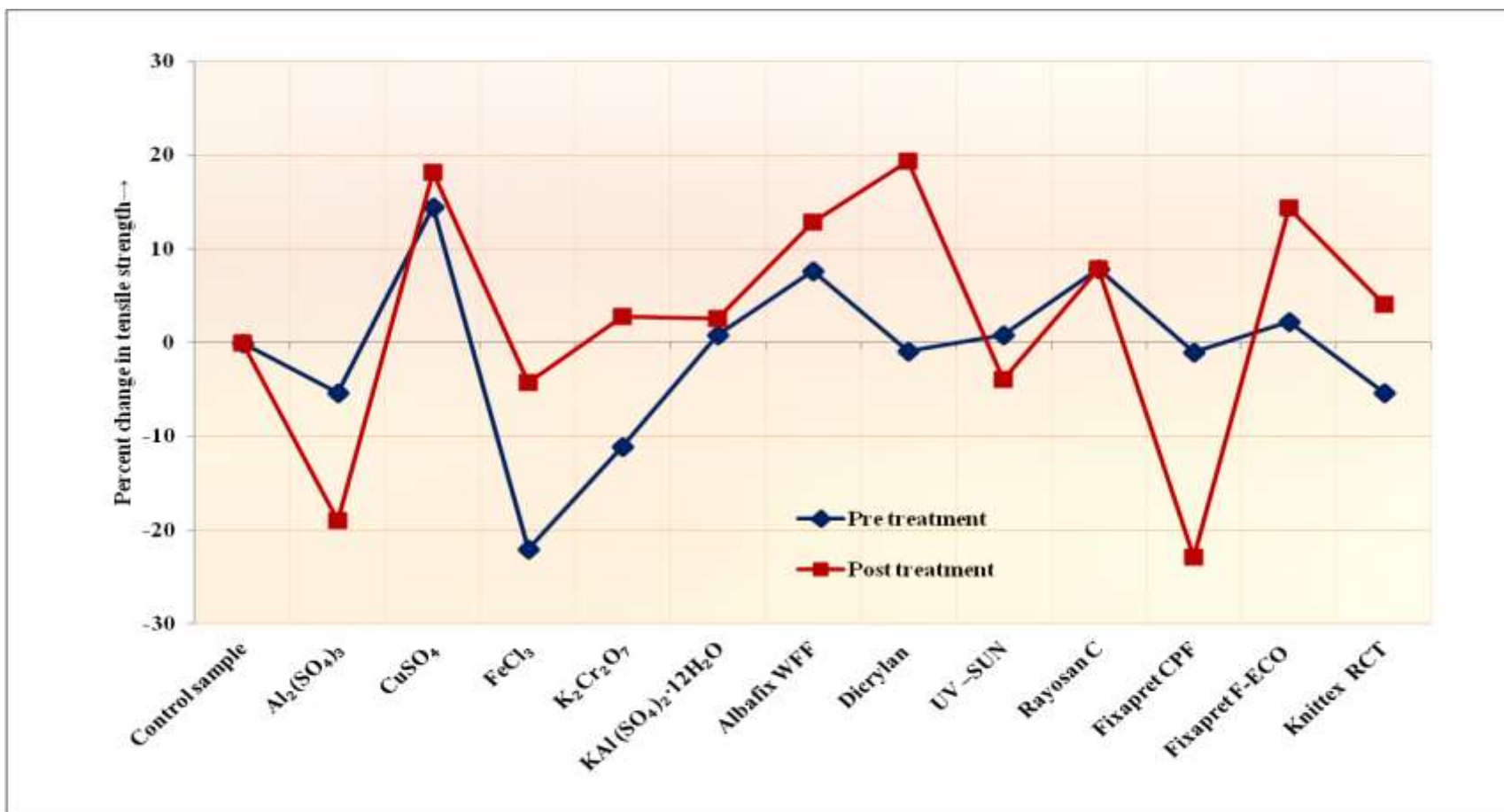


Figure 3.11: Effect of various dyeing auxiliaries on the tensile strength of cotton samples dyed with root extracts of *Acacia catechu* by pad-steam method.

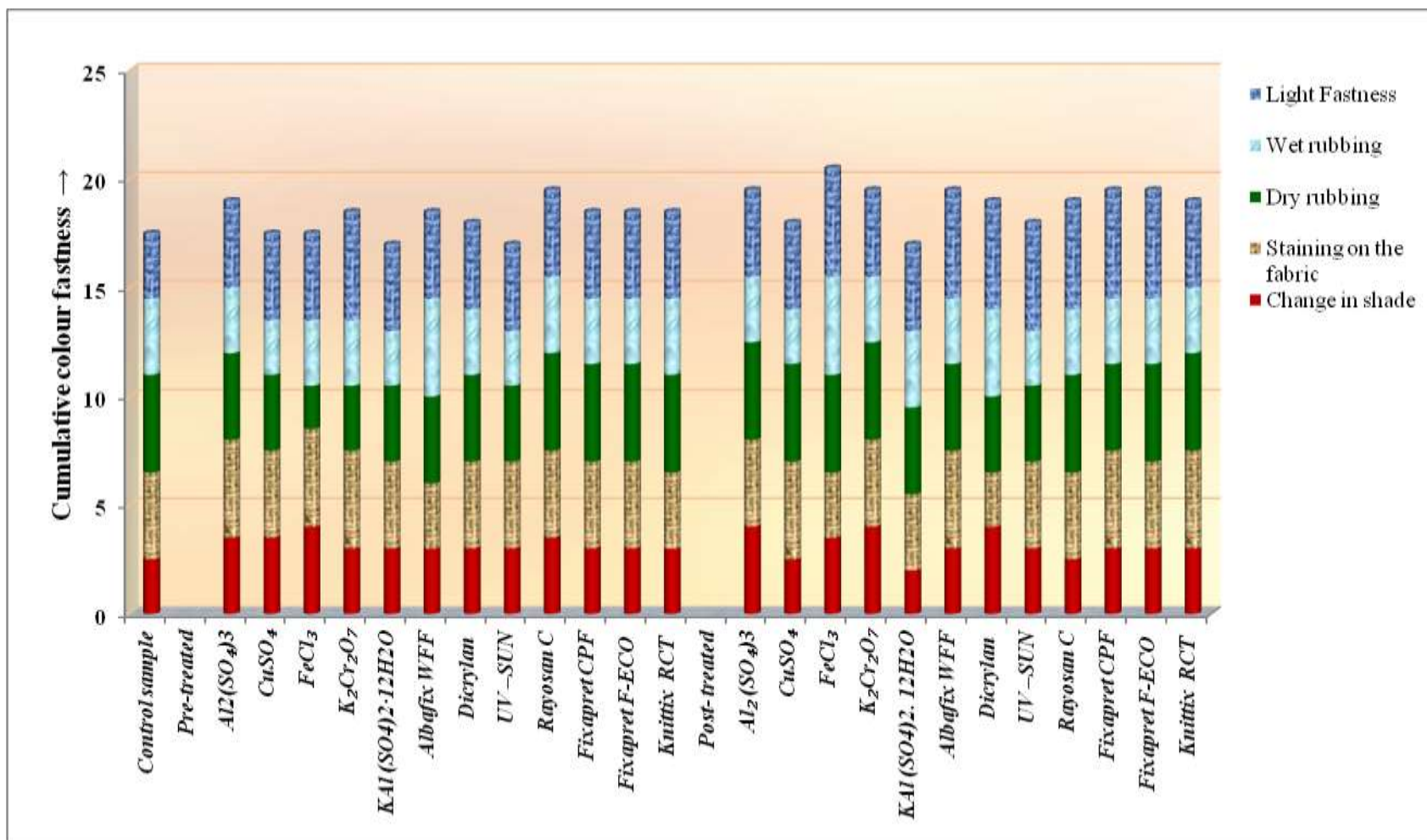


Figure 3.12: Comparative analysis of cumulative colour fastness of cotton dyed with various dye formulations of *Acacia catechu*

It was also very soft and smooth fabric with pleasant appearance. Slightly lighter than the post-padded potassium dichromate sample was the one which was dyed with the pre- treatment of Albafix. Samples dyed with the treatment of post Albafix and pre Dicrylan were unleveled, unattractive and reddish brown in shade. Medium brown shade was observed in the dyed samples achieved from the pre- padding with alum, and Fixapret CPF. All the remaining samples dyed with natural extracts of cutch extracts were designated as light brown.

3.2.2 Wash fastness of cutch dyed cotton samples

Wash fastness of control (untreated) sample of cutch dyed cotton was observed to be 3 on Grey-Scale (Tables 3.11- 3.13).

Exhibit 3.2: Shades produced by cotton samples dyed with natural extracts of cutch under different conditions. Minimum change in shade of 4 GS due to washing was exhibited by cutch dyed samples assisted by the dyeing auxiliaries of pre-mordanting of copper sulphate and post-mordanting of aluminium sulphate and hydrated potassium aluminium sulphate. This good wash fastness performance was followed by 3-4 GS change in shade recorded by pre-mordanting of aluminium sulphate and pre and post-mordanting of ferric chloride. Maximum change in shade due to washing among this group was shown by samples pre-mordanted with alum, post-mordanted with CuSO_4 and both pre and post-mordanted with $\text{K}_2\text{Cr}_2\text{O}_7$. Their score was 3 GS, identical with the scoring of the control sample. The change in shade due to washing of samples which were pre-treated with UV-SUN (Table 3.12) and Rayosan C was also the same as that of untreated sample. A good wash fastness, equivalent to 4 on Grey-Scale was displayed by samples dyed with a combination of cutch dye with pre-treatment of Dicrylan and post-treatment of UV-SUN in the dyeing formulas.

Fairly good wash fastness of 3-4 GS was obtained from cationizing of cotton (both pre and post-treatment) with Albafix WFF as well as post finishing with Dicrylan and Rayosan C. Change in shade due to washing in the remaining samples dyed with cutch and various auxiliaries was 3 GS, similar to the performance of control sample only. Among the group of dyeing auxiliaries of crosslinking agents, the data revealed

(Table 3.12) that the maximum change in shade equal to 3 GS was produced from the pre-treatment of all these products i.e. Fixapret CPF, Fixapret F- ECO and Knittex RCT. However, their pre-treatment displayed 3-4, 4 and 3-4 GS by Fixapret CPF, Fixapret F- ECO and Knittex RCT, respectively.

Regarding staining on the adjacent white fabric as part of the wash fastness test, best result of minimum staining was depicted from cutch dyed samples, the one which was pre-mordanted with alum and the other one, which had a treatment of post- padding with CuSO_4 . A rating of 4 GS was presented by samples, pre-mordanted with $\text{Al}_2(\text{SO}_4)_3$, CuSO_4 , FeCl_3 and post-mordanted with $\text{K}_2\text{Cr}_2\text{O}_7$. This performance was followed by a staining rated as 3-4 GS, available from samples having potassium dichromate as pre-mordant and alum as a post-mordant in the dye formulation. This scoring was similar to the staining shown by cutch dyed control sample. Maximum staining of 3 GS ranking was visible from samples having post-mordanting treatment with aluminium sulphate and ferric chloride in the dyeing recipes.

Among the dyeing auxiliary group of finishes and UV absorbers, good results (only 4 GS staining) were shown by post finished sample with Dicrylan and Rayosan C, whereas, maximum staining (3 GS) in this group was given by the post-cationized (Albafix WFF) cutch dyed sample. Remaining samples dyed with cutch and treated with auxiliaries of this group gave staining equal to 3-4 GS. These were namely pre-treatment with Albafix WFF, Dicrylan and both pre and post-treatment through UV-SUN. Crosslinkers applied as pre or post-treatment on cutch dyed cotton samples exhibited good to very good rating of staining on the adjacent white cloth. The performance of these agents was 4-5 GS from post-treatments of Fixapret F- ECO and Knittex RCT and 4 GS from pre and post-treatment of Fixapret CPF, pre-treatment of Fixapret F- ECO and Knittex RCT, respectively.

3.2.3 Crocking fastness of cotton dyed with extracts of cutch roots.

The information related to the crocking or rub fastness of cotton samples dyed with natural extract of cutch reveal that very good performance of 4-5 GS was displayed by sample pre-mordanted alum. The same result was also exhibited by the control sample of cutch dye. Moreover, good dry rubbing fastness equivalent to 4 on Grey-Scale was

recorded from the samples coloured with dyeing recipe having pre-mordanting of alum and post-mordanting of Aluminium sulphate and ferric chloride. This performance was slightly inferior to the fastness displayed by the control sample (4-5 GS). Lowest fastness due to dry rubbing was recorded by sample post-mordanted with CuSO_4 (2-3 GS). All other treatments related to pre and post-mordanting among this group could produce only 3 GS rating of dry rubbing fastness. These were pre-mordanting with $\text{Al}_2(\text{SO}_4)_3$, CuSO_4 , FeCl_3 and the sample which was post-mordanted with $\text{K}_2\text{Cr}_2\text{O}_7$.

Maximum wet rubbing fastness of 3-4 GS was given by post-mordanted cutch dyed sample with alum. Control sample and the one, post-mordanted with potassium dichromate managed to get a score of 3 GS. All other treatments among this group (Table 3.11) presented inferior wet rubbing as compared to the reference or control sample. Lowest wet rubbing fastness of only 2 GS was revealed by CuSO_4 as a mordant (both pre and post-treatments), pre-mordanting of alum and post-mordanting of ferric chloride. Remaining samples of this group (dyed with the assistance of ferric chloride and potassium dichromate as pre-mordant and aluminium sulphate as pre or post-mordant) demonstrated only 2-3 GS rating of wet rubbing fastness. Among the auxiliary group of finishes and UV absorbers applied with cutch dye, maximum wet rub fastness of 3-4 GS was available from the treatments including post finishing of Dicrylan and UV-SUN, whereas, lowest fastness due to wet crocking was shown by post-treatment of Rayosan C which was only 2 GS. A wet rub fastness ranking of 3 GS was presented by untreated, pre-cationized (Albafix WFF) and pre-treated Rayosan C samples. Remaining samples dyed with cutch and planned formulas of this group managed only 2-3 GS wet rub ranking, which included post-cationized Albafix WFF, pre finished Dicrylan and pre-treated UV-SUN. Wet rubbing fastness of samples dyed with the aid of crosslinkers displayed 3-4 GS performance from pre-treatment of Knittex RCT; 3 GS from the pre-treatment of Fixapret CPF, Fixapret F-ECO and untreated samples and 2-3 GS resulted from the post-treatment of Fixapret CPF, Fixapret F- ECO and Knittex RCT, respectively.

3.2.4 Light fastness of cutch dyed cotton

Fastness of control sample to light (which was dyed only with cutch dye i.e. without any treatment) could match ranking 3 of Blue Wool Standard. However, an exhibition of best light fastness equal to 6 Blue Wool Standard (very good performance) was made by samples dyed with cutch and alum (hydrated potassium aluminium sulphate). Good light fastness of standard number 5 was displayed by samples pre-mordanted with aluminium sulphate and hydrated potassium aluminium sulphate. All other dyed samples which were pre-mordanted with copper sulphate and potassium dichromate; both pre and post-mordanted with ferric chloride; and post-mordanted with aluminium sulphate were assigned 4 Blue Wool Standard which represents fair light fastness.

Cotton sample which was pre-cationized with Albafix WFF made its way in achieving light fastness of 6 Blue Wool Standard. Likewise, the sample dyed with formulation of post-treatment of Rayosan C, also reached to 6 standard of light fastness. This very good performance was followed by another treatment attaining standard number 5, i.e. good lightfast cutch dyed samples and this result was produced by post finished Albafix WFF, Dicrylan, UV-SUN and pre-treated Rayosan C samples when tested for light fastness. Pre-cationized Albafix WFF treatment yielded 4 Blue Wool Standard light fastness from dyeing with natural extracts of cutch dye.

Very good light fastness equivalent to standard number 6 was recorded by cutch dyed cotton samples having pre-treatment of Fixapret F- ECO and post-treatment of Knittex RCT in their dyeing formulas. All other recipes of crosslinkers applied in combination of cutch dye displayed 5 Blue Wool Standard, presenting good light fastness. Moreover, the reference or untreated sample had only 3 Blue Wool Standard of light fastness.

3.2.5 Analysis of cumulative fastness of cutch dyed samples: t-test

Cumulative colour fastness of cotton samples dyed with cutch root extracts with the help of various dyeing auxiliaries has been displayed in Figure 3.12. Paired sample t-test was carried out on the cumulative colour fastness of cotton fabrics, dyed with cutch

and various pre and post-treated dyeing aides. The relevant data is included in Table 3.14 and 3.15. Paired sample statistics conveyed that the mean (cumulative colour fastness) of pre-treated samples was 18.25 and that of post-treated samples came out to be 19.04 with a mean difference of- .79 and standard deviation of 1.72. With $t = -1.93$ and $p = 0.080$, these results propose non- significant difference between the pre and post-treatment of dyeing aides. Significance testing of the colour fastness of cutch dyed cotton fabric samples was carried out by applying t-test on control and pre-treated samples as well between control and post-treated samples (Table 3.15). Significant difference was found between the strength of control and pre-treated samples as well as between the control and post-treated fabric samples.

3.2.6 Colour coordinate values of cutch dyed cotton

Data related to colour strength and other colour coordinates of cutch dyed samples is presented through Tables 3.18 - 3.20. Considering the lightness of shade (L^*), it was noticed that the minimum colour yield was attained by the cutch dyed sample which was post-mordanted with potassium dichromate and the highest yield or darkness of the shade was displayed by the treatment of post-padded alum on cutch dyed sample. The values of a^* were all in the region of positive side presenting red-purple tone. Similarly, b^* values were also positive from all the treatments of mordants, pointing towards the yellow tone of the cutch dye. The shade purity or chroma values lied in the range of 13.22 to 31.28 with the maximum being attained by the post-treatment of alum. Colour hue (h°) was the highest from the treatment of post- padding ferric chloride, followed by aluminium sulphate and alum. Whereas, a minimum colour hue was noticed from the pre-mordanting copper sulphate. Mordanting of cotton samples with alum could produce the least colour strength (K/S) in the cutch dyed samples among this group. Maximum colour strength of cutch dyed cotton was visible from the data when it was padded (both pre and post-mordanting) with ferric chloride.

Colour coordinate values of cutch dyed samples with the assistance of finishes and UV absorbers are listed in Table 3.15. Lightness values ranged between 40.11 and 53.42. The highest colour yield was available from the post-treatment of UV-SUN. The data depict that a^* and b^* values were all positives, i.e. in the range of red and yellow

tones. The values of C^* seemed large, ranging from 18.30 to 25.24. Pre finishing of cotton samples with Dicrylan and padding with natural extracts of cutch presented highest value of C^* and h° among this group of dyed samples. Colour strength (K/S) was the greatest from the post- padding of cutch dyed sample with Albafix WFF.

Lightness (L^*) value of cutch dyed cotton samples with the aides of crosslinkers ranged from 40.11 to 55.34. Greater colour yield was available from post- padding of Fixapret F-ECO. The values of a^* and b^* coordinates were all positive, whereas C^* was almost similar from the all the pre-treatments of crosslinkers as well as untreated sample (20.0 -20.1). However, with post-treated crosslinkers, it was slightly high i.e. in the range 24.8 -25.7. The value of h° was also the highest form the post- padding of Fixapret F-ECO. The K/S data of this group (crosslinkers and cutch dye) ranged from 4.47-7.65; with the highest being available from the post-treatment of Knittex RCT.

3.2.7 Tensile strength of cotton dyed with cutch

Percent change in tensile strength of cutch dyed cotton samples is exhibited through Figure 3.10. A loss in strength due to various auxiliaries employed with cutch dye was 23 percent from the post-treatment of cross linker Fixapret CPF, followed by 22 percent from the pre-mordanting of ferric chloride and 19 percent from the post-mordanting of aluminium sulphate. Pre-mordanting of $K_2Cr_2O_7$ decreased the tensile strength of cotton upto 11 percent. Similarly, the amount of 5 percent loss of strength was evidenced from pre-treatment of aluminium sulphate and Knittex RCT. On the other hand, Maximum increase in tensile strength of 19 percent was exhibited by the pre-padding of Dicrylan. Gain in tensile strength of 18 percent was demonstrated by the post-treatment of copper sulphate and 14.5 percent by pre-treatment of copper sulphate. An increase in strength of 14 percent due to the use of various auxiliaries in dyeing was displayed by the post-treatments of Fixapret F-ECO and 13 percent from Albafix WFF. Rayosan C enhanced the strength of cutch dyed cotton equal to 8 percent.

Paired sample t-test shows insignificant difference at 5% level of significance from the results of tensile strength of pre-treated and post-treated samples. Significance testing of the tensile strength of cutch dyed cotton fabric samples was also carried out by applying t-test on control sample and pre-treated samples as well between control and

post-treated samples (Table 5.3). Insignificant difference was found between the strength of control and pre-treated samples as well as between the control and post-treated fabric samples.

3.3 DYEING OF COTTON WITH MADDER (*RUBIA TINCTORUM*)

Cotton samples were also coloured with madder root extracts with help of various mordants, fixative, finishes UV absorbers and crosslinkers, all applied both as before as well as after dye padding. Findings available from the colour fastness of madder dyeing cotton are presented in Tables 3.21 to 3.30 and Figures 3.13-3.18

3.3.1 Shades obtained with madder root extracts

Madder dyeing resulted in reddish and purplish shade samples of dyed cotton. The most reddish shade was presented by the sample obtained from the dye formulation having post- mordanting with copper sulphate (Exhibit 3.3). Similar shades were characterized by post- cationizing with Albafix. Orange-red tone was available from the treatment of post-mordanting with alum. Pre- padding with Knittex produced yellow-orange shade and the dyeing was uneven. Dark, reddish- grey shade was introduced by the post-mordanting of ferric chloride. All other recipes produced purplish or light reddish shades which were not very attractive.

3.3.2 Wash fastness of madder dyed cotton

It can be noticed from the result that the untreated sample which was dyed without any treatment for colour improving, could attain only 2 Grey- Scale rating of change in shade due to washing. This was the minimum fastness and was also available from all the pre-mordanted samples dyed with madder. The same (minimum fastness of only 2 GS) was also noticeable from the post-mordanting of copper sulphate and alum. The only sample dyed with madder, which could produce 3 GS i.e. good wash fastness was the one which was post-mordanted with ferric chloride.

Exhibit 3.3: Shades produced by cotton samples dyed with natural extracts of madder under different conditions.

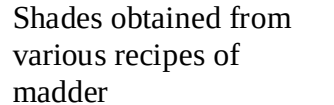
			
	Control sample	CuSO ₄ pre-mordanting	CuSO ₄ post-mordanting
			
	Alum pre-mordanting	Albafix post-treatment	Knittex pre-treatment
			
	K ₂ Cr ₂ O ₇ pre-mordanting	Al ₂ (SO ₄) ₃ post-mordanting	FeCl ₃ post-mordanting
			
	K ₂ Cr ₂ O ₇ post-mordanting	Al ₂ (SO ₄) ₃ pre-mordanting	Fixapret CPF pre-paddind
			
	Shades obtained from various recipes of madder		

Table 3.21: Fastness and tensile properties of cotton fabric dyed with root extracts of *Rubia tinctorum* using various mordants.

Method	Mordant	Wash Fastness		Crocking Fastness		Light Fastness	Tensile strength (lb)	Elongation (%)
		Change in shade	Staining on fabric	Dry rubbing	Wet rubbing			
Pre-mordanting	Al ₂ (SO ₄) ₃	2	2-3	3	2	4	41.2	8.25
	CuSO ₄	2	3	3	2	4	46.8	8.25
	FeCl ₃	2	3	3-4	2-3	5	23.1	2.75
	K ₂ Cr ₂ O ₇	2	3-4	3-4	2	3	45.7	7.25
	KAl(SO ₄) ₂ ·12H ₂ O	2	3	3-4	2-3	4	33.4	4.25
Post-mordanting	Al ₂ (SO ₄) ₃	2-3	3-4	3-4	2	5	34.3	7.38
	CuSO ₄	2	3	2	2	3	33.7	9.38
	FeCl ₃	3	2-3	3-4	3	5	44.8	7.25
	K ₂ Cr ₂ O ₇	2-3	3-4	2-3	2	5	49.7	8.75
	KAl(SO ₄) ₂ ·12H ₂ O	2	3	3	2-3	4	30.5	7.63
No mordanting	Control sample	2	2-3	3	2	4	37.5	7.25

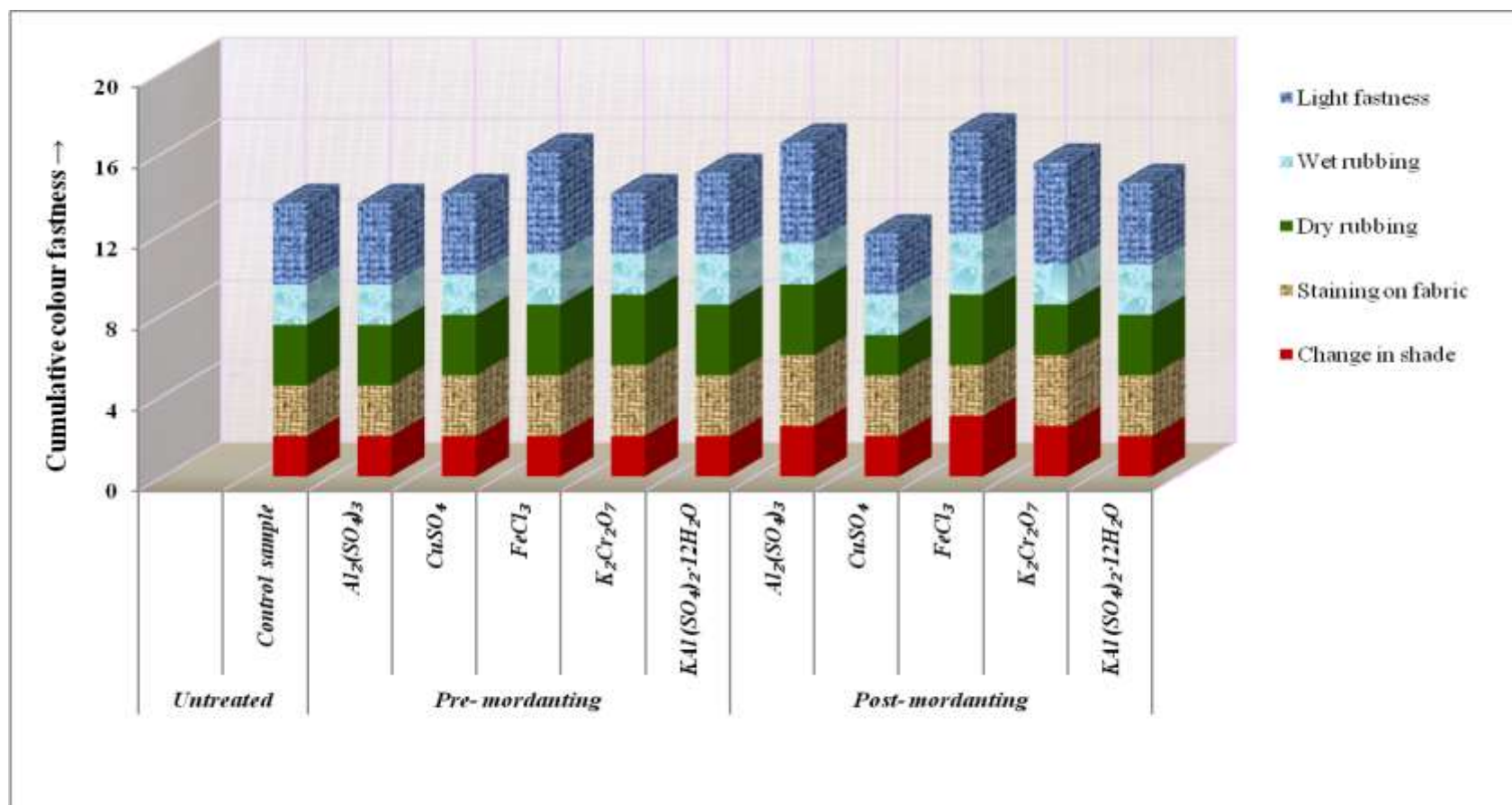


Figure 3.13: Cumulative colour fastness of cotton samples dyed with root extracts of *Rubia tinctorum* using various mordants.

Table: 3.22 Fastness and tensile properties of cotton fabric dyed with root extracts of *Rubia tinctorum* using various finishes and UV absorbers.

Product	Method	Wash Fastness		Crocking Fastness		Light Fastness	Tensile strength (lb)	Elongation (%)
		Change in shade	Staining on fabric	Dry rubbing	Wet rubbing			
Albafix WFF	Pre cationizing	1-2	4-5	3-4	2	3	45.6	7.25
	Post cationizing	3	4-5	3-4	2-3	3	37.5	6.88
Dicrylan	Pre finishing	2	4-5	3	3	3	35.3	7.88
	Post finishing	2	4-5	3	3	4	48.2	5.00
UV –SUN	Pre-treatment	2	4-5	3	2	3	40.1	8.00
	Post-treatment	2	4-5	3	3	4	43.9	6.00
Rayosan C	Pre-treatment	2-3	4-5	2-3	2-3	4	50.5	8.00
	Post-treatment	2-3	4-5	3	3	4	50.3	4.88
Control sample	Untreated	2	4-5	3	2	4	37.5	7.25

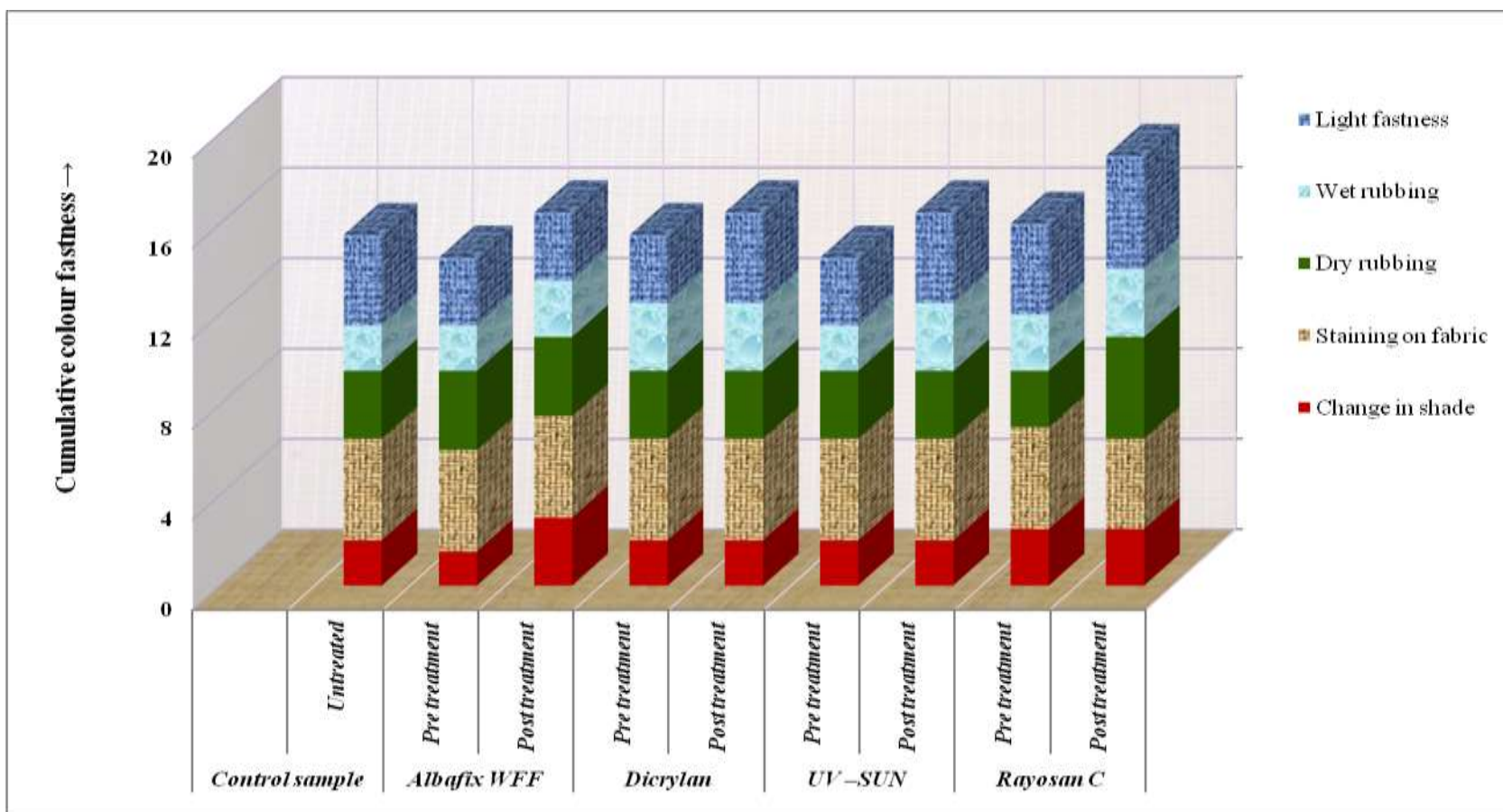


Figure 3.14: Cumulative colour fastness of cotton samples dyed with root extracts of *Rubia tinctorum* using various finishing agents and UV absorbers

Table: 3.23 Fastness and tensile properties of cotton dyed with root extracts of *Rubia tinctorum* using various crosslinking agents.

Product	Method	Wash fastness		Crocking fastness		Light fastness	Tensile strength (lb)	Elongation (%)
		Change in shade	Staining on fabric	Dry rubbing	Wet rubbing			
Fixapret CPF	Pre-treatment	1*	4	3	2-3	3	41.7	7.88
	Post-treatment	3	4	3-4	3	4	43.0	8.75
Fixapret F-ECO	Pre-treatment	2*	4	3	2	3	47.7	8.13
	Post-treatment	3	4	3-4	3	4	47.9	8.25
Knittex RCT	Pre-treatment	2*	4	2-3	2	4	30.5	7.38
	Post-treatment	3	4-5	3	3	4	31.0	7.50
Control sample	Untreated	2	2-3	3	2	4	37.5	7.25

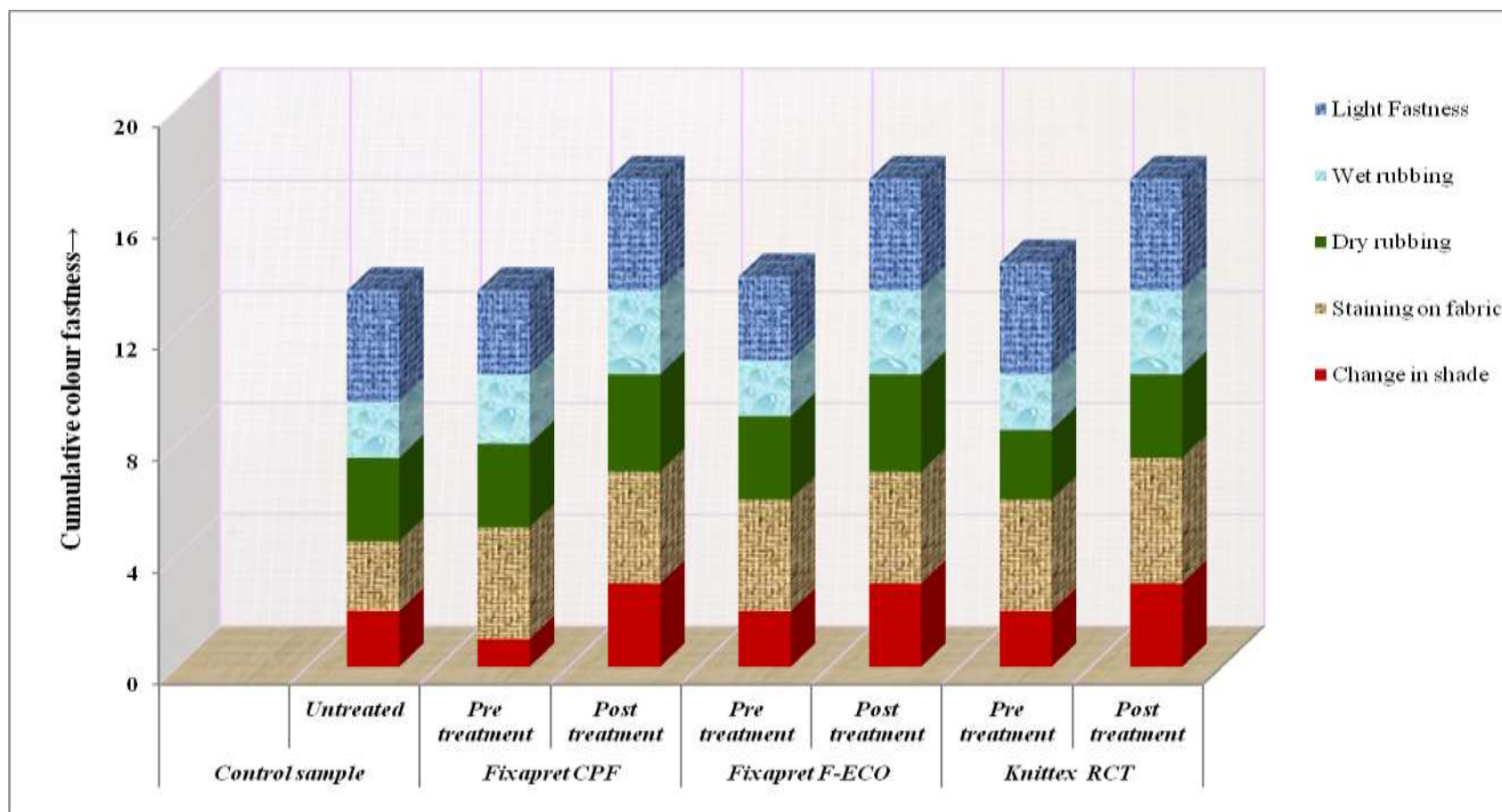


Figure 3.15: Cumulative colour fastness of cotton dyed with root extracts of *Rubia tinctorum* using various cross linking agents

Table 3.24: Paired sample statistics for cumulative colour fastness of cotton dyed with *Rubia tinctorum* (madder).

Treatment	Mean	N	Std. Deviation	Std. Error Mean
T 1*	12	14.58	0.87	0.25
T 2	12	16.21	1.59	0.46

*T 1 = Pre-treatment; T 2= Post-treatment

Table 3.25: Significance testing of cumulative colour fastness of cotton fabric samples dyed with madder.

(a) Paired sample 2- tailed t- test for cumulative colour fastness: paired differences

Treatments	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
T 1 - T 2	-1.37	2.00	0.58	-2.65	0.10	-2.38	11	0.037

(b). One-Sample t-test: cumulative colour fastness

Cumulative colour fastness	Control sample = 13.5					
					95% Confidence Interval of the Difference	
	t	df	Sig. (2-tailed)	Mean Difference	Lower	Upper
T1	4.29	11	.001	1.08	0.53	1.64
T2	5.91	11	.000	2.71	1.70	3.72

Table 3.26: Paired sample statistics for tensile strength of cotton dyed with *Rubia tinctorum* (madder).

Treatment	Mean	N	Std. Deviation	Std. Error Mean
T 1	40.13	12	8.12	2.34
T 2	41.56	12	7.34	2.12

Table 3.27: Significance testing of tensile strength of cotton fabric samples dyed with madder.

(a) Paired sample 2- tailed t- test for tensile strength: paired differences

Treatments	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
T 1 - T 2	-1.42	9.28	2.68	-7.33	4.47	-0.53	11	0.61

(b). One-Sample t-test: tensile strength of madder dyed cotton

Tensile strength	Control sample = 37.5					
					95% Confidence Interval of the Difference	
	t	df	Sig. (2-tailed)	Mean Difference	Lower	Upper
T1	1.12	11	0.28	2.63	-2.52	7.79
T2	1.91	11	0.08	4.06	-0.60	8.72

Table 3.28: Colour coordinate values of *Rubia tinctorum* dyed cotton fabric samples using various mordants.

Method	Mordant	Colour coordinates					
		L*	a*	b*	C*	h°	K/S
Pre-mordanting	Al ₂ (SO ₄) ₃	48.30	19.64	15.31	29.90	37.94	4.73
	CuSO ₄	46.27	18.87	9.12	20.96	25.80	4.39
	FeCl ₃	45.44	8.35	10.25	13.22	50.84	7.23
	K ₂ Cr ₂ O ₇	47.88	16.46	9.72	19.11	30.56	4.15
	KAl(SO ₄) ₂ ·12H ₂ O	51.49	19.92	15.15	25.02	37.26	3.63
Post-mordanting	Al ₂ (SO ₄) ₃	52.03	15.77	23.77	28.49	56.40	4.40
	CuSO ₄	43.07	18.85	12.33	22.32	33.19	6.71
	FeCl ₃	43.47	6.05	11.20	12.73	61.64	8.39
	K ₂ Cr ₂ O ₇	42.96	16.40	11.00	19.75	33.84	5.75
	KAl (SO ₄) ₂ ·12H ₂ O	56.55	19.58	24.20	31.12	51.03	3.22
No mordanting	Control sample	41.30	17.02	10.90	20.21	32.64	6.62

Table 3.29: Colour coordinate values of *Rubia tinctorum* dyed cotton fabric samples using various UV absorbers.

Product	Method	Colour coordinates					
		L*	a*	b*	C*	h°	K/S
Albafix WFF	Pre cationizing	41.23	16.43	11.07	19.81	33.96	6.67
	Post cationizing	42.26	15.80	9.20	18.28	30.21	5.45
Dicrylan	Pre finishing	49.63	15.42	13.33	20.38	40.85	7.71
	Post-treatment	71.37	3.09	39.98	40.10	85.58	6.07
UV –SUN	Pre-treatment	47.48	15.93	11.07	19.40	34.79	6.57
	Post-treatment	78.81	-1.09	41.37	41.39	91.22	6.43
Rayosan C	Pre-treatment	78.33	-0.86	39.33	39.84	91.24	4.43
	Post-treatment	79.31	-1.24	40.36	40.39	92.19	4.14
Control sample	Untreated	41.30	17.02	10.90	20.21	32.64	6.62

Table 3.30: Colour coordinate values of *Rubia tinctorum* dyed cotton fabric samples using various crosslinkers.

Product	Method	Colour coordinates					
		L*	a*	b*	C*	h°	K/S
Fixapret CPF	Pre-treatment	47.61	16.08	11.18	19.58	34.81	4.48
	Post-treatment	77.94	-0.63	40.67	40.67	90.89	4.57
Fixapret F-ECO	Pre-treatment	46.73	16.29	11.92	20.18	36.20	4.95
	Post-treatment	75.15	1.15	39.74	39.76	88.35	4.64
Knittex RCT	Pre-treatment	48.66	15.82	12.17	19.96	37.57	4.35
	Post-treatment	76.94	-0.07	41.77	41.77	90.10	5.18
Control sample	Untreated	41.30	17.02	10.90	20.21	32.64	6.62

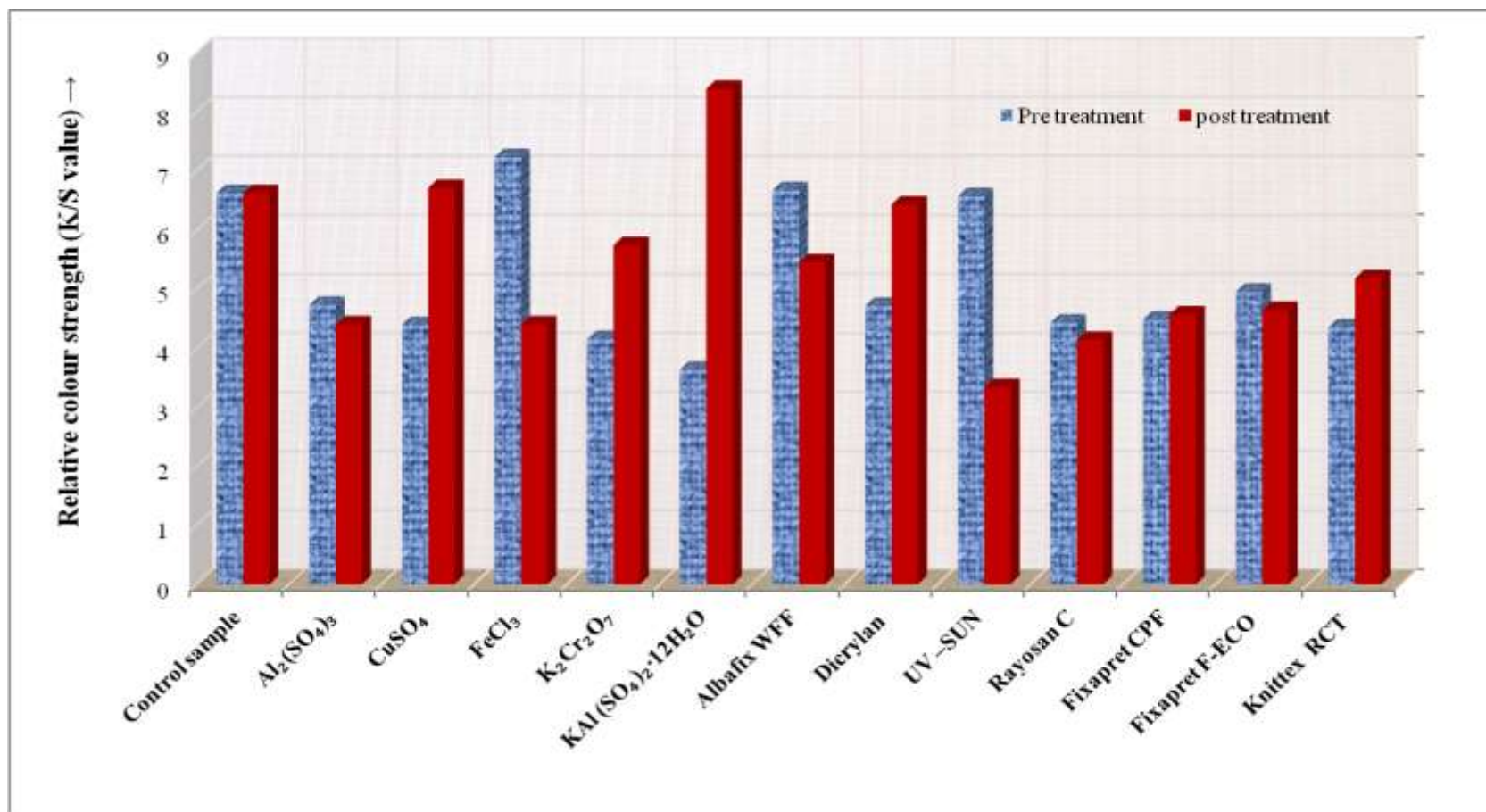


Figure 3.16: Effect of various dyeing auxiliaries on the colour strength of cotton samples dyed with root extracts of *Rubia tinctorum* by pad- steam method.

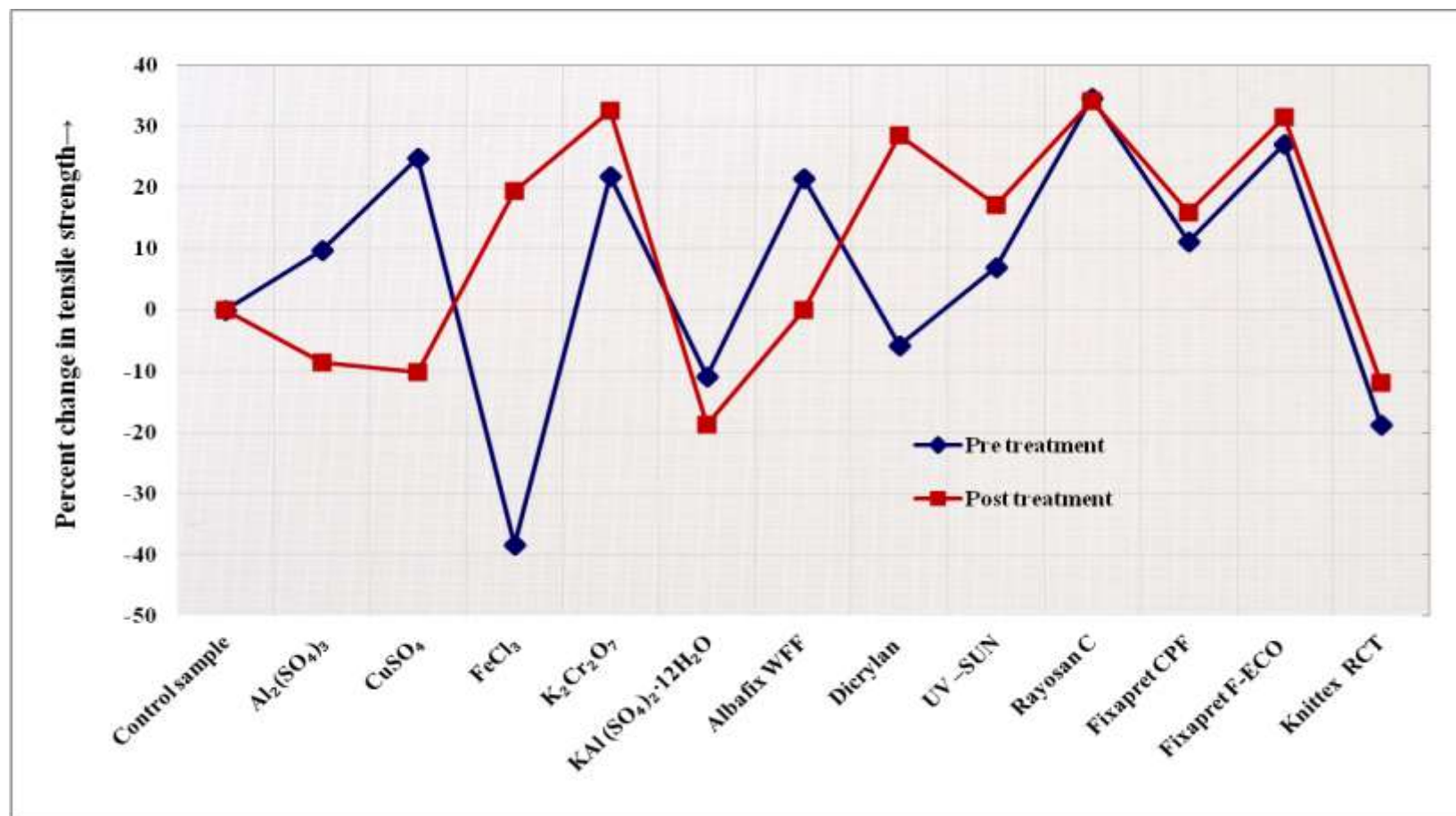


Figure 3.17: Effect of various dyeing auxiliaries on the tensile strength of cotton samples dyed with root extracts of *Rubia tinctorum* by pad-steam method.

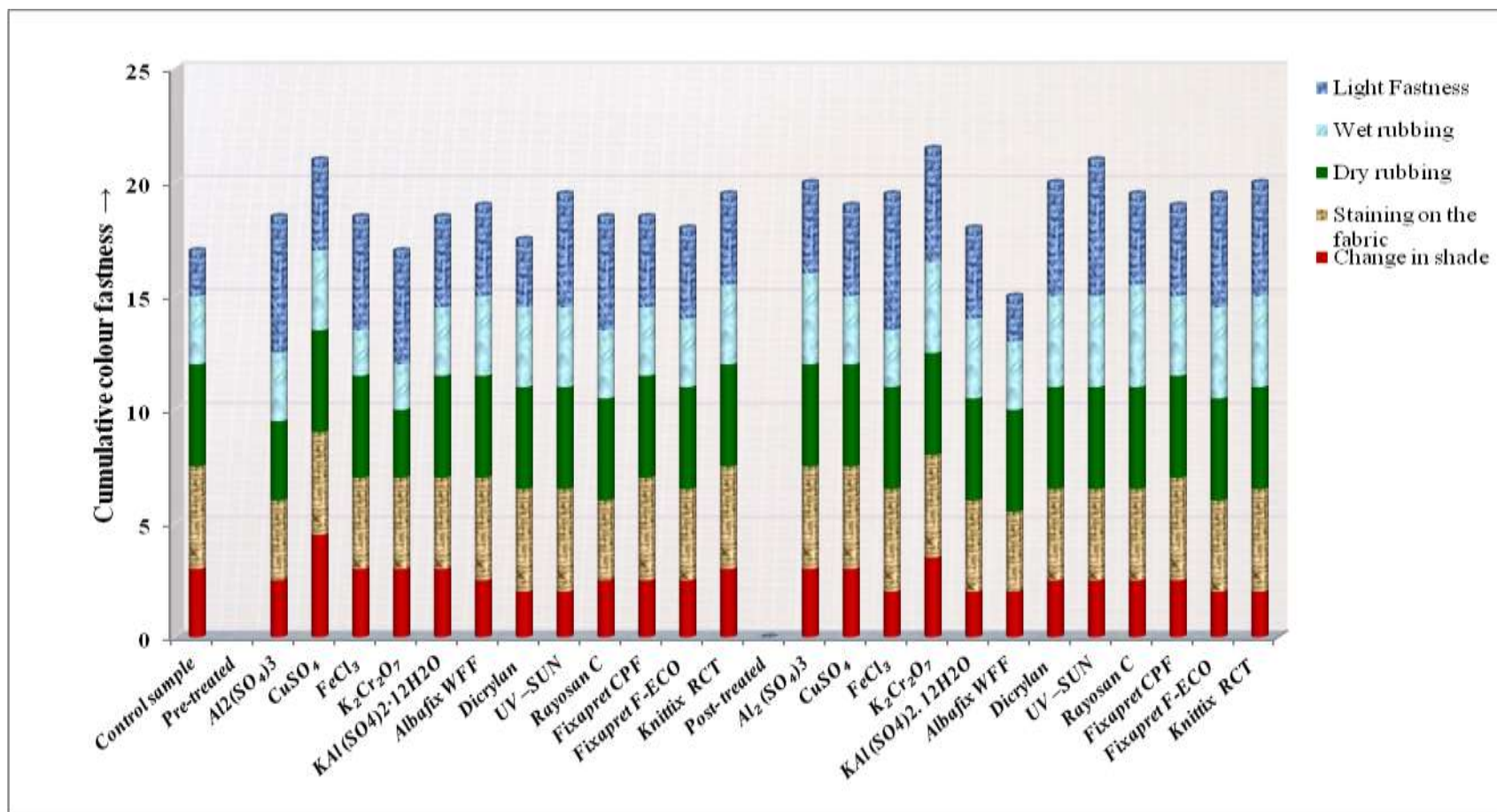


Figure 3.18: Comparative analysis of cumulative colour fastness of cotton dyed with various dye formulations of *Rubia tinctorum*.

Post-mordanting of madder dyeing samples with aluminium sulphate and potassium dichromate yielded 2-3 GS change in shade due to washing. Among the auxiliaries group of finishes and UV absorbers, the post-treatment of Albafix on dyed cotton sample (cationized) posed minimum change in the shade of 3 GS. Unpredictably, maximum change in shade (equal to 1-2 GS) was exposed by the same auxiliary, i.e. Albafix, when it was applied prior to the padding of madder extracts. Change in shade of 2-3 GS was caused by pre and post-treated Rayosan C. All other dyeing formulas employed for the dyeing of cotton with madder yielded the dyed samples with the wash fastness just as the fastness of control or untreated sample. These were pre and post-finishing with Dicrylan and UV- SUN. Samples dyed with the help of crosslinkers Fixapret CPF, Fixapret F-ECO and Knittex RCT presented 3 GS wash fastness rating. As far as staining on the adjacent white cloth is concerned, maximum staining of 2-3 GS was exposed by control; pre-mordanted with aluminium sulphate; and post-mordanted with ferric chloride samples in the application of natural extracts of madder. Lowest staining of 3-4 GS among this group of the samples was achieved by pre and post-treatment of potassium dichromate and post-mordanting of aluminium sulphate.

The remaining samples which resulted from the pre and post-mordanting of copper sulphate, alum and pre-treatment of ferric chloride stained the adjacent white cloth equal to 3 GS, thereby representing fair fastness to washing. Staining on the adjacent white sample from the testing of madder dyed samples with various finishes and UV absorbers was very mild and dyed samples by all the dyeing recipes were graded as 4-5 GS (representing very good fastness performance). Staining from the madder dyed samples with the use of crosslinkers was also very little. Minimum staining of 4-5 GS was noticed from the samples which was madder dyed and post-treated with Knittex RCT. All other samples dyed with pre and post-treatment of crosslinkers were rated as 4 GS showing good fastness due to staining on the adjacent white cloth.

3.3.3 Rubbing or crocking fastness of madder dyed cotton

The data related to rub or crocking fastness of cotton samples dyed with natural extracts of madder is listed in Tables 3.21. Good dry rubbing of 3-4 GS was offered by samples which were pre-padded with potassium dichromate, alum, post-mordanted with

aluminium sulphate and both pre and post-padded with ferric chloride. Lowest dry rubbing of only 2 GS was given by CuSO_4 , when it was post-padded. The dry rubbing rating from post-mordanted with $\text{K}_2\text{Cr}_2\text{O}_7$ was 2-3 GS. Remaining mordanted samples produced a rub fastness of 3 GS which was just identical to the dry fastness rating of control sample. Wet crock fastness of madder dyed cotton samples ranged between 2 GS and 2-3 GS. Pre-mordanted ferric chloride and both pre and post-mordanted alum could produce samples with 2-3 GS wet rub fastness. The fastness rating due to wet rub of all other mordanted samples was 2 GS, similar to the performance of control sample.

Dry rubbing fastness of cotton samples dyed with a combination of natural extracts of madder and various finishes and UV absorbers ranged between 2-3 and 3-4 on Grey- Scale. The dry crocking rating assigned to untreated dyed specimen was 3 GS, which was matched with the performance of samples pre- finished with Dicrylan, UV-SUN and post-treated with Rayosan C. Maximum dry fastness in the this group was available from the cationized sample (both pre and post-padded) by Albafix and the grade allotted was 3-4 GS, while lowest score of 2-3 GS dry fastness was exposed by sample which was pre-treated with Rayosan C. As wet rubbing of the control sample was 2 GS, the treated samples could slightly forward this scoring to a figure of 3 GS which was offered by the treatment of Dicrylan (both pre and post-padding) and post-treatment of UV- SUN and Rayosan C. The resultant cotton samples from the madder extracts dyeing and treatments of pre-cationizing of Albafix and pre-treatment of UV-SUN could attain only 2 GS wet rub fastness. Whereas, the post-cationizing of Albafix and pre-treatment of Rayosan C yielded samples with 2-3 wet rub fastness on Grey-scale.

As far as, the rubbing fastness of cotton treated with various crosslinkers is concerned, it ranged from 2-3 to 3-4 GS in case of dry crocking and 2 to 3 GS in case of wet rub fastness. Good dry fastness of 3-4 GS was presented by the post-treatments of Fixapret CPF and Fixapret F-ECO in the dye formulation. Lowest dry rub fastness was shown by madder dyed cotton sample, pre-padded with Knittex RCT where the rating was 2-3 GS. In case of wet rubbing, the post-treatment from all the crosslinkers presented samples with fastness rating equal to 3 GS, whereas, the rating attained by the control sample was 2 on Grey-scale. The pre-treatments of Fixapret F-ECO and Knittex RCT

also produced samples with a 2 GS rating. Whereas, crosslinker Fixapret CPF offered 2-3 GS wet fastness rating for the madder dyed cotton sample.

3.3.4 Light fastness of cotton dyed with madder root extracts

Light fastness of madder dyed cotton samples ranged between the standard 3 and standard 5. Fastness to light yielded by control sample was equal to 4 Blue Wool Standard, whereas, cotton samples padded with ferric chloride (both pre and post) and post-padded with mordants aluminium sulphate and potassium dichromate bestowed light fastness of standard number 5. Lowest fastness to light of madder dyed cotton samples using mordants was exposed from the pre-mordanting of $K_2Cr_2O_7$ and post-mordanting of $CuSO_4$. These samples showed matching with standard number 3. The light fastness rating of the remaining samples dyed with the help of mordants was similar to that of untreated samples i.e. standard 4.

In case of dyeing of the cotton fabric with the aid of finishes and UV absorbers, the fastness standard resulted from Rayosan C was identical to the untreated sample. The post-treatment of Dicrylan and UV-SUN also produced cotton dyed samples with 4 Blue Wool Standard. Lowest light fastness of standard 3 was displayed by samples dyed with the assistance of pre and post-padding of Albafix and pre-treatments of Dicrylan and UV-SUN among this group. Crosslinkers in the dyeing formulas also manifest 3 to 4 standard of light fastness from madder dyed samples. Standard 4 was registered by Knittex RCT and post-padding of Fixapret CPF and Fixapret F-ECO in case of light fastness of cotton samples coloured with natural extracts of madder roots. However, the pre-treatment of Fixapret CPF and Fixapret F-ECO could manage light fastness of only 3 Blue Wool Standard on madder dyed cotton fabric sample.

3.3.5 Analysis of cumulative fastness of madder dyed samples: t-test

Cumulative colour fastness (lightfastness and wash, crock) of cotton samples dyed with madder dye with the help of various dyeing auxiliaries has been displayed in Figure 3.18. Paired sample statistics of the cumulative colour fastness resulted from 2-tailed t-test (Table 3.25) displayed a mean value of 14.583 for the pre-treatment and 15.958 for the post-treatment of various auxiliaries. The paired sample test showed a

mean difference of -2.380. The t- value conveyed significant result at the 5 % level of significance (as 0.037 is less than 0.05), suggesting a significant difference between the pre and post-treatments of various dyeing auxiliaries employed with the application of dye from madder root extracts. Significance testing of the cumulative colour fastness of madder dyed cotton fabric samples was made by applying t-test on control sample and pre-treated samples as well between control and post-treated samples (Table 3.25). Significant difference was found between the fastness of control and pre-treated samples as well as between the control and post-treated fabric samples.

3.3.6 Colour coordinates values of madder dyed cotton

Data in respect of the effect of pre and post-treatments on L^* , a^* , b^* , C^* , h° and K/S value of madder dyed cotton samples is enclosed in Tables 3.28-3.30. The darkness of shade (L^* value) ranged from 41.30 (control sample) to 56.55 (post-treatment of alum). Post-treatment of aluminium sulphate also gave 52.03 value of L^* representing lightness in shade. The values of coordinate, a^* were all positive displaying redder shades of dyed samples. The most near towards red was available from the treatment of post alum having a value of 19.92 whereas, the lowest figure of 6.05 was observed from the sample which was treated with post ferric chloride. The values of b^* from madder dyed cotton were all positive. Chroma or C^* was also found the highest (31.12) in the sample dyed with the aid of post-mordanted alum. The same sample also gave better h° (hue) value. However, maximum h° was available from post-mordanted ferric chloride which was 61.64. In case of K/S or relative colour strength, maximum value of 8.39 was presented by the same madder dyed cotton sample (post-mordanted ferric chloride) which had a the highest hue (h°) value. The K/S of samples dyed with alum was registered as the lowest among this group of auxiliaries. These were 3.22 and 3.63 for post and pre-treated alum, respectively.

The colour coordinate values of dyed cotton with various finishes and UV absorbers are listed in Table 3.29. Lightness was minimum (L^* value of 41.23) in the sample dyed with pre-cationizing Albafix. The most light shaded sample turned out to be the one which was post-treated with Rayosan C (79.3 L^*). The values of a^* from post-treated UV- SUN and both pre and post-treated Rayosan C were negative presenting or

greener shade. All other samples posed positive values of a^* . The maximum value was attained by control sample showing more redness. The findings from b^* were all positive from madder dyed cotton samples of this group displaying yellowness in the tone.

Purity of colour, C^* was maximum from the sample dyed with post-treatment of UV-SUN. Hue or shade (h°) ranged from 30.21 (from post-cationizing Albafix WFF) to 92.19 (post-treatment of Rayosan C). The relative colour strength or K/S was greatest from pre-treated UV- SUN sample, followed by pre-treated Albafix (6.67) and untreated sample (6.62). The L^* value from madder dyed cotton with the aid of crosslinkers ranged between 41.30 for control sample to 77.94 for post-treated Fixapret CPF. The values of a^* were negatives from the samples post-treated with Fixapret CPF and Knittex RCT presenting greener shade. All other samples got positive a^* values, with control sample having the maximum redness (17.02). Similarly, b^* was also positive for this group and C^* (chroma) was maximum from the sample, post-treated with Knittex RCT. The result of hue or shade was found the highest from the sample post-padded with crosslinker Fixapret CPF. However, the K/S value was found to be the highest from the control sample. The pre-treatment of Knittex RCT produced sample with lowest K/S value among this group.

3.3.7 Tensile strength of cotton dyed with madder root extracts

The data related to the tensile strength of madder dyed cotton is displayed in Figure 3.17 which reveals that most of the dye formulations resulted in increase in the tensile strength of the samples. Maximum gain in strength due to dyeing was available from the sample dyed with combination of natural extracts of madder roots and Rayosan C, where the increase in strength was 34.7 percent from its pre-treatment and 34.1 percent from its post-treatment. Increase in tensile strength of 32.5, 31.5, 28.5, 27.2, 24.8, 21.9, 21.6, 19.4, 17.0, 16.0 and 11.2 percent from $K_2Cr_2O_7$ (post- padding), Fixapret F-ECO (post- padding), Dicrylan (post- padding), Fixapret F-ECO (pre-treatment), $CuSO_4$ (pre-treatment), $K_2Cr_2O_7$ (pre-treatment), Albafix (pre-treatment), $FeCl_3$ (post- padding), UV –SUN (post- padding) and Fixapret CPF (post- padding), correspondingly. Samples Statistics from t-test shows insignificant result at 5% level of significance between the pre-treated and post-treated samples. Significance testing of the tensile strength of

madder dyed cotton fabric samples was carried out by applying t-test on control sample and pre-treated samples as well between control and post-treated samples (Table 3.27). The outcome showed insignificant difference between the strength of control and pre-treated samples as well as between the control and post-treated fabric samples.

3.4 DYEING COTTON WITH MARIGOLD FLOWER (*TEGETES ERECTA*)

The information related to the colour fastness, colour coordinates and tensile strength of cotton fabric samples dyed with marigold flower extract with the aid of various pre and post-treated auxiliaries are included in Tables 3.31-3.39 and displayed in Figures 3.19 -3.24.

3.4.1 Shades obtained with marigold flower extracts

Sun yellow dye or marigold flower extracts mostly produced yellow shade samples. The prettiest and dark yellow sample was achieved from the pre- treatment of alum (Exhibit 3.4). Similarly, the post-mordanting of alum also presented beautiful yellow sample with lesser intensity of the same shade. Entirely changed shades (other than yellow) were created from the pre-mordanting of copper sulphate and pre-treatment of Albafix; Khaki from pre and post-mordanting of potassium dichromate and post-mordanting of copper sulphate, and greenish-khaki from the pre and post-mordanting of ferric chloride. All other treatments produced samples in light but pleasant yellow shade.

3.4.2 Wash fastness of cotton samples dyed with marigold flower extracts

Data related to fastness properties of marigold flower dyed cotton fabric is presented in Tables 3.31-3.33. The untreated or control sample which was dyed without any colour improving ancillaries, presented moderate wash fastness equal to 3 on Grey-scale. The minimum change in shade due to washing resulted from the pre-mordanting of copper sulphate. The fastness rating measured from this treatment was equivalent to 4 Grey-scale (G.S), represented good performance of wash fastness. Similarly, the maximum change in shade of 2-3 GS, due to wash fastness was resulted from the post-treatment of aluminium sulphate on dyed cotton.

Exhibit 3.4: Shades produced by cotton samples dyed with natural extracts of marigold flower under different conditions.

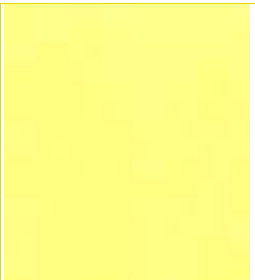
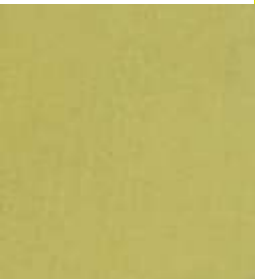
			
	Control sample	Alum- post-mordanting	Alum- pre-mordanting
			
	$\text{Al}_2(\text{SO}_4)_3$ - post-mordanting	$\text{Al}_2(\text{SO}_4)_3$ - pre-mordanting	$\text{K}_2\text{Cr}_2\text{O}_7$ - pre-mordanting
			
	Albafix- pre-treatment	FeCl_3 - post-mordanting	FeCl_3 - pre-mordanting
			
Shades from various recipes of sun-yellow dye	Knittex- pre-treatment	CuSO_4 - pre-mordanting	$\text{K}_2\text{Cr}_2\text{O}_7$ - post-mordanting

Table 3.31: Fastness and tensile properties of cotton fabric dyed with extracts of *Tegetes erecta* flower using various mordants.

Method	Chemical/ Mordant	Wash Fastness		Crocking Fastness		Light Fastness	Tensile strength (lb)	Elongation (%)
		Change in shade	Staining on fabric	Dry rubbing	Wet rubbing			
Pre-mordanting	Al ₂ (SO ₄) ₃	3	4	3-4	3	6	41.9	4.37
	CuSO ₄	4	4-5	4-5	3-4	5	59.6	4-5
	FeCl ₃	3	4	4-5	2-3	5	42.7	4.25
	K ₂ Cr ₂ O ₇	3	4	3	2-3	5	60.7	6.25
	KAl(SO ₄) ₂ ·12H ₂ O	3	3-4	4-5	3	4	47.7	4-5
Post-mordanting	Al ₂ (SO ₄) ₃	2-3	4	4	4	4	53.9	3.75
	CuSO ₄	3-4	4-5	4-5	3-4	4	59	5.63
	FeCl ₃	3	4	4-5	3	5	40.2	5.75
	K ₂ Cr ₂ O ₇	3	4	3-4	3-4	4	59.5	5.13
	KAl (SO ₄) ₂ ·12H ₂ O	3	4	4-5	3-4	4	57.3	6.63
No mordanting	Control sample	3	4	4	3	3	56.8	5.25

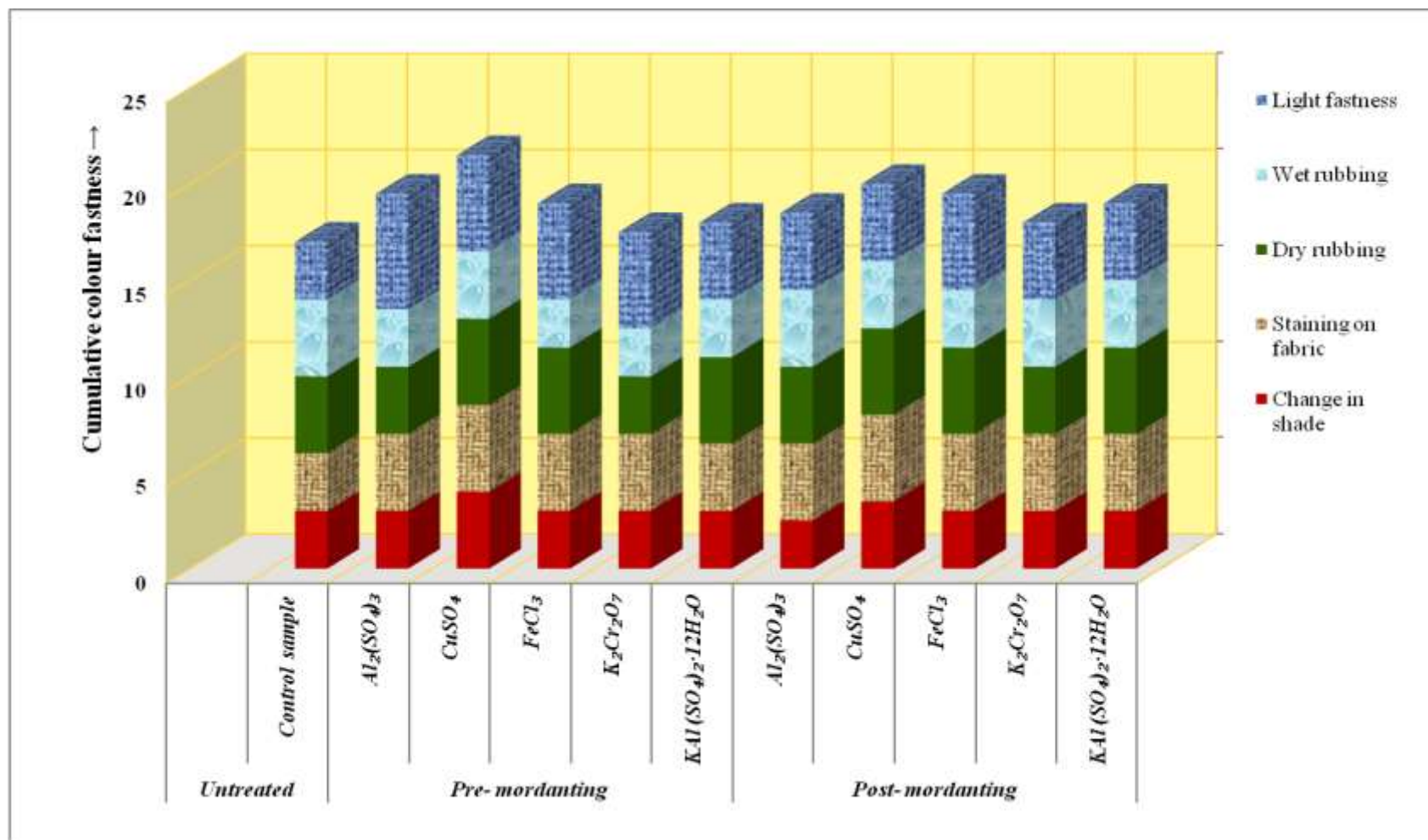


Figure 3.19: Cumulative colour fastness of cotton samples dyed with extracts of *Tegetes erecta* flower using various mordants.

Table: 3.32 Fastness and tensile properties of cotton fabric dyed with extracts of *Tegetes erecta* flower using various finishes and UV absorbers.

Product	Method	Wash Fastness		Crocking Fastness		Light Fastness	Tensile strength (lb)	Elongation (%)
		Change in shade	Staining on fabric	Dry rubbing	Wet rubbing			
Albafix WFF	Pre cationizing	3	4	4	3-4	3	60.6	6.00
	Post cationizing	3	4	4-5	3-4	4	59.5	6.00
Dicrylan	Pre finishing	3	4-5	4	3-4	4	58.6	5.50
	Post finishing	3-4	4-5	4-5	4	4	60.0	5.75
UV –SUN	Pre-treatment	3	4-5	4-5	3-4	5	58.8	5.38
	Post-treatment	3	4	4-5	4	6	50.0	4.75
Rayosan C	Pre-treatment	3	3-4	4	4	5	59.0	4.88
	Post-treatment	3	4	4-5	4-5	5	47.7	5.38
Control sample	Untreated	3	4	4	3	3	56.8	5.25

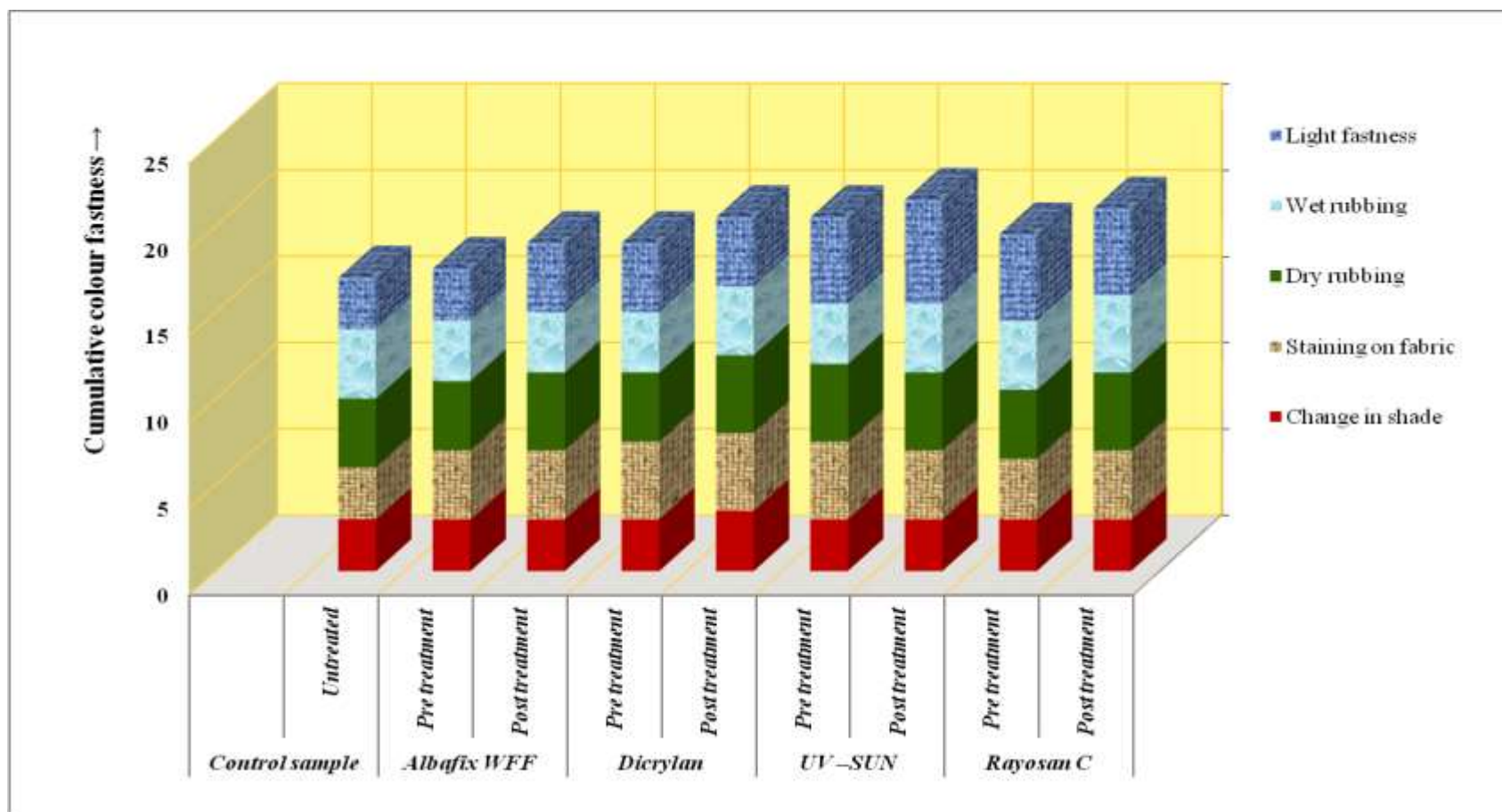


Figure 3.20: Cumulative colour fastness of cotton samples dyed with extracts of *Tegetes erecta* flower using various finishing agents and UV absorbers

Table: 3.33 Fastness and tensile properties of cotton dyed with extracts of *Tegetes erecta* flower using various crosslinking agents.

Product	Method	Wash fastness		Crocking fastness		Light fastness	Tensile strength (lb)	Elongation (%)
		Change in shade	Staining on fabric	Dry rubbing	Wet rubbing			
Fixapret CPF	Pre-treatment	3	3-4	4	3	4	48.4	4.25
	Post-treatment	3	3-4	4	3-4	5	62.8	4.88
Fixapret F-ECO	Pre-treatment	3	4	4	3	4	47.8	5.25
	Post-treatment	3	3-4	3-4	3-4	5	59.5	6.38
Knittex RCT	Pre-treatment	3	3-4	4	3-4	4	64	4.38
	Post-treatment	2-3	3	3-4	3-4	4	57.2	6.13
Control sample	Untreated	3	3	4	4	3	56.8	5.25

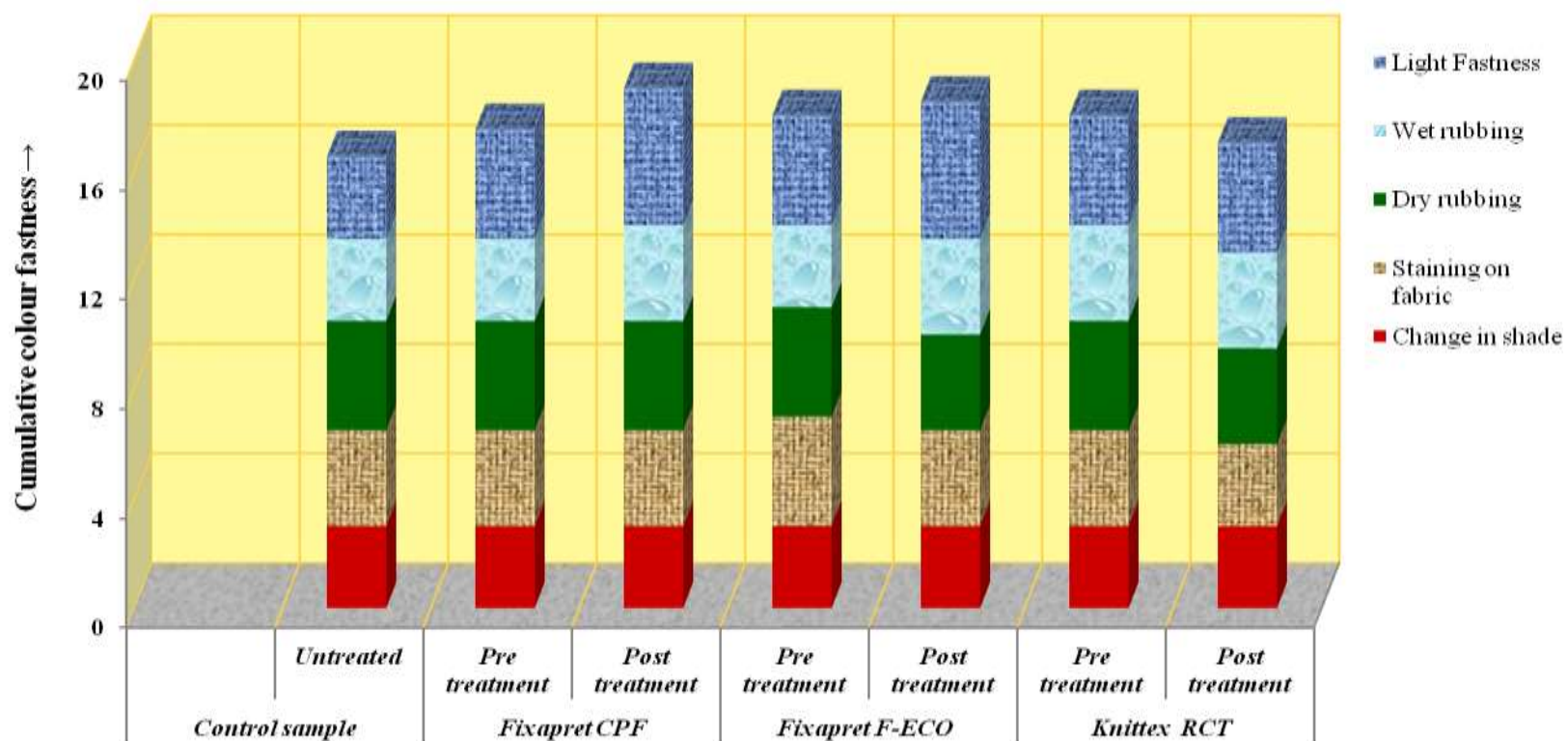


Figure 3.21: Cumulative colour fastness of cotton dyed with extracts of *Tegetes erecta* flower using various crosslinking agents.

Table 3.34: Paired sample statistics for cumulative colour fastness of cotton dyed with *Tegetes erecta* (marigold flower).

Treatment	Mean	N	Std. Deviation	Std. Error Mean
T 1*	12	18.79	1.29	0.37
T 2	12	19.25	1.37	0.40

*T 1 = Pre-treatment; T 2= Post-treatment

Table 3.35: Significance testing of cumulative colour fastness of cotton fabric samples dyed with marigold flower.

(a) Paired sample 2- tailed t- test for cumulative colour fastness: paired differences

Treatments	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
T 1 - T 2	-0.67	2.15	0.62	-2.03	0.70	-1.08	11	0.305

(b). One-Sample t-test: cumulative colour fastness

Cumulative colour fastness	Control sample = 17					
					95% Confidence Interval of the Difference	
	t	df	Sig. (2-tailed)	Mean Difference	Lower	Upper
T1	4.82	11	.001	1.79	0.97	2.61
T2	5.67	11	.000	2.25	1.38	3.12

Table 3.36: Paired sample statistics for tensile strength of cotton dyed with *Tegetes erecta* (marigold flower).

Treatment	Mean	N	Std. Deviation	Std. Error Mean
T 1	12	54.15	7.82	2.26
T 2	12	55.55	6.52	1.88

Table 3.37: Significance testing of tensile strength of cotton fabric samples dyed with marigold flower.

(a) Paired sample 2- tailed t- test for tensile strength: paired differences

Treatments	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
T 1 - T 2	-1.40	8.63	2.49	-6.88	4.08	-0.56	11	0.58

(b). One-Sample t-test: tensile strength

Tensile strength	Control sample = 56.8					
					95% Confidence Interval of the Difference	
	t	df	Sig. (2-tailed)	Mean Difference	Lower	Upper
T1	-1.17	11	0.26	-2.65	-7.62	2.32
T2	-0.66	11	0.52	-1.25	-5.39	2.89

Table 3.38: Colour coordinate values of *Tegetes erecta* flower dyed cotton fabric samples using various mordants.

Method	Mordant	Colour coordinates					
		L*	a*	b*	C*	h°	K/S
Pre-mordanting	Al ₂ (SO ₄) ₃	55.46	-1.16	28.71	28.73	92.31	10.26
	CuSO ₄	61.95	3.60	29.97	30.19	83.15	7.12
	FeCl ₃	36.81	1.70	9.93	10.07	80.26	5.52
	K ₂ Cr ₂ O ₇	55.85	4.20	28.53	28.84	81.62	5.21
	KAl(SO ₄) ₂ ·12H ₂ O	71.05	0.86	45.00	45.04	87.63	4.29
Post-mordanting	Al ₂ (SO ₄) ₃	58.56	-3.68	21.87	22.17	99.54	3.36
	CuSO ₄	59.19	7.46	32.41	33.26	77.06	8.57
	FeCl ₃	49.18	-0.88	11.27	11.30	94.46	7.41
	K ₂ Cr ₂ O ₇	59.52	2-33	26.54	26.66	84.55	4.18
	KAl (SO ₄) ₂ ·12H ₂ O	74.40	0.37	43.61	43.61	89.51	3.01
No mordanting	Control sample	71.15	2.75	35.78	35.89	85.61	4.29

Table 3.39: Colour coordinate values of *Tegetes erecta* flower dyed cotton fabric samples various dyeing auxiliaries.

Product	Method	Colour coordinates					
		L*	a*	b*	C*	h°	K/S
Albafix WFF	Pre cationizing	67.79	2.96	33.45	33.48	84.94	5.33
Dicrylan	Pre finishing	72.82	1.64	36.01	36.05	87.36	5.03
UV –SUN	Pre-treatment	71.84	1.20	32.35	32.38	84.94	3.06
Fixapret CPF	Pre-treatment	68.62	2.78	32.74	32.86	85.15	4.23
Fixapret F-ECO	Pre-treatment	72.31	0.98	33.21	33.23	88.31	3.13
Knittex RCT	Pre-treatment	74.42	1.15	36.47	36.49	88.19	3.47
Albafix WFF	Post cationizing	69.33	3.46	37.64	37.81	84.59	5.70
Control sample	Untreated	71.15	2.75	35.78	35.89	85.61	4.29

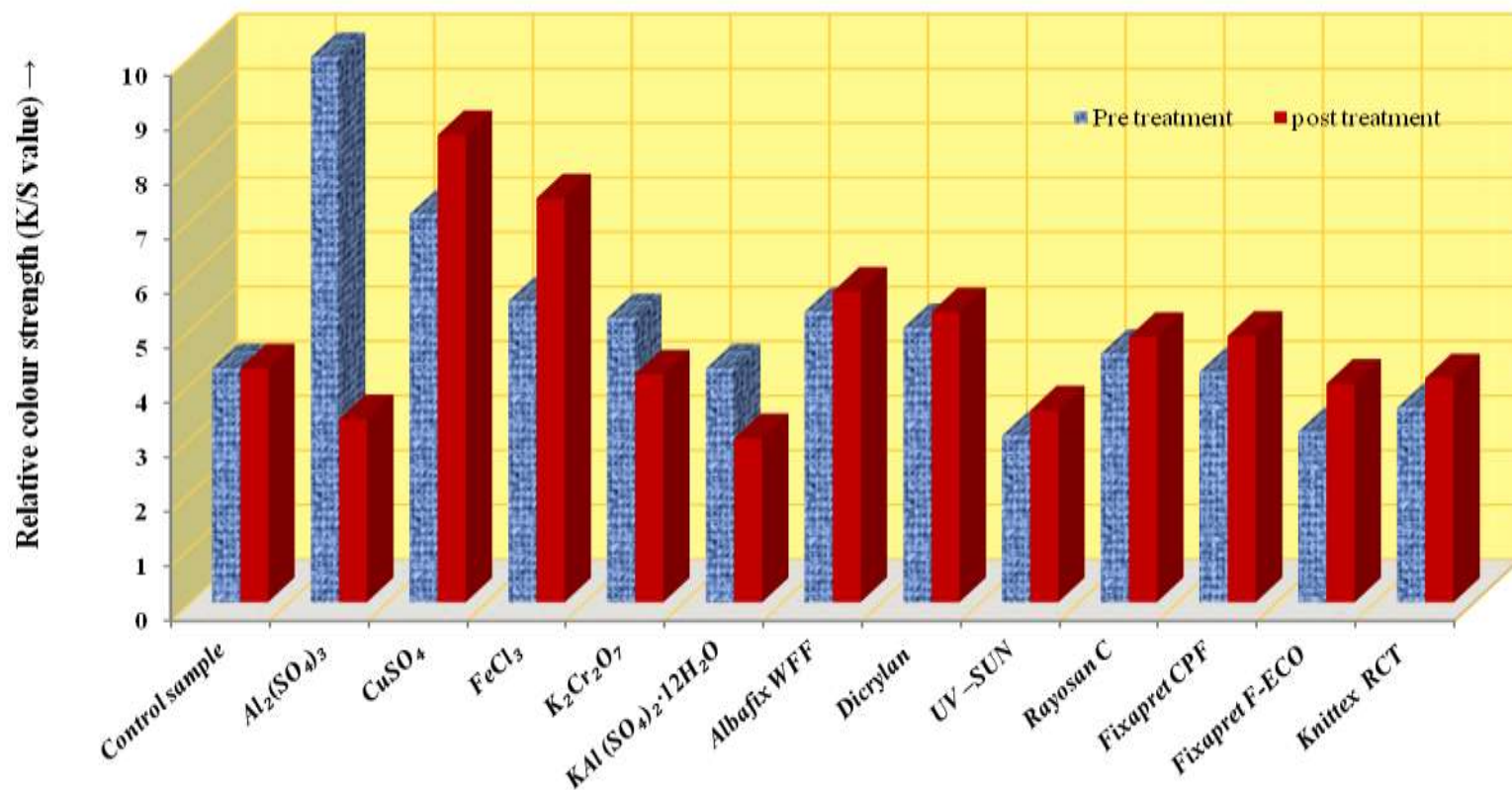


Figure 3.22: Effect of various dyeing auxiliaries on the colour strength of cotton samples dyed with extracts of *Tegetes erecta* flower by pad-steam method.

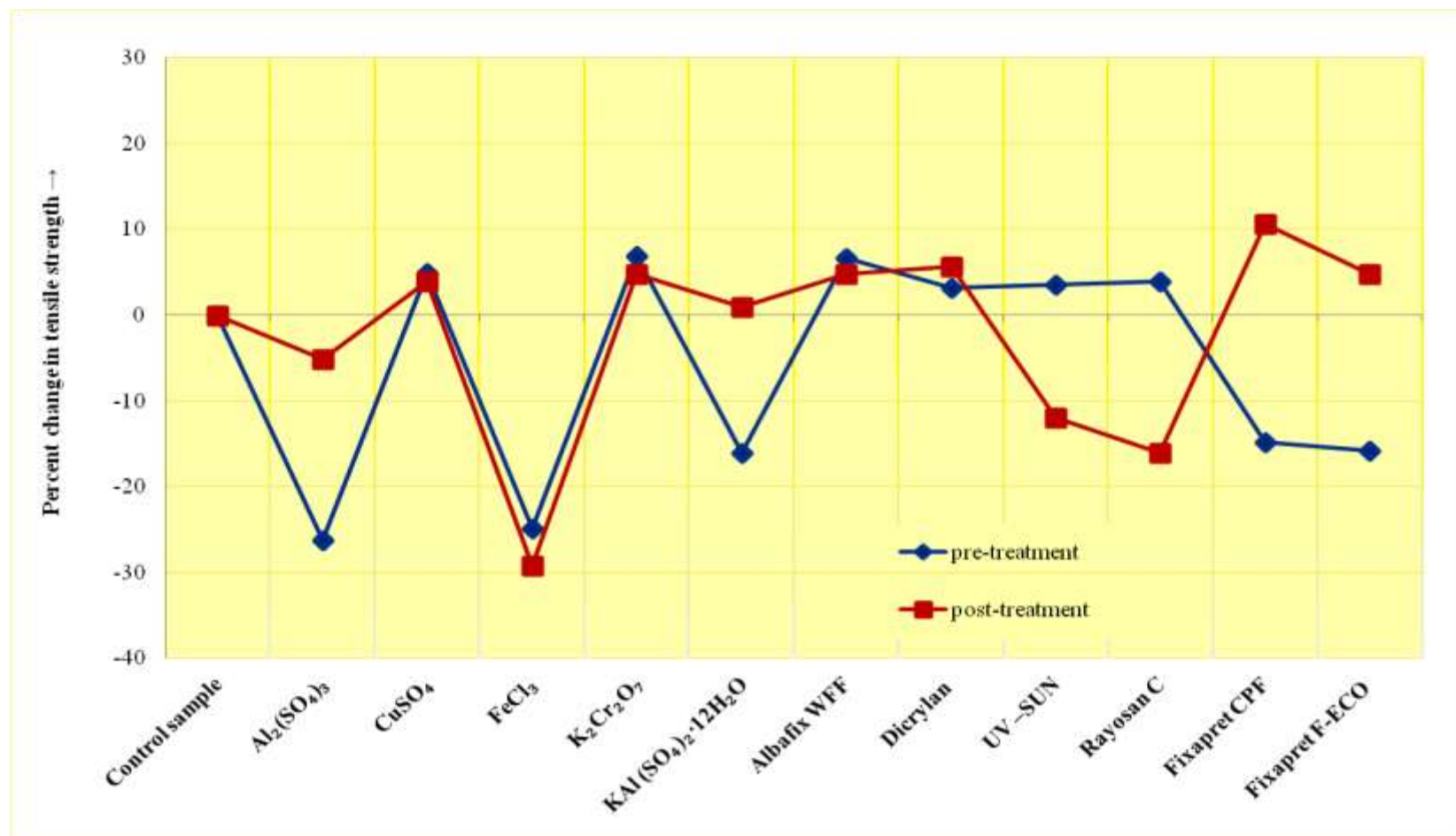


Figure 3.23: Effect of various dyeing auxiliaries on the tensile strength of cotton samples dyed with extracts of *Tegetes erecta* flower by pad-steam method.

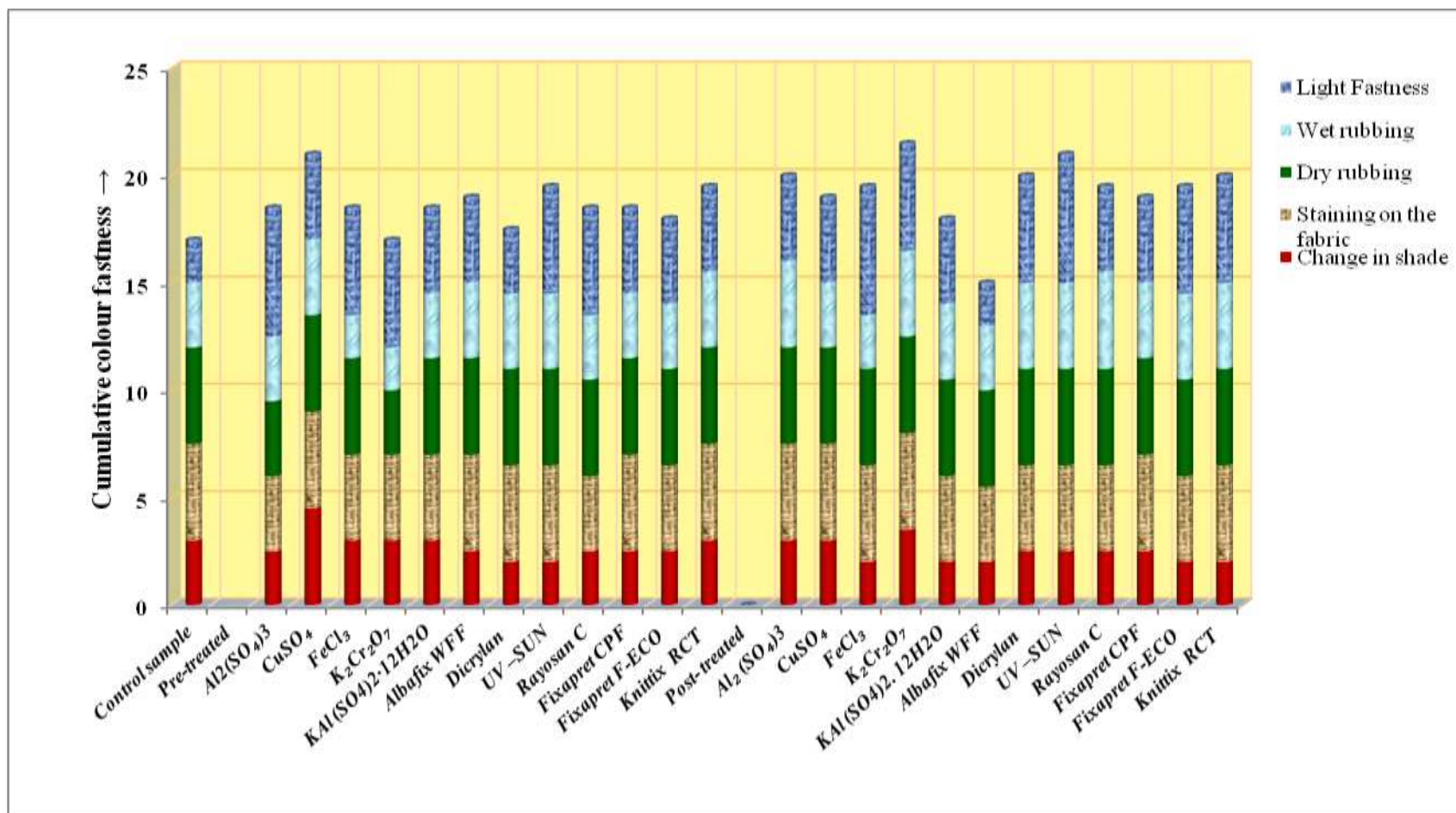


Figure 3.24: Comparative analysis of cumulative colour fastness of cotton dyed with various dye formulations af *Tegetes erecta*.

A change in shade of 3 GS was also revealed from cotton samples which were pre-mordanting by aluminium sulphate, ferric chloride, potassium dichromate, hydrated potassium aluminium sulphate as well as post-mordanting of ferric chloride, potassium dichromate and hydrated potassium aluminium sulphate (alum). In case of post-mordanting with CuSO_4 , the rating was 3-4 GS, i.e., slightly superior to the wash fastness of control or untreated sample.

Post-treatment of marigold flower extracts dyed cotton with Dicrylan recorded the wash fastness rating of change in shade equal to 3- 4GS, which is considered to be fairly good fastness. Post-mordanting of cotton sample with Knittex and dyeing with marigold flower extracts exposed 2-3 GS rating of change in shade due to washing. All other dyeing formulas among this group, produced cotton samples with a fastness rating of 3 GS change in shade. These included the pre-treatment with Knittex RCT, post-treatment with Dicrylan and both pre as well as post-treatments of Albafix WFF, UV-SUN, Rayosan C, Fixapret CPF and Fixapret F-ECO.

As far as staining on the adjacent white fabric is concerned due to wash test, best result (minimum staining) was displayed by the sample dyed with formula of pre and post-mordanting of CuSO_4 in the recipes where the rating was 4-5 GS. This was followed by a rating of 4 GS available from control sample, pre and post-mordanting with $\text{Al}_2(\text{SO}_4)_3$, FeCl_3 , $\text{K}_2\text{Cr}_2\text{O}_7$ and post-mordanting with $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. Maximum staining of 3-4 GS among this group was rendered by sample dyed with marigold flower extracts and pre-mordanted $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

To compare the staining that resulted from the treatment of various finishes and crosslinkers, very little staining equivalent to 4-5 GS was perceptible from the tested samples dyed with a combination of marigold flower extracts and pre and post-cationizing of Dicrylan and pre-treatment with UV-SUN. Good wash fastness performance related to 4 GS was offered by samples having pre and post-treatment with Albafix WFF, pre-treatment with Fixapret F-ECO, as well as post-treatment of UV- SUN and Rayosan C. Staining of 3-4 GS was disclosed by the cotton sample dyed with the aid of pre-treated Rayosan, pre and post-treatment of Fixapret CPF, pre-treatment of knittex and post-treatment of Fixapret F-ECO in the dyeing formulas. Post-padding of cotton

with Knittex stained the adjacent white sample similar to the control sample and was rated as 3 GS which was the maximum staining recorded on the adjacent white fabric from the samples of this group.

3.4.3 Crocking fastness of cotton dyed with marigold flower extracts

As looked upon the results of dry rubbing fastness of cotton samples dyed with marigold flower extracts and various mordants, it is evident from the tabulated data (Table 3.31) that the pre and post-mordanting with CuSO_4 , FeCl_3 and $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ produced samples with dry rubbing equal to 4-5 on GS, representing very good dry rubbing fastness of dyed articles. In the same group, the sample which faded the most due to dry crocking was the one which had a treatment of pre-mordanting at $\text{K}_2\text{Cr}_2\text{O}_7$ in the dye formulation. The dry rubbing rating of this dyed sample was recorded as 3 on Grey scale. Fastness rating of cotton samples dyed with a combination of pre-mordanted of $\text{Al}_2(\text{SO}_4)_3$ and marigold flower extracts yielded dry rub fastness similar to 4 GS. Dry crock fastness rating equal to 3-4 GS was available from the pre-treatment with $\text{Al}_2(\text{SO}_4)_3$ and post-treatment of cotton sample with $\text{K}_2\text{Cr}_2\text{O}_7$ as mordants.

As regards to the dry rubbing fastness of cotton with treatments of UV absorbers, crosslinkers and other finishes, very good performance of only 4-5 GS rating was exhibited by those cotton samples which were dyed with recipes having UV-SUN both as pre and post-treatments as well as pre-treatment of Dicrylan and post-treatments of Albafix WFF and Rayosan. This was followed by acquiring dry rubbing of 4 GS from the pre and post-treatments of Fixapret CPF; pre-treatments of Albafix WFF, Rayosan C, Fixapret CPF, Fixapret F-ECO, Knittex RCT; post-treatment of Dicrylan. Minimum dry rubbing fastness in this group was 3-4 GS attained by the samples which had the post-treatments of Fixapret F-ECO, Knittex RCT.

Considering the wet rubbing fastness performance of cotton samples coloured with marigold flower extracts, the rating of 3 GS was assigned to the control sample and those which were pre-mordanted with aluminium sulphate and hydrated potassium aluminium sulphate. In comparison, cotton sample resulting from the pre and post-mordanting of CuSO_4 and post-mordanting of $\text{K}_2\text{Cr}_2\text{O}_7$ and $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ had been able to produce wet rubbing fastness greater than the wet fastness of the control sample

(i.e. 3 GS). All other mordants in the dyeing formulas produced cotton with lesser wet rub fastness. The most faded samples due to wet rubbing (2-3 GS) were those which had been coloured with pre-mordanting with FeCl_3 and $\text{K}_2\text{Cr}_2\text{O}_7$.

Wet rubbing fastness of 4-5 GS was demonstrated by cotton dyed with natural extracts of marigold flower assisted by the post-treatment of Rayosan C. This exhibition of the best fastness to wet rubbing was followed by 4 GS, resulting from dyeing with pre-treated Dicrylan and Rayosan as well as post-treated UV-SUN. Lowest fastness due to wet rubbing of 3 GS among this group of dyeing auxiliaries was found in samples dyed with pre-treatments of Fixapret CPF and Fixapret F-ECO. Wet fastness of 3-4 GS was offered by both pre and post-treatments of Albafix WFF and Knittex RCT. Pre-treatment of UV-SUN and post-padding of Dicrylan, Fixapret CPF and Fixapret F-ECO in the dye formulations also yielded samples with 3-4 GS wet rubbing fastness.

3.4.4 Light fastness of cotton dyed with marigold flower extracts

Evaluating the light fastness performance related to dyed cotton samples with marigold flower extracts are listed in Tables 3.31. Without any additional dyeing assisting, the control sample could achieve only 3 Blue Wool Standard light fastness. Highest light fastness was exhibited by the cotton sample dyed with a combination of natural extracts of marigold flower and pre-mordanting of aluminium sulphate and the sample was rated as standard 6 (very good light fastness property). Pre-mordanting with $\text{K}_2\text{Cr}_2\text{O}_7$, both pre and post-mordanting with FeCl_3 and post-mordanting with CuSO_4 , with the application of marigold flower extracts posed light fastness of 5 Blue Wool Standard which represent a good performance. All other mordants employed with the application of marigold flower extracts, i.e., pre and post-mordanting with hydrated potassium aluminium sulphate and post-mordanting with aluminium sulphate, copper sulphate and potassium dichromate caused light fastness of 4 Blue Wool Standard which is a fairly good performance.

A very good light fastness of standard 6 was displayed by the post-padding of UV-SUN. Similarly, a fastness rating of 5 Blue Wool Standard was revealed from cotton samples with marigold flower extracts which were pre and post-treating with Rayosan; pre-padded with UV-SUN; and post-treated with Fixapret CPF. Light fastness equivalent

to standard 4 was yielded by samples dyed with marigold flower extracts and pre as well as post-treatment of Rayosan C and Knittex RCT; pre-padding of crosslinkers Fixapret CPF and Fixapret F-ECO; and post-treatment of Albafix WFF in the dye formulations. However, the pre-treatment of Albafix WFF, utilized to assist dyeing could not push the light fastness ahead of the control or reference sample and they were allotted 3 on Blue Wool Standard.

3.4.5 Cumulative fastness of marigold flower dyed samples: t-test

Cumulative colour fastness of cotton samples dyed with marigold flower dye with the help of various dyeing auxiliaries has been displayed in Figure 3.24. The highest cumulative colour fastness of cotton dyed with marigold flower with the use of various auxiliaries was displayed by the pre-mordanting of copper sulphate and post-treatment of potassium dichromate and UV-SUN. Lowest performance in this regard was shown by post padding of Albafix. Paired sample t-test was applied to evaluate the cumulative colour fastness of cotton samples dyed with marigold flower with various dyeing aides. There was no significant difference in the rating of pre and post-treatment on the cumulative colour fastness of dyed samples. The mean values were 18.67 and 19.33, available from pre-treatments and post-treatments. The mean difference was computed as -0.67, with standard deviation = 2.1, $t = -1.07$ and $p = 0.305$. The data showed non-significant difference (as 0.305 is greater than 0.05), between the outcome of pre and post-treatments. Significance testing of the cumulative colour fastness of marigold flower dyed cotton fabric samples was also carried out by applying t-test on control sample and pre-treated samples as well between control and post-treated samples (Table 3.37). Significant difference was found between the fastness of control and pre-treated samples as well as between the control and post-treated fabric samples.

3.4.6 Colour coordinates of cotton fabric dyed with marigold flower extracts

Good colour yield was manifested by most of the samples dyed with the extracts of marigold flower (*Tagetes erecta L.*). In the presence of various dyeing ancillaries, the L^* was towards the high region. It ranged from 36.81 to 74.42. The L^* for control sample was 71.15. Samples dyed with the combination of marigold flower and other dyeing auxiliaries such as pre-treatment of UV-SUN, Fixapret F-ECO, Dicrylan and Knittex

RCT were characterized by colour yield lower than the control sample. Their L^* values were 71.82, 72.31, 72.82, 74.40 and 74.42, respectively. Colour production from alum was also low and the L^* value was 71.05 and 74.40 from its pre and post-mordanting, respectively. Better colour yield (low lightness) was displayed by mordanting with ferric chloride, particularly the combination of marigold flower and pre-mordanting with ferric chloride posed the lowest L^* value. Colour coordinate a^* was negative in samples dyed by using $Al_2(SO_4)_3$ as pre or post-mordant as well as ferric chloride as post-mordant indicating greener tone. All other dyed samples were in the region of redder tone. However, the values of b^* were positive (yellow tone) from all the dyed samples of marigold flower with the highest of 45.0 being offered by pre-mordanting of alum, followed by 43.6, available from post-mordanting of alum.

Purity of shade (C^*) was maximum from a sample dyed with marigold flower and pre finished with Dicrylan indicating value of 36.0. The readings of C^* of samples obtained from the pre-treatment with Albafix WFF, Fixapret F-ECO, Fixapret CPF and UV-SUN were 33.48 33.23, 32.86 and 32.38, respectively. Post-mordanted sample with copper sulphate also yielded 33.26 value of chroma, presenting better shade purity. The values of h° were all high in respect of marigold flower dyed samples and ranged from 77.06- 99.54. As far as the K/S or colour strength of dyed samples are concerned, the pre-mordanting of $Al_2(SO_4)_3$ managed to yield a cotton fabric sample with the highest value of 10.26 followed by 8.57 K/S value, attained by a sample which was post-mordanted with $CuSO_4$. Moreover, good result was also communicated by a sample which was pre-mordanted with copper sulphate.

3. 4.7 Tensile strength of cotton dyed with natural extracts of marigold flower

The majority of the auxiliaries employed with marigold flower dyeing in this study resulted in improving the tensile strength of coloured cotton samples. However, a loss in strength was also registered in some cases. Maximum gain in tensile strength of cotton samples due to dyeing with the help of various auxiliaries was about 15.8 percent from $K_2Cr_2O_7$ (post-mordanting). Increase in strength from the treatments of post-padding of UV-SUN, Fixapret CPF (post- padding) and Knittex RCT (post-treatment) was 11.5, 6.0 and 5.7 percent, respectively. A loss in tensile strength of about 28 percent

from potassium dichromate (pre-mordanting), 25 percent from FeCl_3 (pre-treatment) and 17.5 percent from CuSO_4 was also caused due to dyeing. Overall, pre-treated samples gave poor strength than post-treated cotton fabric. Samples Statistic from paired sample t-test showed insignificant. Significance testing of the tensile strength of dyed cotton fabric samples was carried out by applying t-test on control sample and pre-treated samples as well between control and post-treated samples (Table 3.37). The outcome showed insignificant difference between the strength of control and pre-treated samples as well as between the control and post-treated fabric samples.

3.5 DYEING OF COTTON WITH TURKEY RED NATURAL DYE (*RUBIA CORDIFOLIA*)

Cotton samples dyed with natural extracts of Turkey red with the utilization of various dyeing auxiliaries were also put through services of physical tests to check the credibility of the dye on cotton. The recorded data are presented in Tables 3.40-3.48 and Figures 3.25 to 3.30.

3.5.1 Shades obtained with Turkey red dye

Natural extracts of Turkey red gave a range of purple shade with most of the dyeing recipes (Exhibit 3.5). Extremely beautiful, attractive, soft textured, smooth and evenly dyed sample in dark purple (signal violet) colour resulted from the dye formulation having pre-mordanting of hydrated potassium aluminium sulphate (alum). Beautiful shade of pure purple colour was displayed by pre-cationized cotton (Albafix WFF) sample dyed with Turkey red extracts. Slightly greater intensity of the same shade was exposed by the pre-treatments of UV-SUN, Dicrylan and Fixapret CPF as well as the post-treatments of Albafix and control sample. Lighter shade of the purple was available from the dyeing recipes of the treatment with Fixapret F ECO, Knittex and post-mordanting of potassium dichromate.

Cationization with Albafix (pre-padding) produced dull purple colour. Reddish purple samples were yielded by treatments of post-mordanting of copper sulphate (dark shade), pre-mordanting with hydrated potassium aluminium sulphate (medium reddish purple) and pre-mordanting by copper sulphate (light shade).

Exhibit 3.5: Shades produced by cotton samples dyed with natural extracts of Turkey red natural dye under different conditions.

			
	Control sample	FeCl ₃ pre-mordanting	Al ₂ (SO ₄) ₃ pre-mordanting
	K ₂ Cr ₂ O ₇ pre-mordanting	CuSO ₄ pre-mordanting	Dicrylan pre-treatment
	Alum post-mordanting	Alum pre-mordanting	Knittex pre-treatment
	Albafix pre-treatment	Albafix post-treatment	FeCl ₃ post-mordanting
	Shades from various recipes of Turkey red		

Table 3.40: Fastness and tensile properties of cotton fabric dyed with root extracts of *Rubia cordifolia* using various mordants.

Method	Chemical/ Mordant	Wash Fastness		Crocking Fastness		Light Fastness	Tensile strength (lb)	Elongation (%)
		Change in shade	Staining on fabric	Dry rubbing	Wet rubbing			
Pre-mordanting	Al ₂ (SO ₄) ₃	3	4	4-5	2-3	3	62.7	4.88
	CuSO ₄	2-3	4	4	2	5	42.0	3.40
	FeCl ₃	4-5	4-5	3-4	2	3	46.4	3.88
	K ₂ Cr ₂ O ₇	4	4	4	2	3	37.0	3.13
	KAl(SO ₄) ₂ ·12H ₂ O	4	4	4-5	2-3	1*	60.2	4.25
Post-mordanting	Al ₂ (SO ₄) ₃	3	4	4	2	5	64.9	5.50
	CuSO ₄	3-4	4	4	2	3	64-5	5.63
	FeCl ₃	1*	4-5	4-5	3	3	64.1	5.00
	K ₂ Cr ₂ O ₇	3	4	4-5	2-3	3	59.4	4.50
	KAl (SO ₄) ₂ ·12H ₂ O	4	4	4	2	3	65.0	5.25
No mordanting	Control sample	3	4	4-5	2-3	3	59.6	4.75

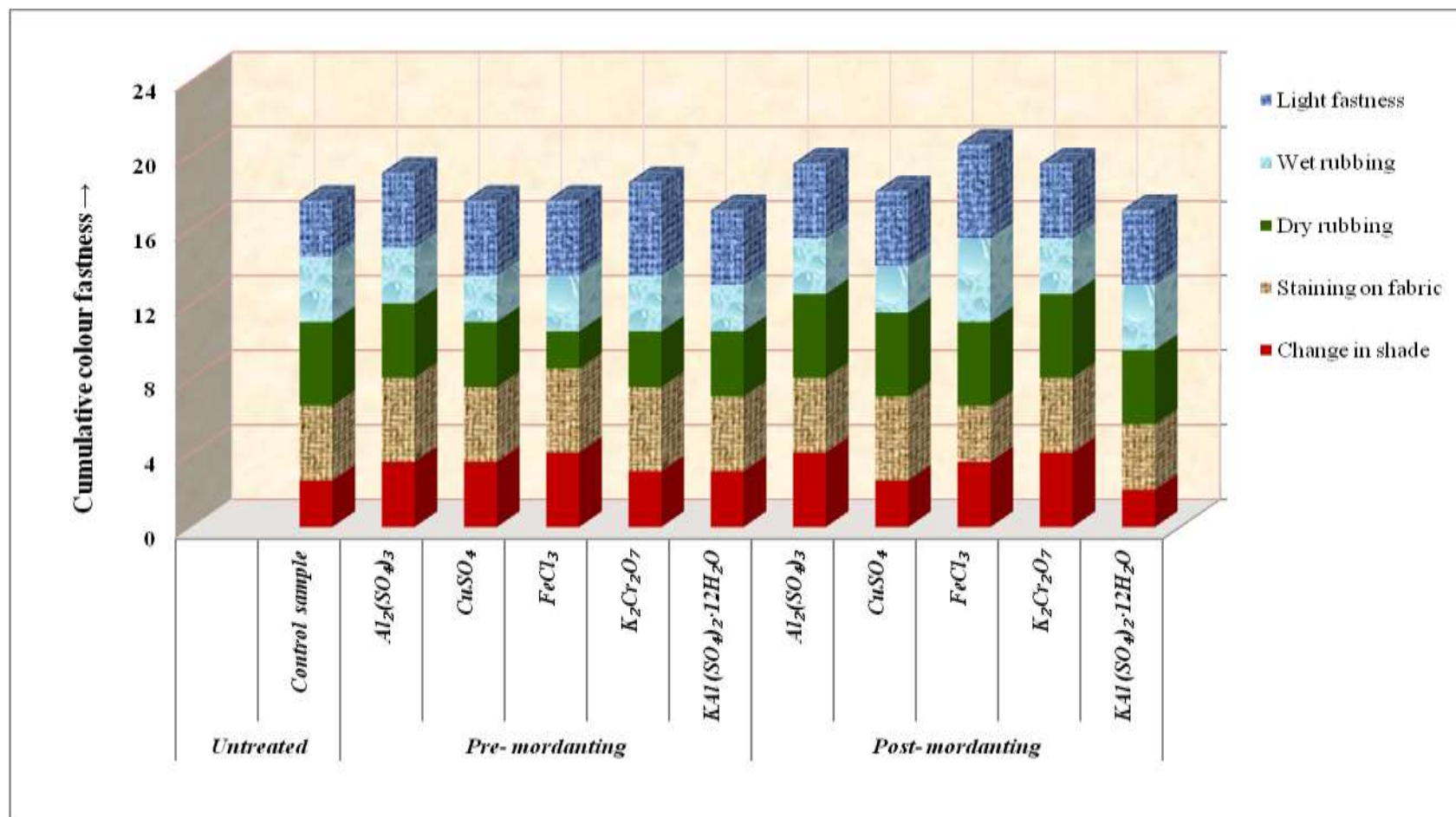


Figure 3.25: Cumulative colour fastness of cotton samples dyed with root extracts of *Rubia cordifolia* using various mordants.

Table: 3.41 Fastness and tensile properties of cotton fabric dyed with root extracts of *Rubia cordifolia* using various finishes and UV absorbers.

Product	Method	Wash Fastness		Crocking Fastness		Light Fastness	Tensile strength (lb)	Elongation (%)
		Change in shade	Staining on fabric	Dry rubbing	Wet rubbing			
Albafix WFF	Pre cationizing	4	4-5	3-4	2	1*	58.6	4.75
	Post cationizing	3	4-5	4-5	2	3	56.3	5.38
Dicrylan	Pre finishing	3	4	3-4	2	4	59.6	5.13
	Post finishing	4	4	4	3	4	60.0	5.25
UV –SUN	Pre-treatment	3	3-4	3-4	2	3	69.6	5.75
	Post-treatment	4	4	4	2	4	69.9	5.88
Rayosan C	Pre-treatment	4	3-4	4-5	2-3	4	66.0	5.63
	Post-treatment	4	4	4-5	2-3	4	67.5	5.37
Control sample	Untreated	3	4	4-5	2-3	3	59.6	4.75

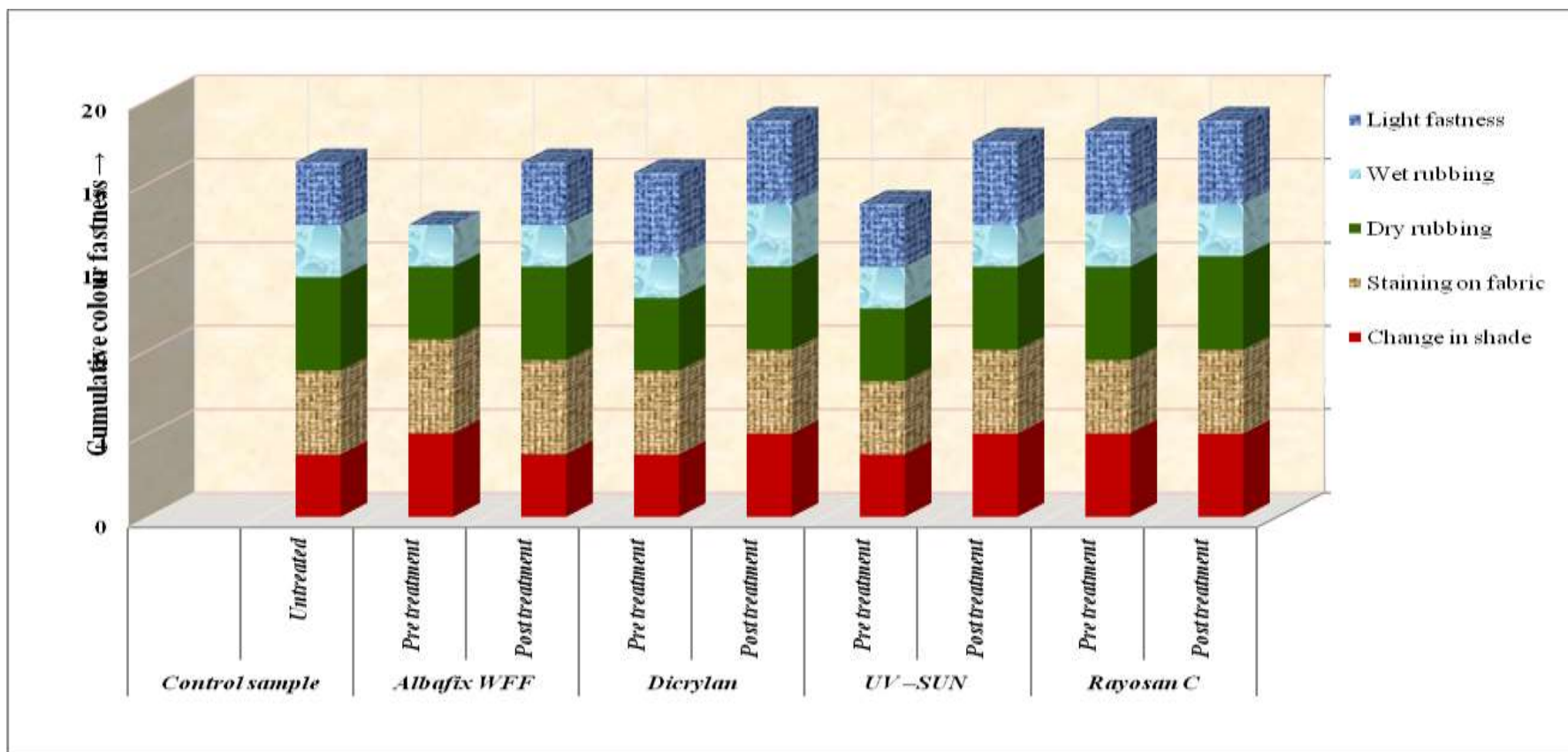


Figure 3.26: Cumulative colour fastness of cotton samples dyed with root extracts of *Rubia cordifolia* using various finishing agents and UV absorbers.

Table 3.42: Fastness and tensile properties of cotton fabric dyed with root extracts of *Rubia cordifolia* using various crosslinking agents.

Product	Method	Wash fastness		Crocking fastness		Light fastness	Tensile strength (lb)	Elongation (%)
		Change in shade	Staining on fabric	Dry rubbing	Wet rubbing			
Fixapret CPF	Pre-treatment	3	3-4	4	2-3	3	45.6	4.38
	Post-treatment	2-3	3-4	3	2	3	56.3	5.38
Fixapret F-ECO	Pre-treatment	3	4	4	2-3	3	40.0	3.38
	Post-treatment	3	4	3	2	3	42.0	3.75
Knittex RCT	Pre-treatment	3	4	4	3	4	53.2	4.37
	Post-treatment	3	4-5	4	2	6	52.0	4.25
Control sample	Untreated	3	4	4-5	2-3	3	59.6	4.75

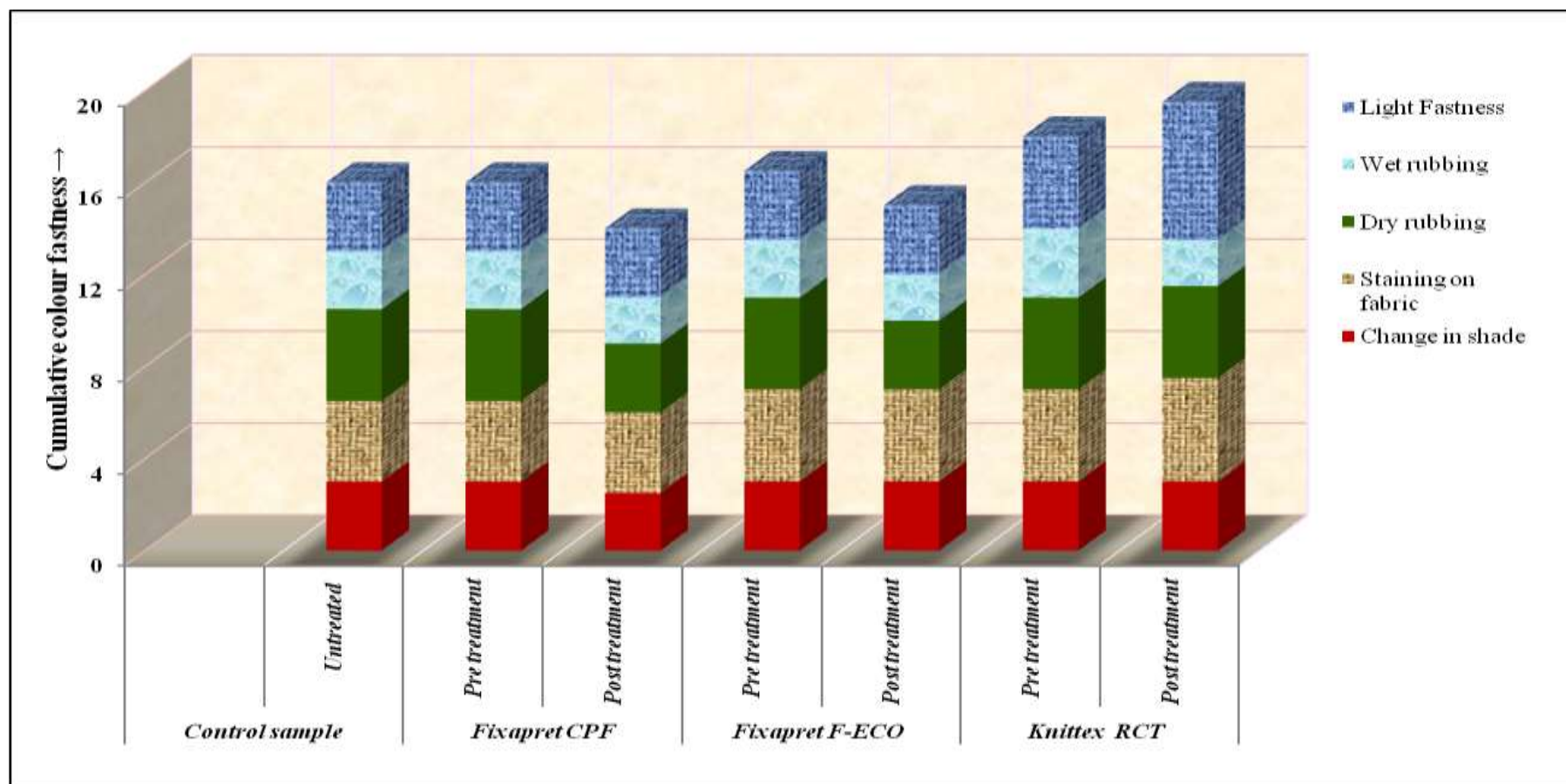


Figure 3.27: Cumulative colour fastness of cotton dyed with root extracts of *Rubia cordifolia* using various crosslinking agents.

Table 3.44: Paired sample statistics for cumulative colour fastness of cotton dyed with *Rubia cordifolia* (Turkey red).

Treatment	Mean	N	Std. Deviation	Std. Error Mean
T 1*	12	16.71	1.10	0.32
T 2*	12	17.17	1.66	0.48

*T 1 = Pre-treatment; T 2= Post-treatment

Table 3.45: Significance testing of cumulative colour fastness of cotton fabric samples dyed with Turkey red.

(a) Paired sample 2- tailed t- test for cumulative colour fastness: paired differences

Treatmen ts	Paired Differences					t	df	Sig. (2- tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
T 1 - T 2	-0.63	1.31	0.38	-1.46	0.21	-1.65	11	0.127

(b). One-Sample t-test: cumulative colour fastness

Cumulative colour fastness	Control sample = 17					
					95% Confidence Interval of the Difference	
	t	df	Sig. (2-tailed)	Mean Difference	Lower	Upper
T1	-0.92	11	.38	-0.29	-0.98	0.41
T2	0.35	11	.73	0.17	-0.88	1.22

Table 3.46: Paired sample statistics for tensile strength of cotton dyed with *Rubia cordifolia* (Turkey red).

Treatment	Mean	N	Std. Deviation	Std. Error Mean
T 1	12	53.41	10.90	3.15
T 2	12	60.16	7.72	2.23

Table 3.47: Significance testing of tensile strength of cotton fabric samples dyed with Turkey red.

(a) Paired sample 2- tailed t- test for tensile strength: paired differences

Treatmen ts	Paired Differences					t	df	Sig. (2- tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
T 1 - T 2	-0.63	1.31	0.38	-1.46	0.21	-1.65	11	0.127

(b). One-Sample t-test: tensile strength

Tensile strength	Control sample = 57.7					
					95% Confidence Interval of the Difference	
	t	df	Sig. (2- tailed)	Mean Difference	Lower	Upper
T1	-1.30	11	0.22	-4.09	-11.01	2.83
T2	1.19	11	0.26	2.66	-2.24	7.56

Table 3.47: Colour coordinate values of *Rubia cordifolia* dyed cotton fabric samples using various mordants.

Method	Mordant	Colour coordinates					
		L*	a*	b*	C*	h°	K/S
Pre-mordanting	Al ₂ (SO ₄) ₃	42.46	20.08	1.26	20.14	355.57	2.83
	CuSO ₄	43.10	21.18	1.68	21.25	4.54	3.64
	FeCl ₃	27.04	12.02	3.23	12.44	344.96	9.46
	K ₂ Cr ₂ O ₇	36.90	23.25	2.33	23.43	7.18	4.88
	KAl(SO ₄) ₂ ·12H ₂ O	31.30	20.46	-7.34	21.73	340.25	1.70
Post-mordanting	Al ₂ (SO ₄) ₃	44.27	19.18	10.47	21.85	28.63	2.80
	CuSO ₄	36.67	15.87	-3.12	16.17	348.87	9.71
	FeCl ₃	40.81	4.99	1.82	5.32	20.37`	7.56
	K ₂ Cr ₂ O ₇	40.59	15.68	-6.88	17.13	336.32	3.73
	KAl (SO ₄) ₂ ·12H ₂ O	52.02	32.73	20.17	41.03	29.44	2.03
No mordanting	Control sample	35.69	15.89	13.41	20.86	319.23	3.17

Table 3.48: Colour coordinate values of *Rubia cordifolia* dyed cotton fabric samples various dyeing auxiliaries.

Product	Method	Colour coordinates					
		L*	a*	b*	C*	h°	K/S
Albafix WFF	Pre cationizing	29.37	13.71	-10.97	17.56	321.34	5.55
Dicrylan	Pre finishing	38.05	13.79	-10.65	17.42	322.33	4.19
UV –SUN	Pre-treatment	36.53	14.05	-10.38	17.47	323.43	3.28
Fixapret CPF	Pre-treatment	37.29	14.18	-11.18	18.06	321.77	3.08
Fixapret F-ECO	Pre-treatment	34.91	14.47	-10.68	17.99	323.46	3.80
Knittex RCT	Pre-treatment	35.18	14.25	-10.54	17.72	323.41	3.73
Albafix WFF	Post cationizing	38.88	14.79	-13.43	20.04	317.56	2.67
Control sample	Untreated	35.69	15.89	13.41	20.86	319.23	3.17

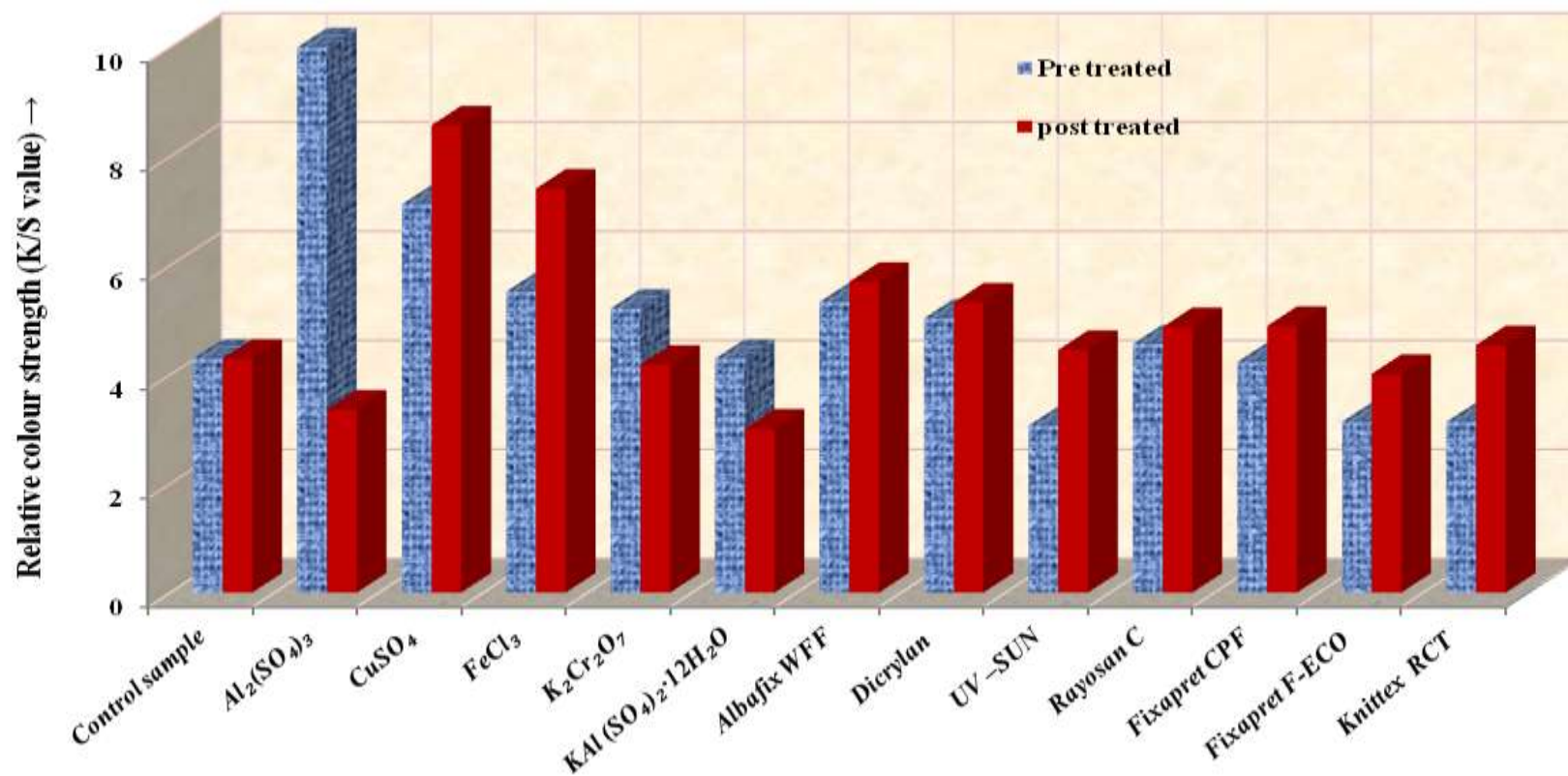


Figure 3.28: Effect of various dyeing auxiliaries on the colour strength of cotton samples dyed with root extracts of *Rubia cordifolia* by pad- steam method.

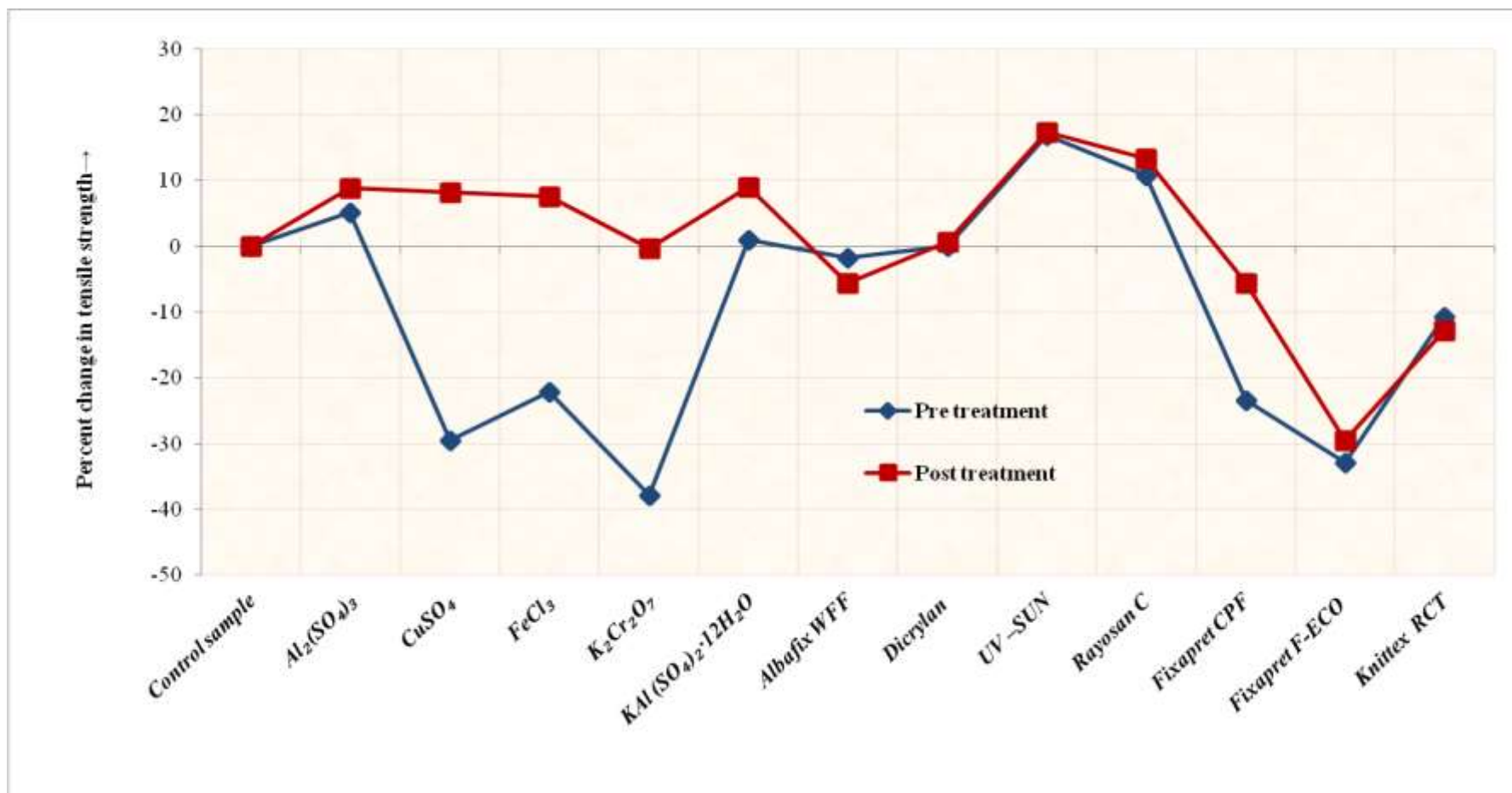


Figure 3.29: Effect of various dyeing auxiliaries on the tensile strength of cotton samples dyed with root extracts of *Rubia cordifolia* by pad- steam method.

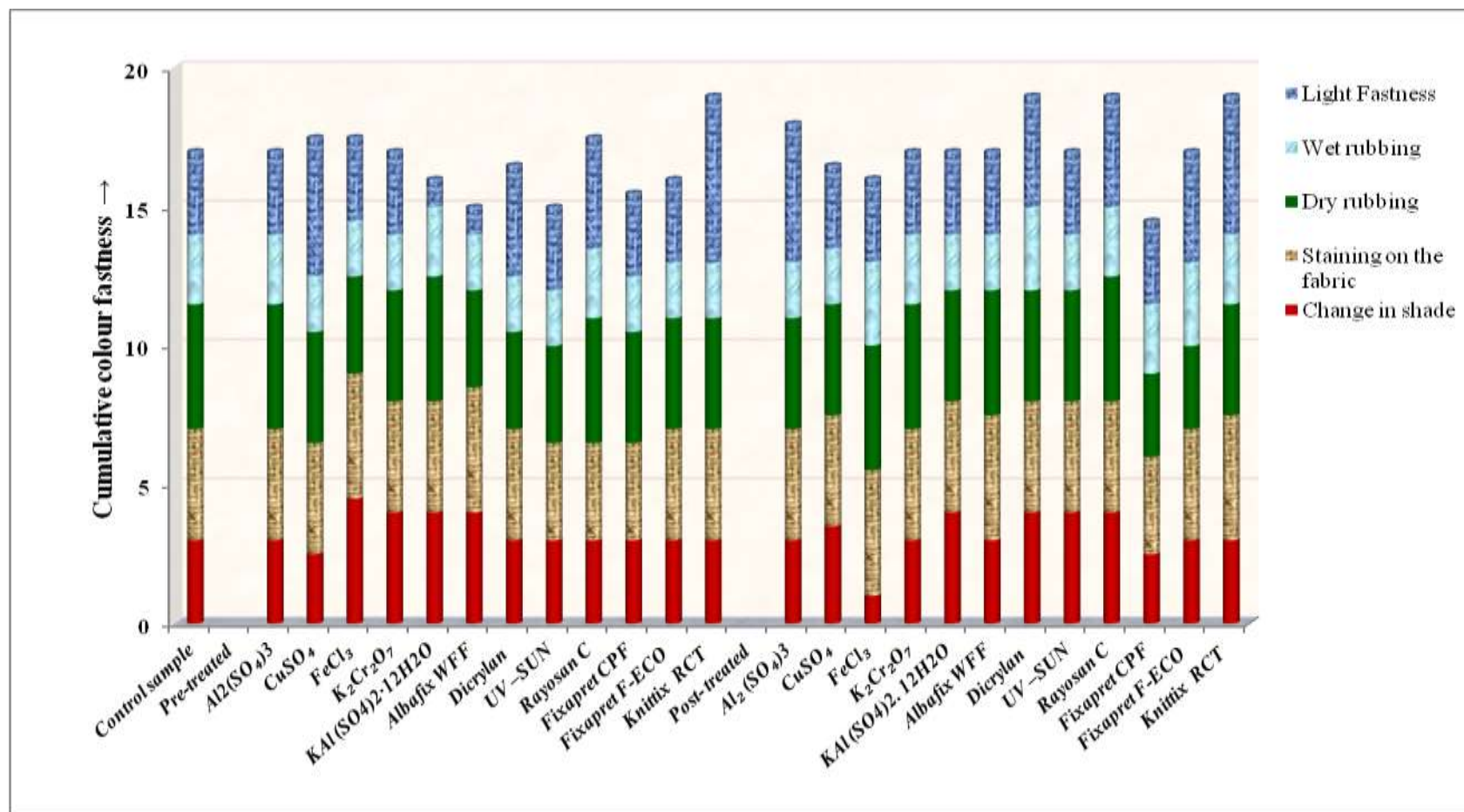


Figure 3.30: Comparative analysis of cumulative colour fastness of cotton dyed with various dye formulations of *Rubia cordifolia*.

Similarly, pre-mordanting with potassium dichromate produced dark maroonish-red shade, whereas, light maroonish-red sample was obtained from post-mordanting of aluminium sulphate. Moreover, post-mordanting of alum produced completely different sample which was reddish orange, even shade having soft handle and pleasant appearance.

3. 5.2 Wash fastness of Turkey red dyed cotton

Table 3.32 carries the results obtained from testing of Turkey red dyed cotton with the use of various pre and post-treated mordants. Change in shade due to wash test of control (untreated) specimen was 3 on Grey- scale representing fair wash fastness. The minimum change in shade of only 4-5 GS was exhibited by Turkey red dyed sample which was pre-mordanted with ferric chloride. This outstanding wash fastness was followed by 4 GS fastness from the samples coloured with dye formulations of pre-mordanting potassium dichromate and both pre and post-mordanting of alum. Mordanting with aluminium sulphate (both pre and post) could not enhance the wash fastness of Turkey red dyed cotton and its rating was identical with the rating of control sample only (i.e. 3 GS).

Among the auxiliaries group of finishes and UV absorbers applied with Turkey red dye, change in shade of 4 GS rating was assigned to sample cationized with Albafix WFF prior to dye padding, post-treating with UV-SUN and both pre and post-treatment with Rayosan C (Table 3.41). Change in shade scoring of the remaining samples dyed with this group of auxiliaries was similar to the grading of control sample. Crosslinkers employed with Turkey red dye also yielded dyed cotton samples identical with control sample in the change in shade rating due to wash test. The post-treatment of CPF showed slightly inferior fastness to washing (2-3 GS) when applied on Turkey red dyed cotton sample.

Assessment of staining on the adjacent white cloth due to wash test was also part of the wash fastness test. Very little staining (4-5 GS) was displayed by dyed samples which were both pre and post-mordanted with ferric chloride. The dyed samples of cotton both pre or post-mordanted with $\text{Al}_2(\text{SO}_4)_3$, CuSO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ and $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ presented

good fastness by showing staining of 4 GS on adjacent white cloth. Staining of the same ranking was also exhibited by untreated sample prepared as reference for Turkey red dyed samples.

Staining of 4-5 GS was also available from cotton samples dyed with Turkey red and finished by Albafix WFF (both pre and post-cationizing). This was an outstanding performance regarding wash fastness. The pre and post finishing of Dicrylan disposed staining of 4 GS. Similarly, the post-treatment of UV-SUN and Rayosan C also yielded 4 GS of staining, presenting good wash fastness. Samples dyed with combination of these two auxiliaries made staining of 3-4 GS on the adjacent white fabric. The same result of 3-4 GS staining was also recorded from the treatment of crosslinker Fixapret CPF employed both as pre and post- padding on Turkey red dyed cotton samples (Table 3.42). Minimum staining equal to 4-5 GS was exhibited by the Turkey red dyed sample, post-treated with crosslinker Knittex RCT. Remaining cotton samples dyed with combination of natural extracts of Turkey red and crosslinkers presented staining on the adjacent white cloth equivalent to 4 GS which is considered to be good performance.

3.5.3 Crocking or rubbing fastness of Turkey red dyed cotton

Crocking or rub fastness has been studied both as dry rubbing and wet rubbing. The relevant findings are tabulated and plotted. Dry rub fastness of control sample, cotton pre-treated with $\text{Al}_2(\text{SO}_4)_3$ and alum and samples post-treated with ferric chloride and potassium dichromate was rated as 4-5 GS, representing very good dry rubbing. A dry rubbing fastness of 4 on Grey-Scale was attained by pre-mordanted CuSO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$ and post-mordanted $\text{Al}_2(\text{SO}_4)_3$, CuSO_4 and $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ cotton samples padded with natural extracts of Turkey red. Lowest dry rubbing fastness among the mordanted samples was 3-4 GS, detected in the cotton pre-mordanted with ferric chloride. Among the UV absorbers group, 4-5 GS, dry rubbing fastness similar to control sample was presented by sample post-cationized with Albafix WFF, and pre and post-treated with Rayosan C. A dry rubbing fastness of 4GS was displayed by samples dyed with the aid of post finishing of Dicrylan and UV-SUN. Remaining samples of this group yielded 3-4 GS dry rub fastness available with the treatment of pre-cationizing Albafix WFF, pre finishing of Dicrylan and UV-SUN. Wet rubbing of all the samples treated with

crosslinkers was inferior to the fastness of control sample (4-5 GS dry rub fastness was given by cotton pre-treated with CPF, ECO and both pre and post-treated with Knittex RCT. Post-treatment of crosslinkers CPF and ECO could provide 3 GS dry rub fastness to the Turkey red dyed cotton samples.

Regarding wet rubbing of cotton dyed with Turkey red and treated with mordants, it is obvious from the data in Table 3.32 that maximum wet fastness of 2-3 GS was available from control sample, pre-mordanted sample of $\text{Al}_2(\text{SO}_4)_3$ and $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ as well as post-mordanted sample of $\text{K}_2\text{Cr}_2\text{O}_7$. All other Turkey red dyed samples produced only 2 GS wet rubbing fastness from the mordanting process irrespective of pre or post- padding of the mordant. In the finishes and UV absorbers group, sample post-padded with Dicrylan had wet rubbing of 3 GS which is considered to be a fair fastness. The performance of Rayosan C was identical to the scoring of untreated sample, i.e. 2-3 on Grey scale. All other auxiliaries managed to fetch only 2 GS wet fastness for the Turkey red dyed cotton samples. In crosslinkers group, only the pre-treatment of Knittex RCT obtained 3 GS rating of wet rubbing. This was followed by 2-3 GS scoring from samples treated with pre Fixapret CPF and Fixapret F-ECO. Other treatments of crosslinkers whether pre-padded or post-treated got only 2 GS wet rubbing fastness on Turkey red dyed cotton.

3.5.4 Light fastness of cotton dyed with Turkey red dye

Mordanting of cotton dyed Turkey red was able to take the light fastness to 5 Blue Wool Standard available from the pre-treatment of CuSO_4 and post-mordanting of $\text{Al}_2(\text{SO}_4)_3$ as compared to 3 standard light fastness of the control sample. This was a good light fastness. However, the fastness rating from all other auxiliary treated cotton was just equal to the control sample. Finishes and UV absorbers also enhanced the light fastness standard of Turkey red dyed cotton samples from 3 to 4 Blue Wool Standard. A light fastness standard equal to 4 was available from the treatment of pre and post finishing of Dicrylan, post- padding of UV-SUN and both pre and post-treatment of Rayosan C. The performance of Albafix WFF treated sample was similar to that of control sample in case of light fastness. Among the group of crosslinkers, post-treatment of Knittex RCT exhibited light fastness of 6 Blue Wool Standard whereas; its pre-treated sample was

rated as standard no. 4 which is also satisfactory performance. All other treatments of crosslinkers on cotton were able to show light fastness of only standard 3 which is a moderate/non satisfactory light fastness rating of fabrics.

3.5.5 Cumulative fastness of Turkey red dyed samples: t-test

Cumulative colour fastness (lightfastness and wash, crock) of cotton samples dyed with Turkey red dye with the help of various dyeing auxiliaries has been displayed in Figure 3.30. For the purpose of comparing the cumulative colour fastness (wash, crock and lightfastness) of Turkey red dyed cotton samples the data was analysed statistically by applying paired samples 2- tailed t-test. Having computation of the results of pre-treatments (mean = 16.63, standard deviation = 1.19); post-treatments (mean = 17.25, standard deviation = 1.13); $t = -1.65$ and $P = 0.127$, the data suggests a non- significant difference in the rating of cumulative colour fastness of cotton from pre and post-treatments of dyeing auxiliaries employed with natural dye from Turkey red. Significance testing of the cumulative colour fastness of Turkey red dyed cotton fabric samples was carried out by applying t-test on control sample and pre-treated samples as well between control and post-treated samples (Table 5.5). The outcome showed insignificant difference between the fastness of control and pre-treated samples as well as between the control and post-treated fabric samples.

3.5.6 Colour coordinate values of Turkey red dyed Cotton

The results related to the colour coordinates of Turkey red dyed cotton samples are displayed through Tables 3.47 & 3.48. The lightness (L^*) values ranged from 27.0 (pre-mordanting Ferric chloride.) to 52.0 (post-mordanting alum). The values of coordinate a^* (which represent tone) was positive denoting red-purple tone. However, some of the samples gave negative values related to the coordinate b^* meaning that the tone was on blue side. Among them the extreme negative was owing to the pre-treatment of Knittex followed by -11 from Fixapret CPF, Albafix, Fixapret F ECO, Dicrylan and UV-SUN. In the positive region of b^* , post-treatment of Albafix was on the top. The C^* or purity of shade ranged from 12.44 because of pre-mordanting of ferric chloride to 41.0 on account of post-mordanting of alum. Lowest hue was noticed from samples which were pre-padded with copper sulphate (4.54) and potassium dichromate (7.18). However,

the post- padding of copper sulphate resulted in maximum h^o value, followed by pre-mordanting with ferric chloride. Relative colour strength ranged between 1.70 (from pre-mordanting with alum) to 9.46 observed from the sample which was pre-mordanted with ferric chloride.

3.5.7 Tensile strength of cotton dyed with Turkey red dye

Tensile strength of Turkey red dyed samples is displayed in Figure 3.29. About 28 percent of the tensile strength of Turkey red dyed cotton was lost due to the pre-treatments of potassium dichromate. Likewise, 25 percent strength on account of pre-treatment of ferric chloride and about 8.0 percent because of copper sulphate was also caused. Some of the dyeing aides managed to enhance the tensile strength of the fabric. The highest value of about 16 percent gain was available from post-treatment of $K_2Cr_2O_7$ and 11.5 percent of post-treated UV-SUN. Paired Samples Statistics from t- test shows significant result between the strength of pre-treated and post-treated samples at 5% level of significance. Significance testing of the tensile strength of Turkey red dyed cotton fabric samples was carried out by applying t-test on control sample and pre-treated samples as well between control and post-treated samples (Table 5.6). The outcome showed insignificant difference between the strength of control and pre-treated samples as well as between the control and post-treated fabric samples.

3.6 PERFORMANCE EVALUATION OF DYEING AUXILIARIES

Apart from the shade or colour, dyeing auxiliaries had their own distinct part to play in the colour fastness and mechanical properties of cotton fabric. Data obtained from testing wash (staining on the adjacent white fabric, change in shade), light and rubbing (both dry and wet) fastness was cumulated and rearranged to study the role of every dye formulation in the application of natural dyes on cotton fabric.

3.6.1 Effect on cumulative colour fastness

The record related to the use of various mordants with natural dyes is presented by Figures 3.31-3.42. Aluminium sulphate improved the cumulative colour fastness of alkanet and marigold flower to a great extent. It also managed to enhance the fastness properties of cutch and Turkey red dyed cotton samples.

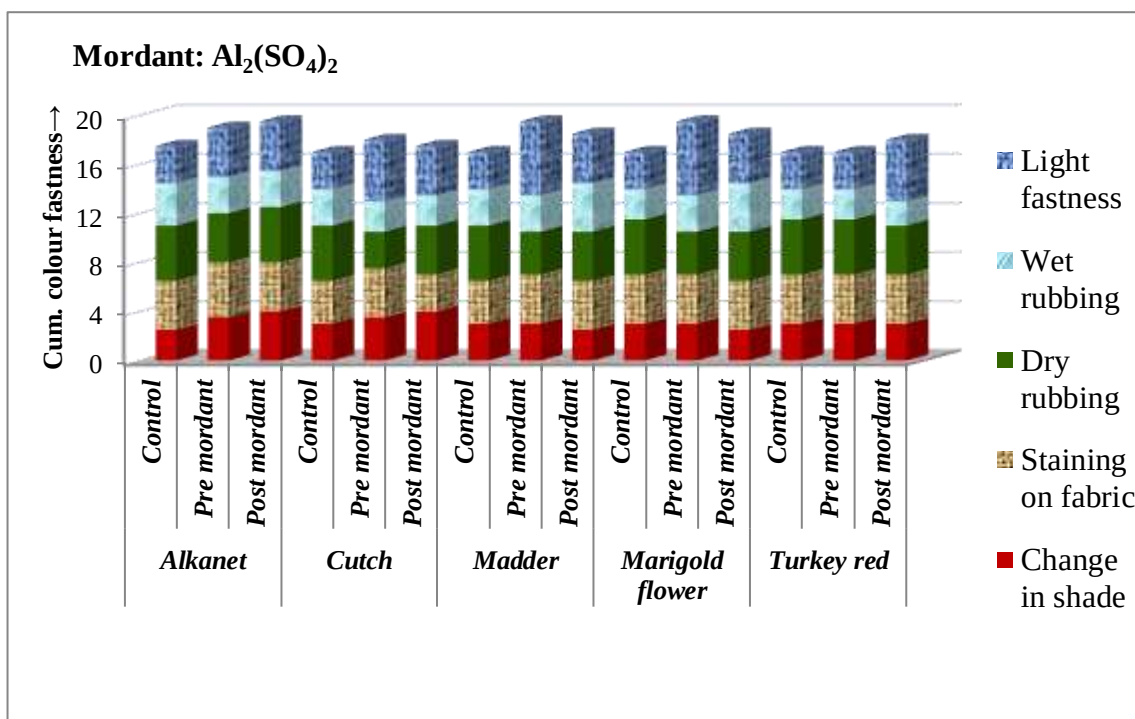


Figure 3.31: Effect of $\text{Al}_2(\text{SO}_4)_3$ on the cumulative colour fastness of cotton samples dyed with various natural dyes.

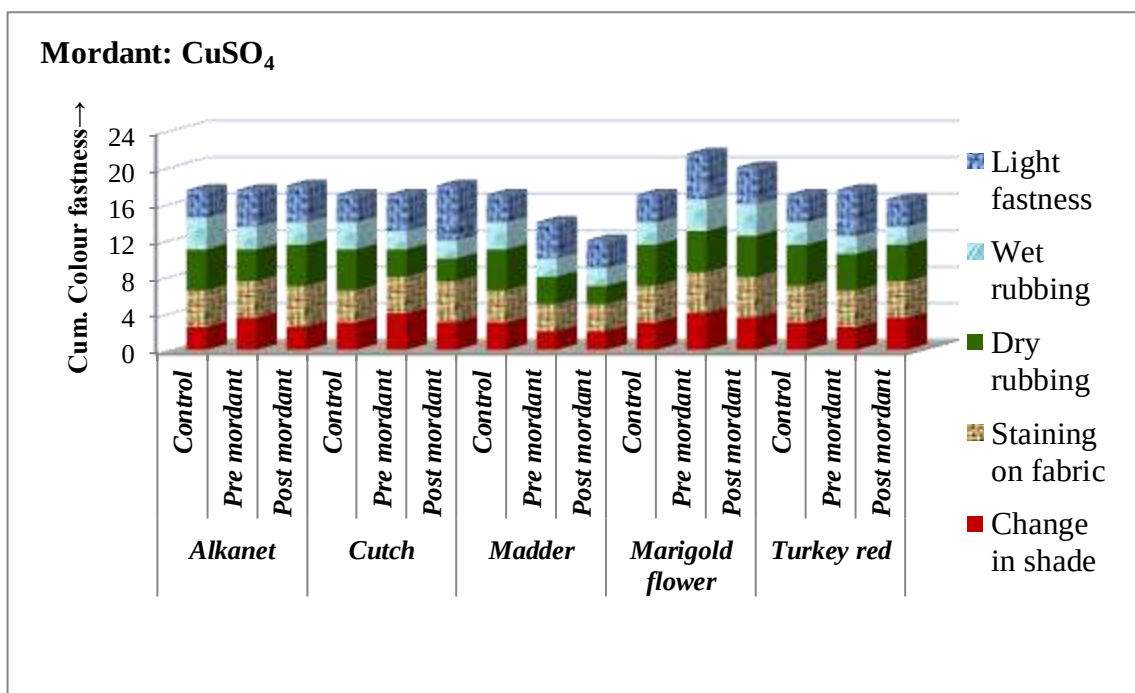


Figure 3.32: Effect of CuSO_4 on the cumulative colour fastness of cotton samples dyed with various natural dyes.

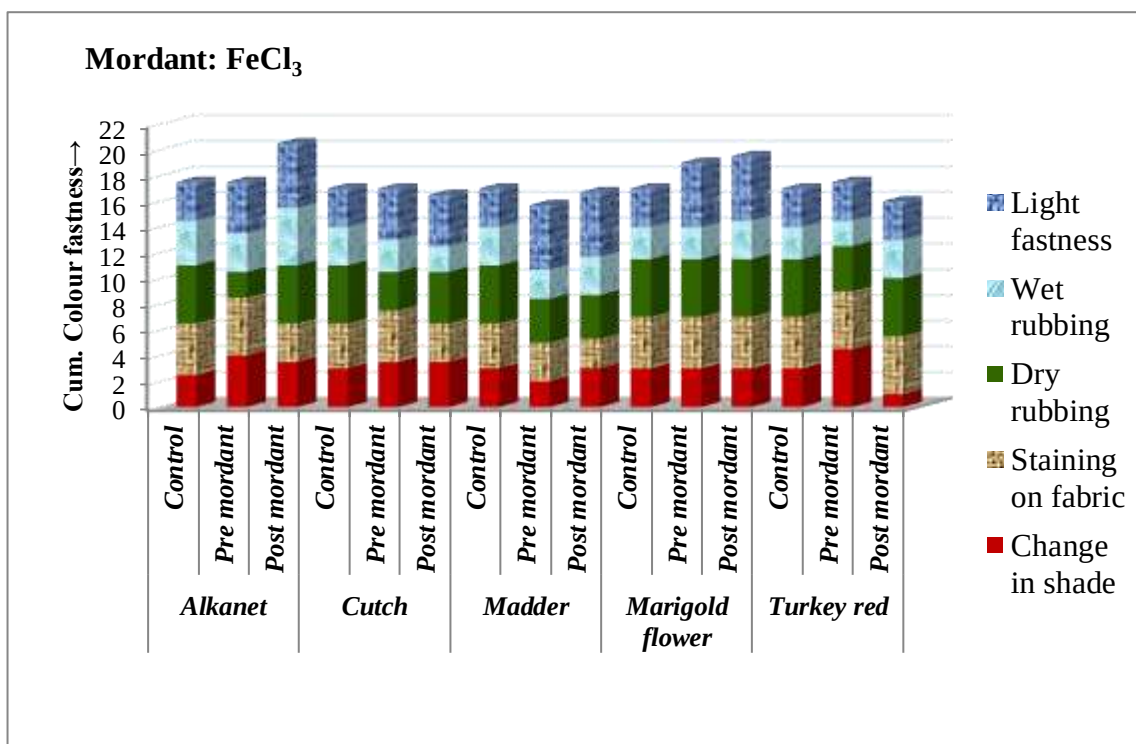


Figure 3.33: Effect of FeCl_3 on the cumulative colour fastness of cotton samples dyed with various natural dyes.

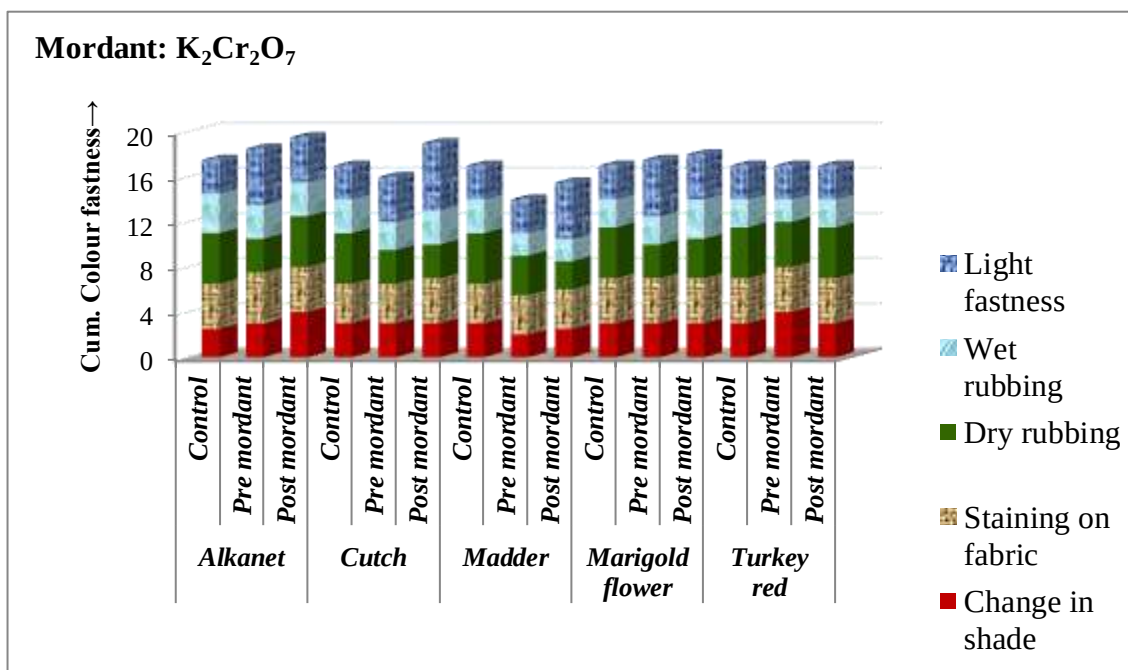


Figure 3.34: Effect of $\text{K}_2\text{Cr}_2\text{O}_7$ on the cumulative colour fastness of cotton samples dyed with various natural dyes.

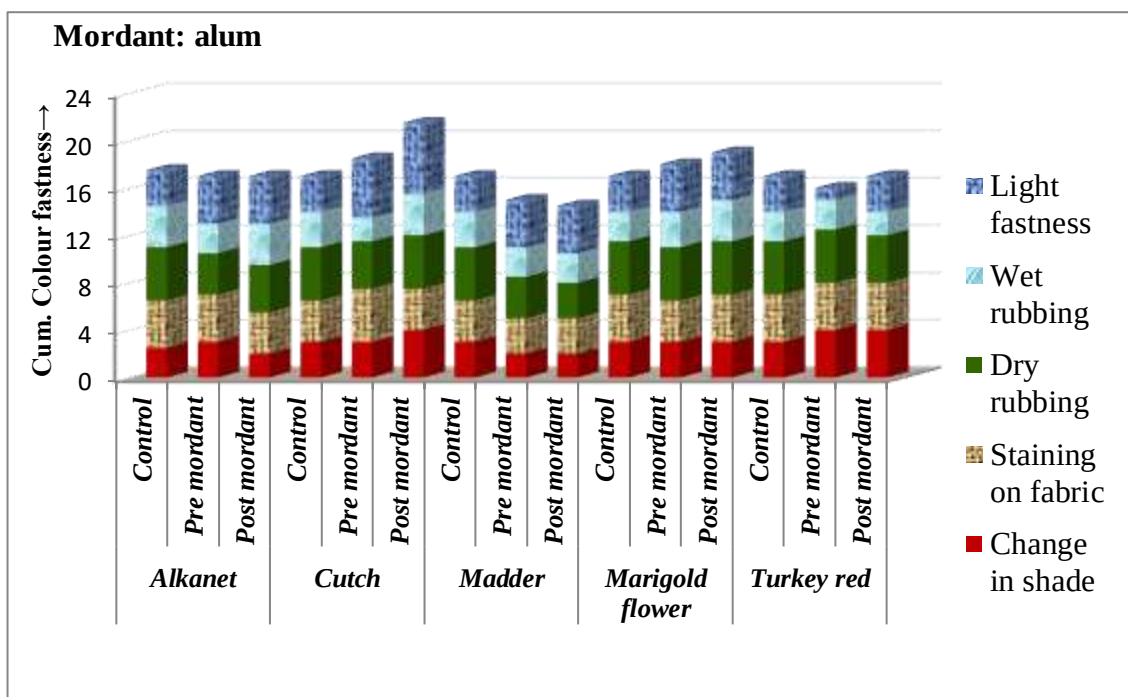


Figure 3.35: Effect of $KAl(SO_4)_2 \cdot 12H_2O$ (alum) on the cumulative colour fastness of cotton samples dyed with various natural dyes.

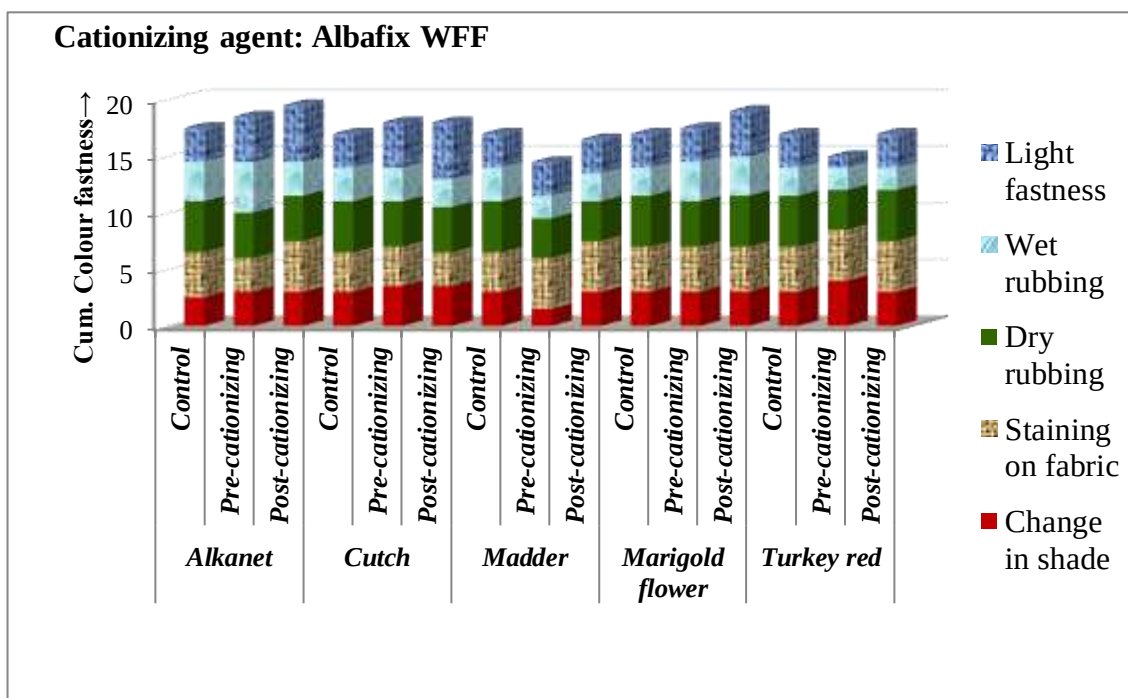


Figure 3.36: Effect of Albafix WFF on the cumulative colour fastness of cotton samples dyed with various natural dyes.

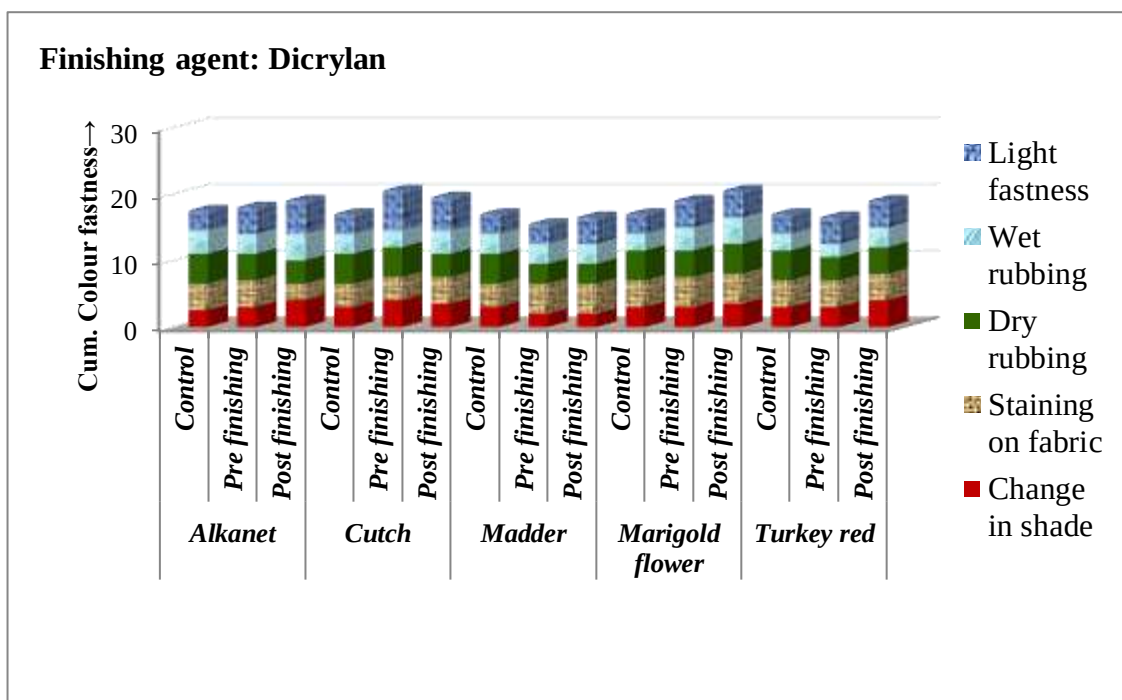


Figure 3.37: Effect of Dicrylan on the cumulative colour fastness of cotton samples dyed with various natural dyes.

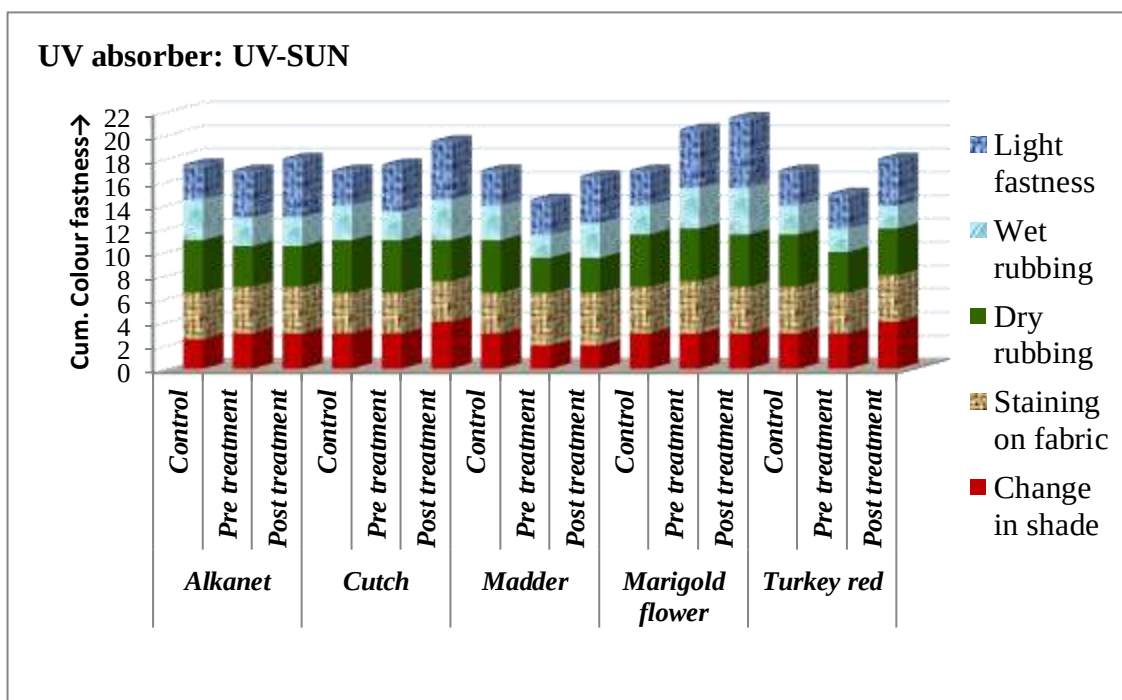


Figure 3.38: Effect of UV-SUN on the cumulative colour fastness of cotton samples dyed with various natural dyes.

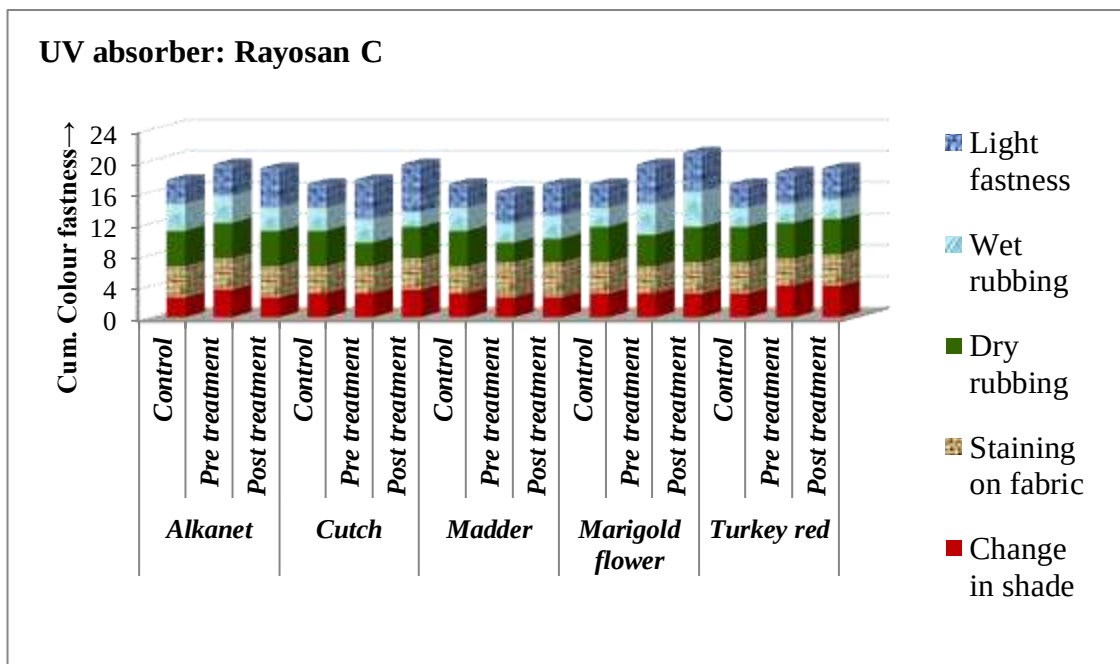


Figure 3.39: Effect of Rayosan C on the cumulative colour fastness of cotton samples dyed with various natural dyes.

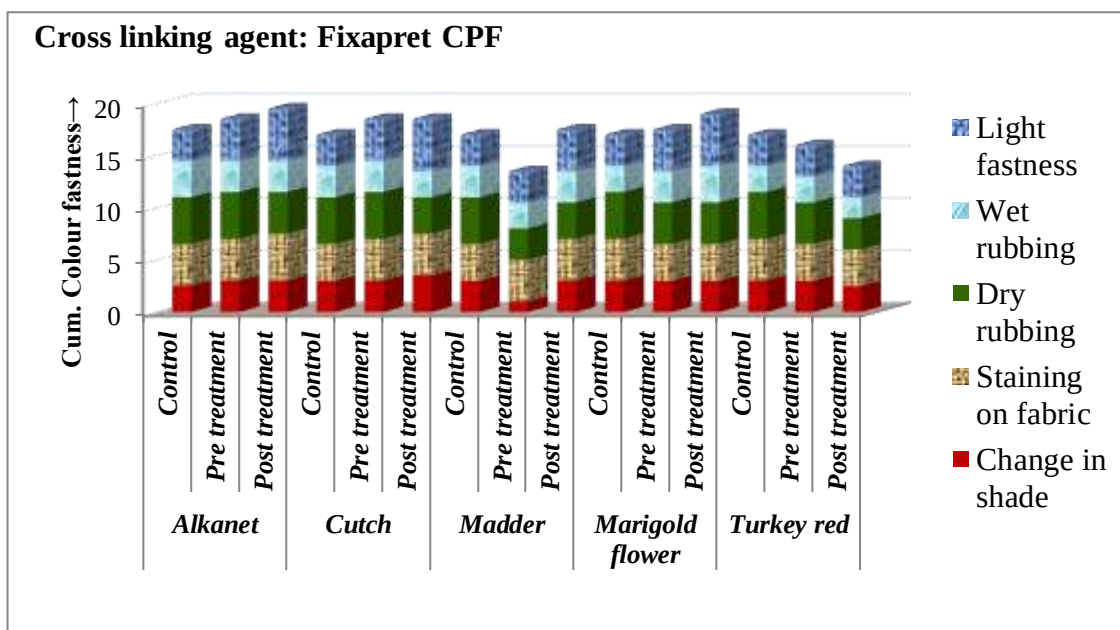


Figure 3.40: Effect of Fixapret CPF on the cumulative colour fastness of cotton samples dyed with various natural dyes.

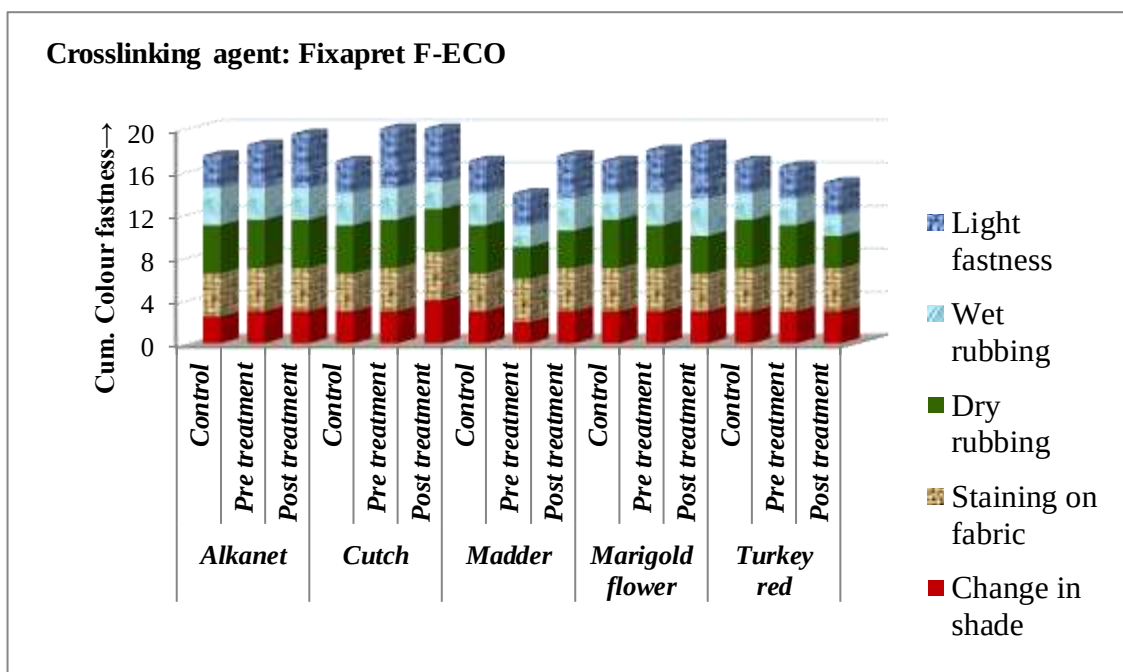


Figure 3.41: Effect of Fixapret F-ECO on the cumulative colour fastness of cotton samples dyed with various natural dyes.

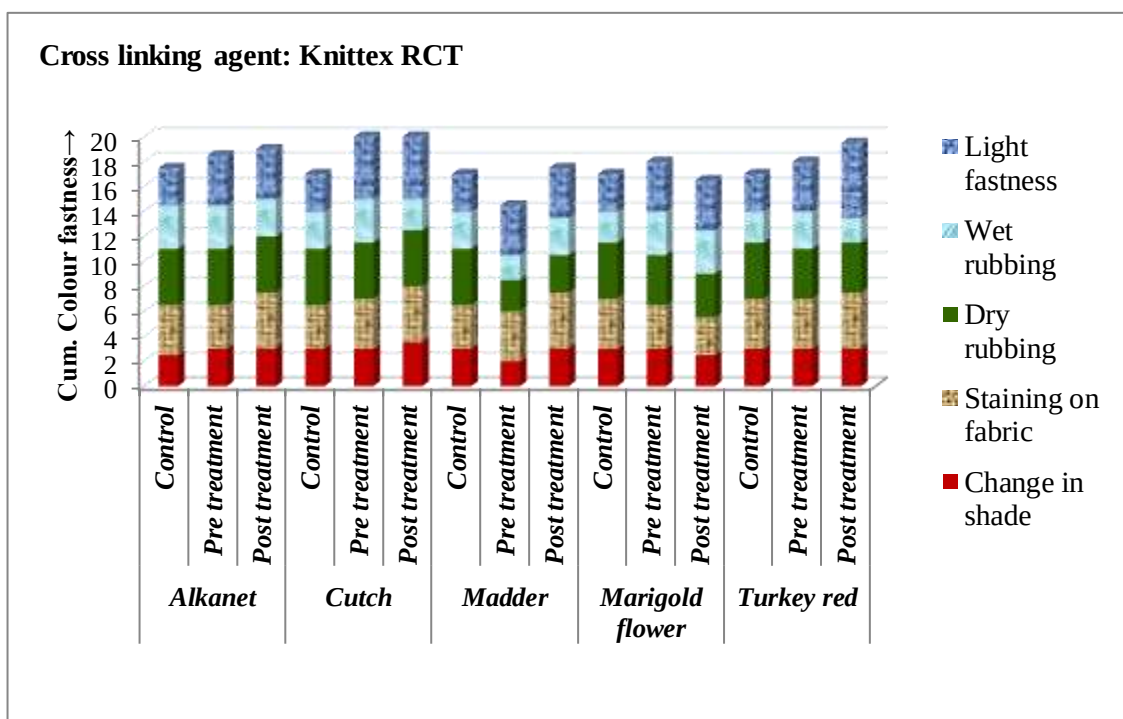


Figure 3.42: Effect of Knittex RCT on the cumulative colour fastness of cotton samples dyed with various natural dyes.

However, it could not play any appreciable role in the colour fastness of madder dyed cotton. Copper sulphate did a better job to assist marigold flower for increasing the colour fastness of cotton fabric. Considerable improvement was also brought about in the samples dyed with alkanet, cutch and Turkey red. FeCl_3 was successful only with the combination of dye formulation of marigold and alkanet. However, $\text{K}_2\text{Cr}_2\text{O}_7$ perked up when employed with all natural dyes except madder. The combination of alum and natural dyes in respect of colour fastness was suitable particularly with cutch (Figure 3.34).

Cationization of cotton proved more useful in revitalizing natural colorants particularly, dyeing with alkanet followed by both cutch and marigold in terms of increased fastness properties. Dicrylan enhanced the colour fastness of cotton when it was used with cutch and marigold. Similarly, both the UV absorbers, UV-SUN and Rayosan proved valuable when used with marigold in improving the colour fastness of cotton samples. Likewise, crosslinkers also made their way to boost up the fastness properties of natural dyes on cotton. In this regard, Fixapret CPF was responsible for increasing the colour fastness of alkanet dyed cotton and with a little difference, produced similar result with cutch dye on cotton. Another crosslinker, Fixapret F-ECO also played its role in enhancing the fastness properties of the same two natural dyes on cotton, but this time the colour fastness of cutch dyed samples was a little higher than the alkanet dyed cotton. Knittex (DHEU) showed the same performance and enhanced the fastness properties of cotton when applied with cutch root extracts.

3.6.2. Role of auxiliaries in tensile strength

Mordants have greatly influenced the tensile strength of the dyed samples. Aluminium sulphate seemed to enhance the strength of madder dyed cotton to a greater extent. Copper sulphate proved harmless for the application of cutch dye on cotton but it greatly decreased the tensile strength of madder and alkanet dyed samples. On the other hand, the tensile strength of Turkey red dyed cotton samples was maintained with the post-mordanting of ferric chloride. The same mordant emerged as the most damaging auxiliary when it was employed as pre-mordant with madder. The post-mordanting

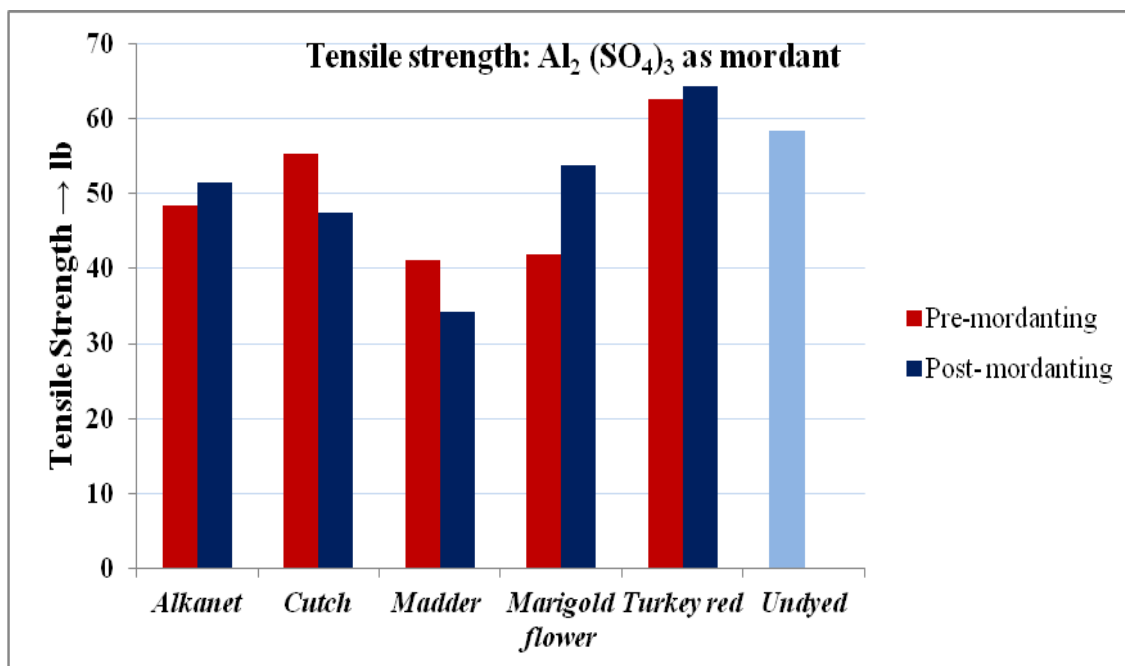


Figure 3.43: Effect of $\text{Al}_2(\text{SO}_4)_3$ on the tensile strength of cotton samples dyed with various natural dyes.

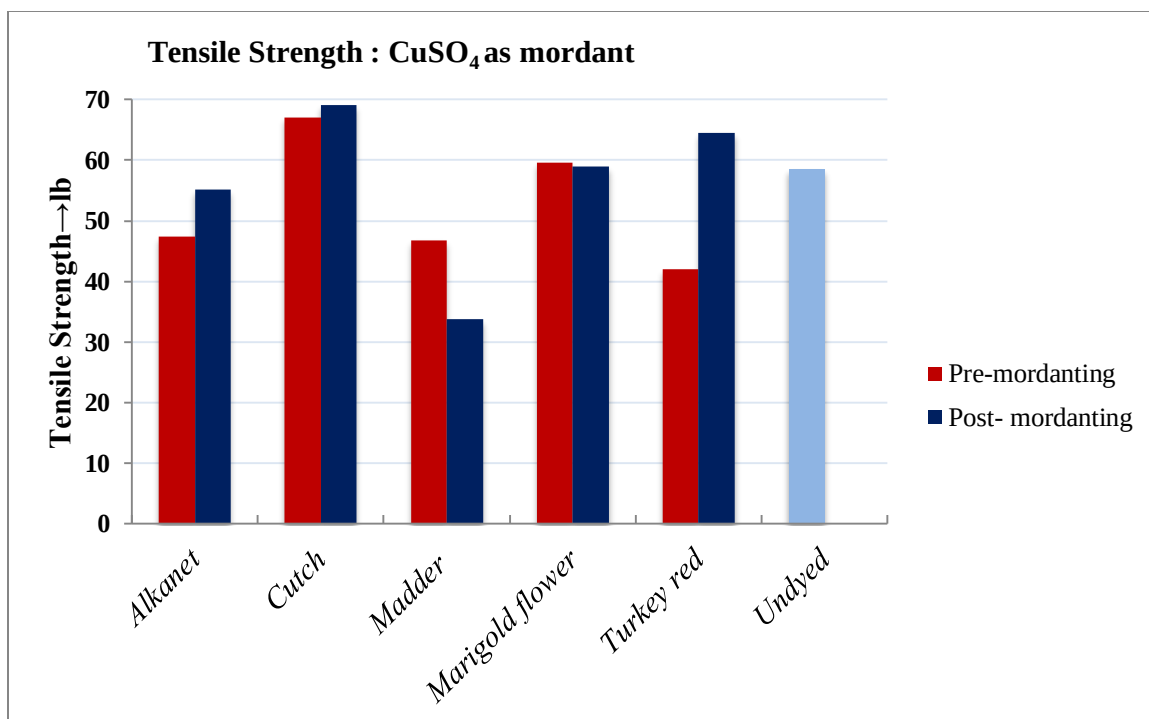


Figure 3.45: Effect of CuSO₄ on the tensile strength of cotton samples dyed with various natural dyes.

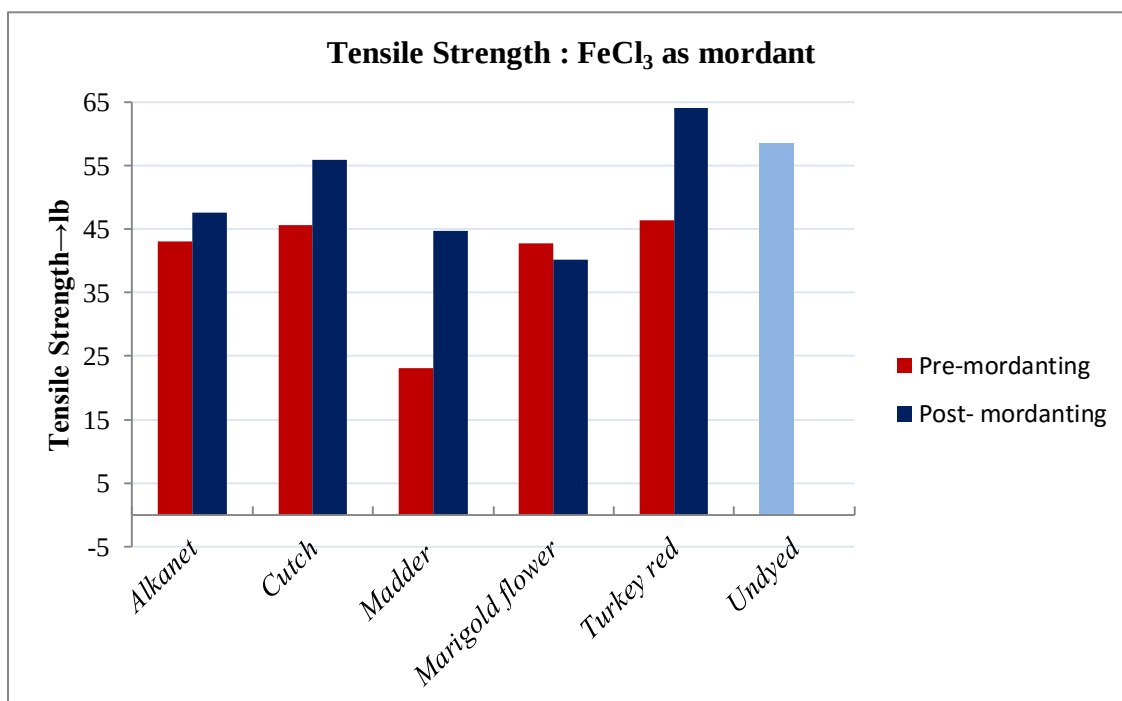


Figure 3.45: Effect of FeCl₃ on the tensile strength of cotton samples dyed with various natural dyes.

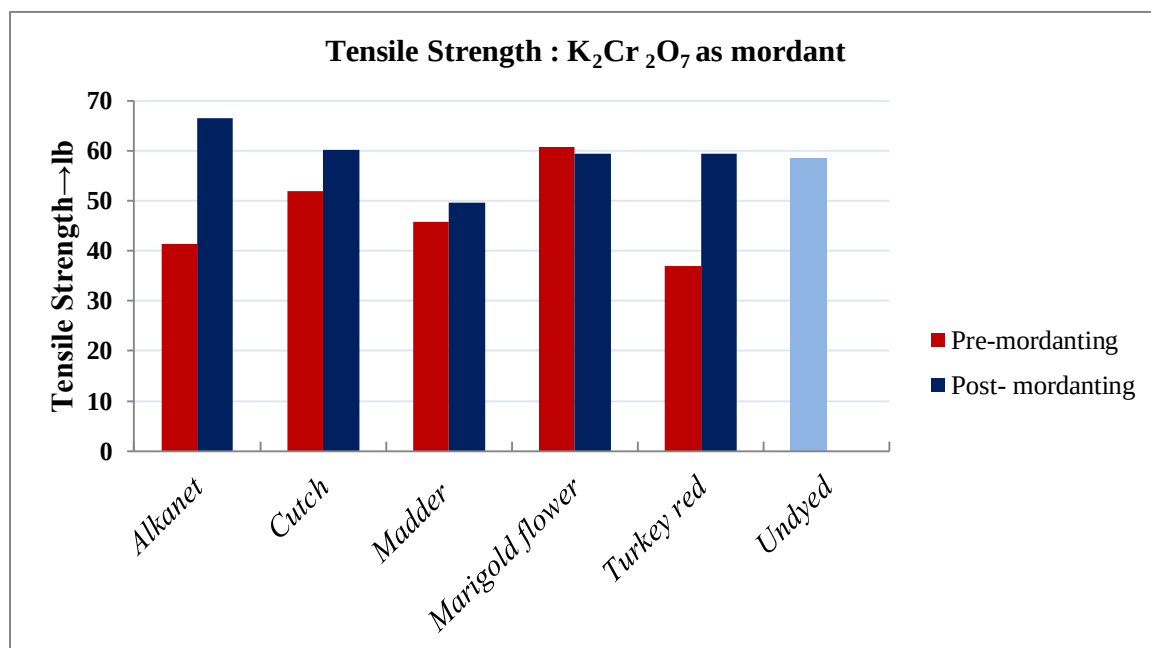


Figure 3.46: Effect of $K_2Cr_2O_7$ on the tensile strength of cotton samples dyed with various natural dyes.

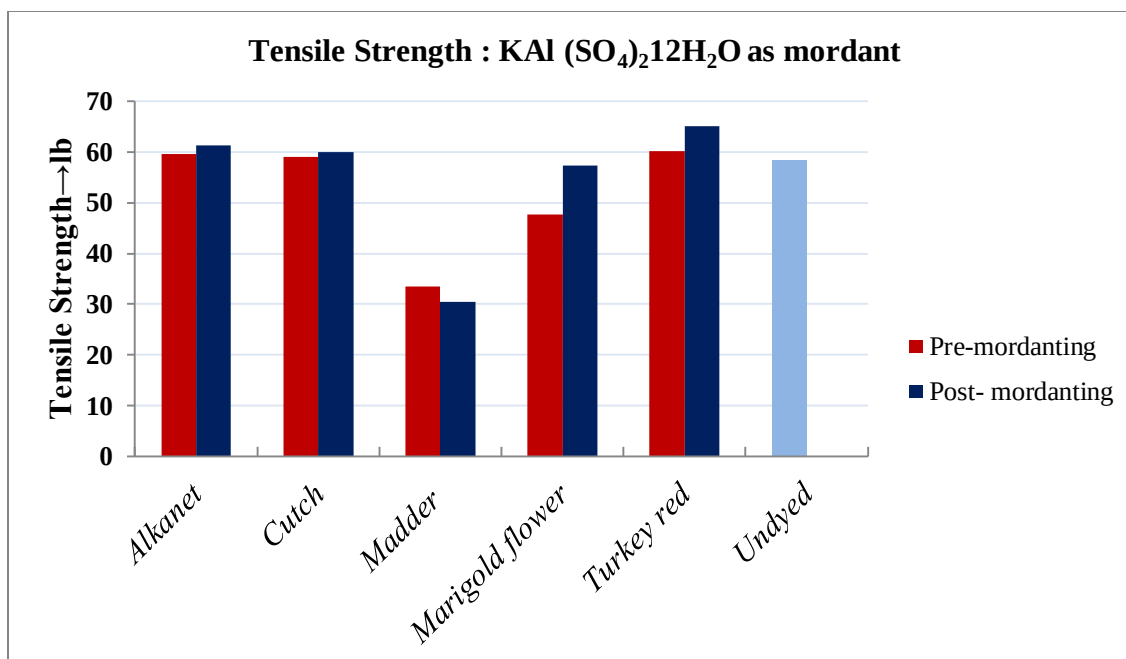


Figure 3.47: Effect of KAl (SO₄)₂.12H₂O on the tensile strength of cotton samples dyed with various natural dyes.

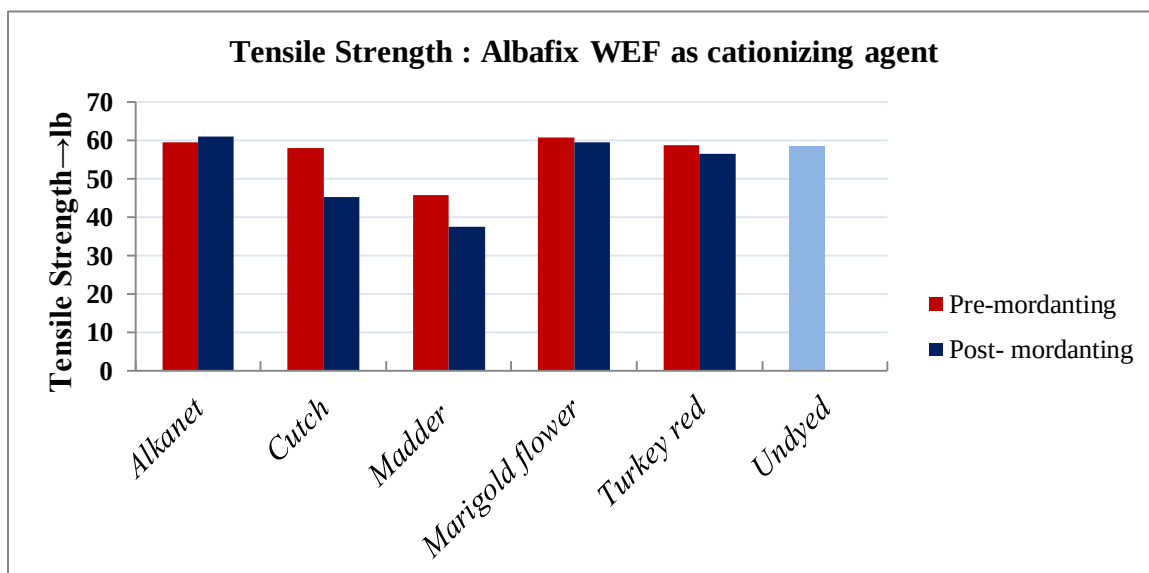


Figure 3.48: Effect of Albafix WEF on the tensile strength of cotton samples dyed with various natural dyes.

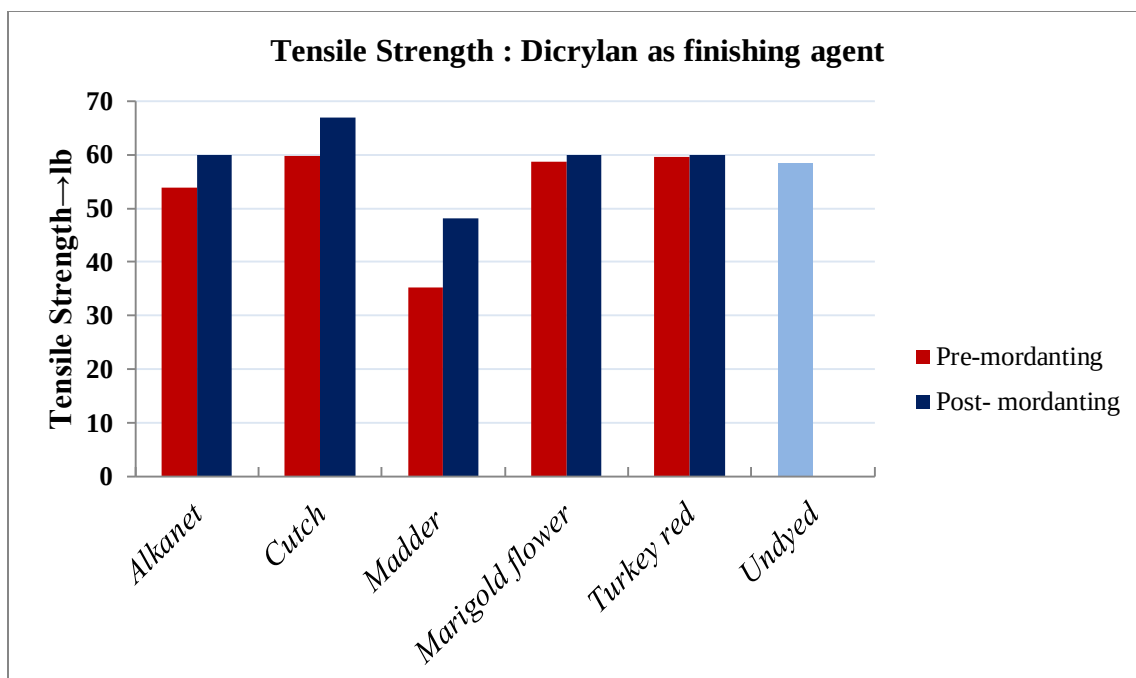


Figure 3.49: Effect of Dicrylan on the tensile strength of cotton samples dyed with various natural dyes.

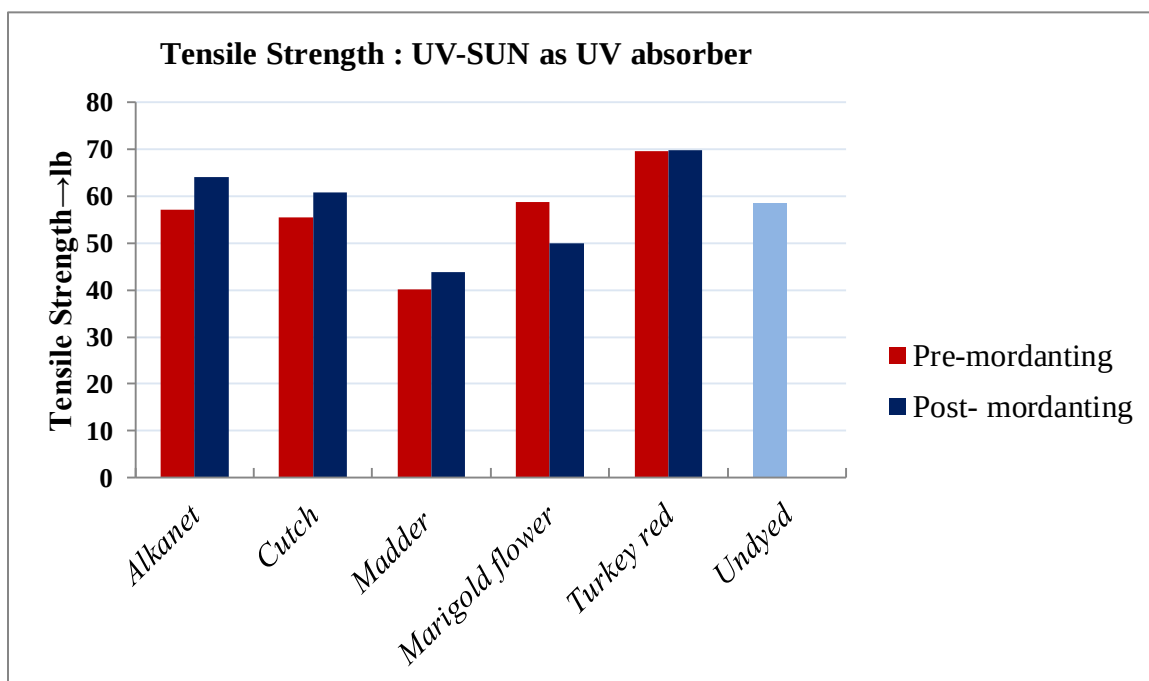


Figure 3.50: Effect of UV-SUN on the tensile strength of cotton samples dyed with various natural dyes.

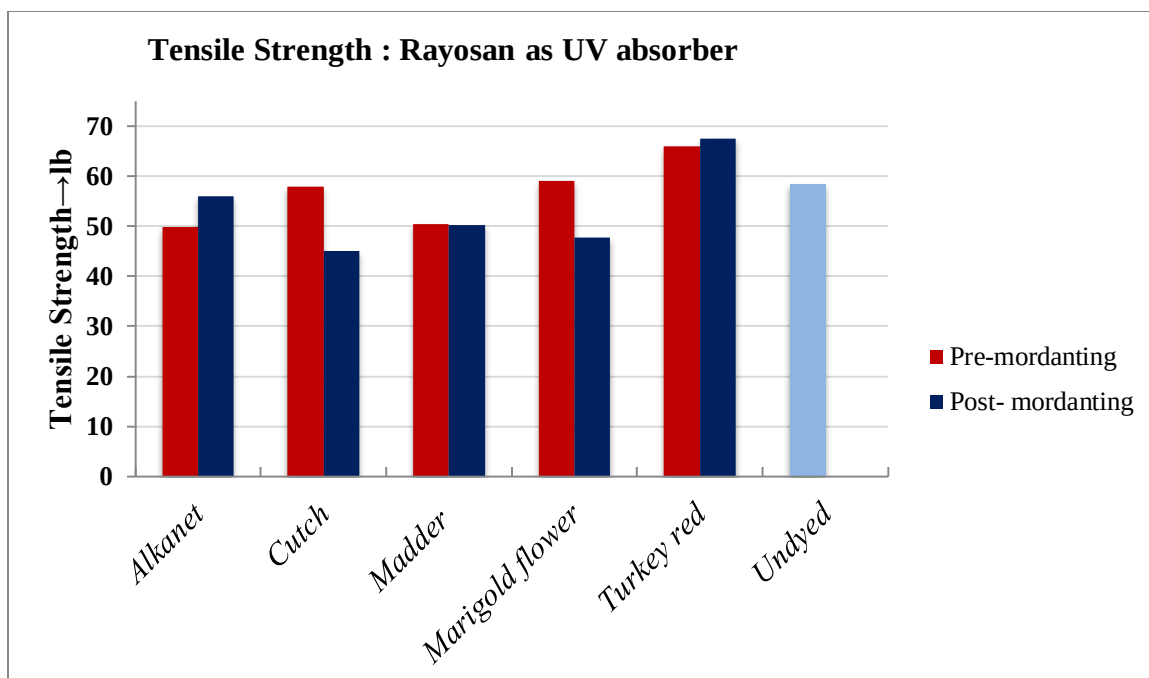


Figure 3.51: Effect of Rayosan C on the tensile strength of cotton samples dyed with various natural dyes.

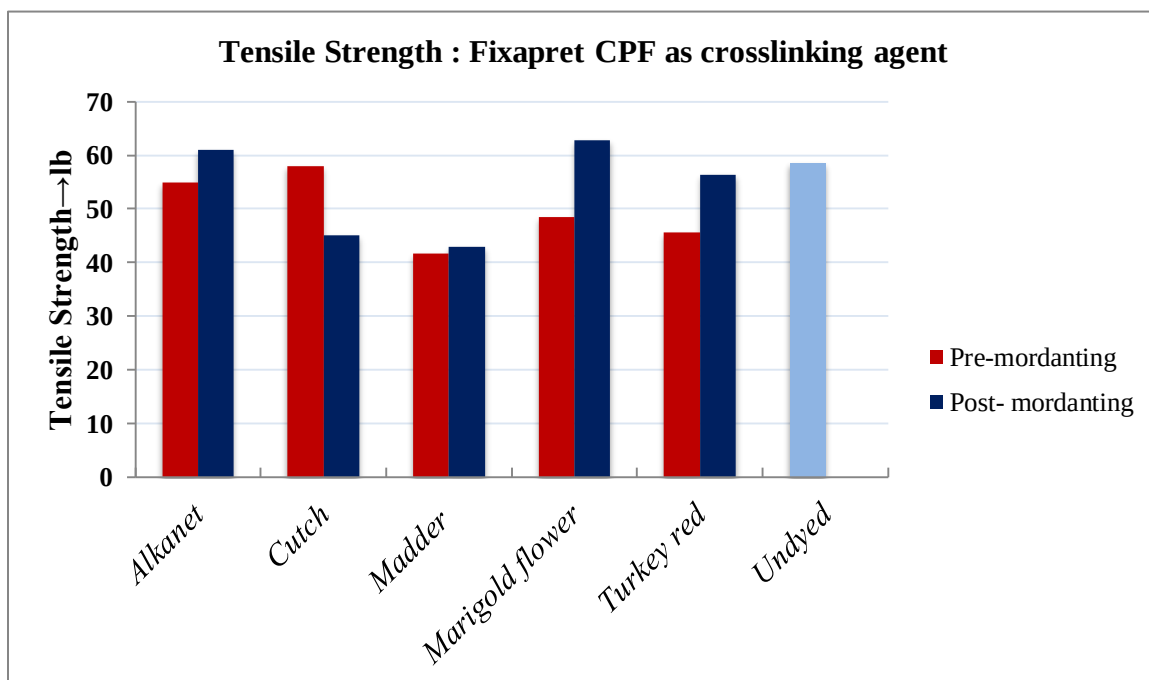


Figure 3.52: Effect of Fixapret CPF on the tensile strength of cotton samples dyed with various natural dyes.

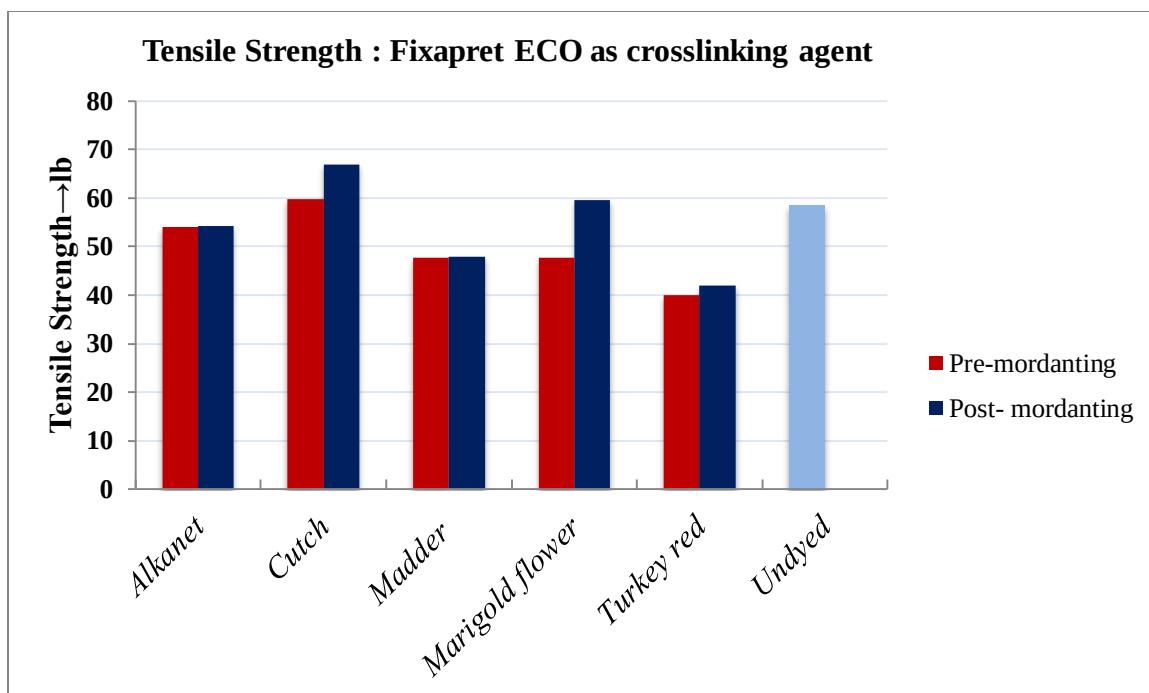


Figure 3.53: Effect of Fixapret F-ECO on the tensile strength of cotton samples dyed with various natural dyes.

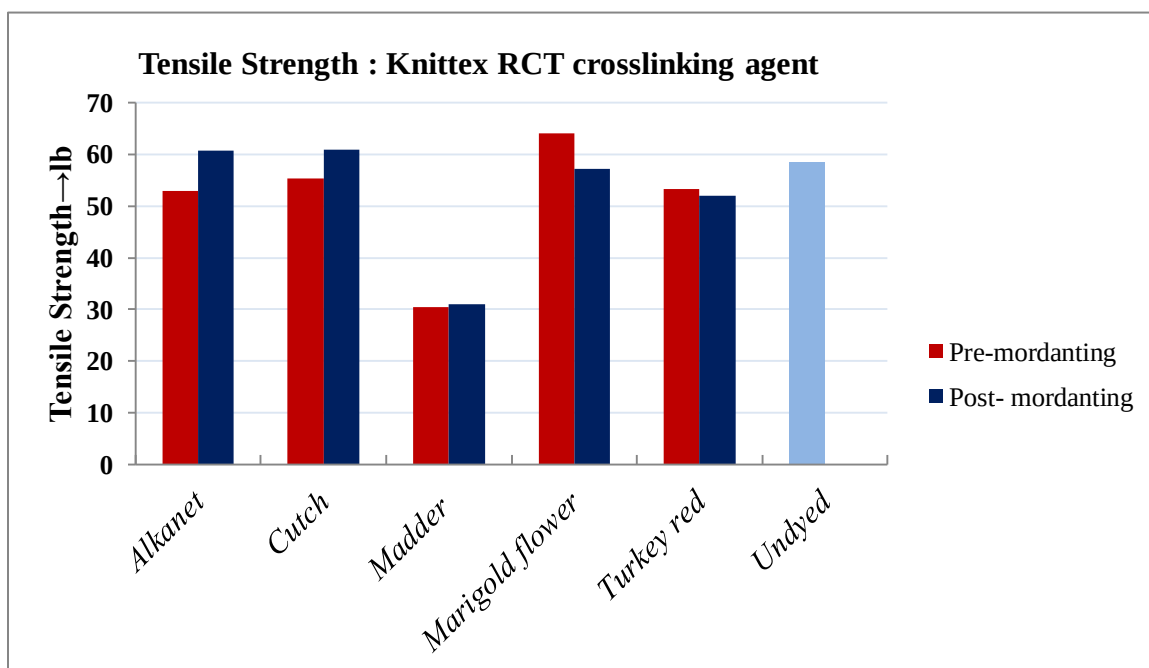


Figure 3.54: Effect of Knittex RCT on the tensile strength of cotton samples dyed with various natural dyes.

treatment of potassium dichromate appeared to be the safest dye formulation particularly in case of alkanet dyed cotton samples. Alum acted as the most damaging mordant when used with madder. Cationization with Albafix increased the strength of dyed samples. The only decrease in tensile strength was accessible from the sample of madder dyed cotton. Finishing with Dicrylan raised the tensile strength of samples dyed with cutch extracts as compared to the strength of undyed samples. Furthermore, the reaction of UV-SUN was identical to Dicrylan. UV absorber Rayosan heightened up the tensile strength of samples coloured with Turkey red, both as pre and post-padding. as far as the role of crosslinkers are concerned, Fixapret CPF and knittex proved better for marigold dye by raising its strength as compared to its original tensile strength and Fixapret ECO played its best role with cutch in raising its tensile strength.

CHAPTER-4

DISCUSSION

Cotton is a very long and linear cellulosic polymer, the repeating unit of which is cellobiose. Its degree of polymerization is about 5000. The most important chemical (functional) groups of the polymer are the hydroxyl groups which are also present as methylol groups ($-\text{CH}_2\text{OH}$). Owing to the many polar $-\text{OH}$ groups in its polymer, the fibre is very absorbent and hygroscopic in nature. Generally, it is considered to be an easy fibre to colour (dye or print). The ease with which cotton takes up the colourants is due to the polarity of its polymer system. There is a great attraction between the fibre polymers and the dye molecules. Therefore, it can be dyed with many classes of dyes such as azoic, direct reactive, sulfur and vat etc. In the present research project, it has been dyed using various plant based natural colorants with the assistance of many dyeing auxiliaries such as different mordants, cationizing agents, finishes, UV absorbers, and crosslinkers.

4.1 DYEING COTTON WITH NATURAL COLOURANTS USING MORDANTS

Since most natural dyes have low colour yields and poor light stability, different mordants play an important role in enhancing wash, light, and crocking as well as colour strength of natural dyes. They are the essential dependant factors responsible for the development of natural colours applied to fabrics. Colour absorption and stability depend both on the natural dye as well as on the mordant. Metal ion can form coordinate bond with dye molecule as it can act as acceptors to the electron donors. Such a bond is water insoluble and therefore, improves the wash fastness of the natural dye.

4.1.1 Role of mordants in the establishment of new shades

The role of mordants in creating variety of shade/ colours from the same dye was obvious from all the five natural dyes utilized in the current study. The effect of mordants and natural dyes on the shade and colour fastness has been widely reported. One of the advantages of natural dyeing is that the same dye yielding plant species produce variety of colours by means of various mordants. Wanyama et al (2010) reported that while each mordant yielded its individual limited range of colour, the range of colours produced by various mordants was remarkable. In the current study also, Alkanet dyed cotton was available in a variety of shades in green such as greyish green, greenish grey, greenish brown and yellowish green etc. In the same way remarkable range of browns was available from Cutch dye on cotton with the use of metallic mordants. These findings are in line with the earlier work of Ratnapandian et al. (2012). While, working on mordants (CuSO_4 , FeSO_4), they reported that the two mordants showed different results in case of shades obtained on cotton fabric dyed with Acacia plant family. They acquired beige shade from this dye with CuSO_4 , whereas, in present case the resultant shade was reddish brown. This may be due to the amount of dye used because they used 10g/l of the dye, whereas, in the present case the dye used was 30 g/l.

The current findings also support the earlier verdict of Bhattacharya and Shah (2000). They produced many colours of cutch on wool with six different mordants. Moreover, they also mentioned their satisfaction with the fastness properties of this dye

with mordants. By means of several of mordants, cutch dye has proved itself as a beautiful brown colorant for cotton in this study. All the mordants had boosted the colour of the dyed cotton. After wash fastness test, they retained the soft and supple hand. The deep and dark browns presented by cutch on cotton in this study with the use of metal mordants may be due to the fact that some transition metal ions make strong bonds with molecule of this dye. The most dark and deep brown colours were produced by copper and iron mordants. Both these metals are well known for making coordination complexes so in the present study also, they may have been readily chelated with the catechu (Bhattacharya & Shah, 2000). The coordination numbers of these mordants are 4 in copper and 6 in iron. Some of the unoccupied coordination sites may have occupied the $-OH$ or $-CH_2OH$ functional groups of cellulose when they have interacted with cotton fibre. These metals may have been able to form coordination complex on one site with Cutch and on the other site with the cellulose, thereby enhancing the interactions between the Cutch and cotton polymer system.

Like other natural dyes applied on cotton in this study, Madder and Turkey red exhibited wide range of red to violet shades. While discussing the effect of mordant on colour, Gupta et al. (2004 b) have reported that a range of colours from purpurin by the use of various mordants was very wide. They obtained brownish red colour by the use of copper sulphate and deep red with alum and other mordants. The present results support their findings as alum produced red (flame red) colour with the use of madder dye on cotton and the post- padding of copper sulphate as mordant yielded brown red.

Variety of shades were displayed by the applications of Marigold flower extracts on cotton fabric with the utilization of various metal mordants applied as pre and post-padding. Pretty yellow, shades were available from copper sulphate as well as pre-mordanting with alum. All the mordants produced their own distinct shades mostly in the range of yellow. The effect of mordants on the shade of natural dyed cotton and other fibres has been widely reported. Wanyama et al. (2010) have mentioned that alum yields bright and clear yellowish green shades. Hence their report is confirmed by the results obtained from the present study.

4.1.2 Role of mordants in the wash fastness of natural dyed cotton

The application of alkanet through pad-steam method on cotton yielded very good wash fastness of the particularly, with ferric chloride (pre-mordanting) and post-mordanting of aluminium sulphate as well as potassium dichromate. Moreover, the post-mordanting of ferric chloride and pre-mordanting of aluminium sulphate were also able to produce cotton sample with 3-4 GS wash fastness. This is also considered to be good wash fastness. Among the mordants applied with Alkanet dye, the post-mordanting with copper sulphate and alum could not be rated properly on Grey-scale because instead of fading, their originally dyed shade was entirely changed after wash test.

The traditional mordant for natural dyes i.e. alum was unsuccessful in presenting any desirable wash fastness on cotton dyed with Alkanet. In a study on the use of tea as natural dye using mordants (Moiz et al, 2009), best results were achieved with copper salts such as CuSO_4 . In the present case, the result of this mordant on cotton with Alkanet dye was very peculiar. Instead of fading, its shade got entirely changed and became clearer and brighter after washing. However, in the case of cutch dye on cotton with CuSO_4 as mordant, the present results confirm the earlier findings of Moiz et al. (2009).

The wash fastness of cotton resulting from a beautiful brown colour natural dye i.e. cutch was also good particularly with the pre-padding of copper sulphate and post-mordanting of aluminium sulphate and alum. The employment of aluminium sulphate as pre-mordant also produced good wash fastness (3-4 GS). Likewise ferric chloride also exposed good results. All the mordants utilized with cutch for cotton dyeing did their job and their performance was not less than satisfactory. On the other hand dyeing with famous madder could not manage to produce wash fast cotton samples with the help of various mordants. In general, wash fastness of samples coloured with madder was low. Heavy staining on the adjacent white sample was also noticeable. However, the use of ferric chloride as post-padding produced a dyed cotton sample with 3 GS i.e. satisfactory wash fastness. Furthermore, Gupta et al. (2004 b) has also concluded that wash fastness of natural dyes was generally improved by mordants. Yet, in the present case the poor wash fastness exposed by madder dye on cotton remained unchanged even with the use of mordants but the wash fastness of Turkey red dyed cotton was improved with some

dye formulations using mordants. On the whole, its wash fastness produced better performance in comparison to madder dyed cotton.

Dyeing of cotton with Sun- yellow (extracts of marigold flower) exposed good wash fastness where the highest fastness due to washing was registered by pre and post-mordanting of copper sulphate. Staining on the adjacent white cloth from these dye formulations were also negligible (only 4-5 GS). Contrary to that, the performance of post-mordanted aluminium sulphate was even lower than that of the control sample, which was not provided with any treatment for the improvement for wash fastness. Heavy staining on the adjacent white cloth was found from the sample which was dyed with pre-mordanted alum.

Cotton dyed with Turkey red exhibited very good wash fastness with the use of mordants particularly with ferric chloride as pre-mordant. The use of potassium dichromate as pre-padding and alum both as pre and post-padding resulted in 4 GS i.e. good fastness to washing. While pre-mordanting with copper sulphate presented wash fastness lower than the untreated cotton sample. Contrary to the best performance with pre-mordanting of ferric chloride, the post-padding of some mordants entirely changed the original dyed shade of the sample due to washing. The current results revealed non-satisfactory wash fastness of Madder dyed on cotton with the use of various mordants.

Generally red dyes among natural colorants have low wash fastness of the dyed fabrics as most of them have high solubility in water (Kongkachuichay et al., 2002). Their fastness however can be improved by conducting dyeing using metal salts such as potassium dichromate and copper sulphate. In the present research study there was no difference between the wash fastness of mordanted and untreated samples of red dye i. e. madder. These findings also support the postulation of Yusuf et al. (2012) who have investigated that the wash fastness of mordanted and un-mordanted madder samples was nearly the same. Moreover, they have reported good wet and dry rubbing fastness from madder dye, while in the present case only the dry crocking fastness of madder dyed cotton was satisfactory. The poor wash fastness of madder dye might be due to the large number by ionizable groups such as $-OH$ and $-COOH$. Yusuf et al. (2012) explained that

at appreciable pH, these ionizable groups became soluble in aqueous solution due to their conversion to anionic form.

For the application of red natural dyes like madder (*Rubia tinctorum*), Vankar (2000) has recommended alum as mordant. However, in the present research work, a slightly enhanced wash fastness (3 GS) of madder dyed cotton was presented by the post-mordanting of ferric chloride and 2-3 GS by the post-mordanting of aluminium sulphate and potassium dichromate. However, alum was successful in improving the rubbing fastness of the dyed cotton samples. In comparison to the fastness properties of madder, the wash fastness presented by Turkey red on cotton was better. Furthermore, washing of pre-mordanted alum sample exposed new results as the fabric became darker due to washing and could not be compared or rated on Grey-scale with the original dyed sample.

Dye molecules containing large number of auxochromes contribute towards its solubility in aqueous media and hence these dyes leave the textile article very easily during washing. Usually these dye anions are attacked by hydrogen bonds and Van der Waal's forces to the cellulose polymers. As both them are weak forces (bonds), they are easily hydrolyse with water which results into fading of textile due to the removal of these dye molecules.

4.1.3. Effect of mordants on rubbing fastness

In the course of dyeing of cotton with plant-based natural dyes mordants displayed variable results. Cotton dyed with alkanet by various mordants revealed good fastness. All the mordants except alum, performed well in enhancing the rubbing fastness of dyed cotton when post-padded. Pre-mordanting of ferric chloride caused the lowering of dry rubbing fastness, whereas, alum decreased both the wet and dry crocking fastness as compared to the control sample.

Dyeing of cotton with cutch generally displayed good rubbing fastness. However, this achievement was not related to the method or type of mordant as the highest rubbing fastness (4-5 GS) was displayed by the control sample. Only the post-mordanting with alum showed identical performance. All other dye formulations related to the combination of mordanting and cutch dyeing could not bring any further improvement in

the dry rubbing fastness of cotton dyed fabric. Wet rubbing fastness of the cutch dyed cotton samples exposed poor performance. Dry rubbing fastness from madder dyed cotton samples was good particularly with pre and post- mordanting of ferric chloride. The rubbing fastness performance of post- mordanting with potassium dichromate and copper sulphate was lower than the control sample.

Dyeing with Sun- yellow was a pleasant experience. It displayed very good rubbing fastness from the dye formulations having pre and post- mordanting with copper sulphate, ferric chloride and alum. Cotton dyed with Turkey red also presented good results of rubbing fastness, especially post- mordanting with ferric chloride, potassium dichromate and pre- mordanting with alum and aluminium sulphate as well as the control sample. They demonstrated 4-5 GS, which is very good fastness of dry rubbing.

4.1.4 Effect of mordants on light fastness

The type and method of various mordants utilized in this study with the five natural dyes behaved in different manner. Generally, they made improvement in the light fastness of cotton fabrics, dyed with natural dyes. In case alkanet extracts, the pre-mordanting of potassium dichromate and post- mordanting of ferric chloride forwarded the light fastness up to standard 5 which is considered to be good performance. The overall performance of alkanet with the use of mordants was also better than the control sample.

Colouring of cotton with extracts of cutch roots by the use of mordants further enhanced the light fastness and the post- mordanting of alum, potassium dichromate and copper sulphate presented an exhibition of performance by recording 6 Blue Wool Standard. As discussed in earlier literature, chromium (if present in the dye molecule) contributes to the very good light fastness (Gohl & Vilensky, 1987) as it increases the stability of chromophore which becomes resistant towards the ultraviolet radiation of sunlight. The pre- mordanting of samples with alum and aluminium sulphate and coloured with cutch dye also displayed good light fastness (standard no. 5). Moreover, the light fastness of all the cutch dyed samples through mordanting was greater than the untreated sample.

The light fastness of cotton sample dyed with madder also brought about 5 Blue Wool Standard with the pre and post- mordanting of ferric chloride and post- padding with aluminium sulphate and potassium dichromate. However, the light fastness of madder dyed samples with the aid of pre- mordanted potassium dichromate and post-mordanted copper sulphate was lower than the performance of control sample. Gupta et al. (2004 b) worked on the dyeing of madder and suggested post-mordanting as the preferred method for using copper and iron salts as they form complexes more effectively. It was confirmed from the less fading and colour change of samples during the present study. They further stated that there was all over greater fading of the samples mordanted with alum. This suggests the formation of lesser resistant metal-ligand chelates to the photo degradation by this mordant. Madder contains munjistin. The poor light fastness may be attributed to the fact that carboxyl groups of munjistin are photosensitive as aromatic carboxylic acids are very prone to de-carboxylation. Gupta et al. (2004 b) assumed immediate structural modification on exposure to light and concluded that in general, munjistin has very poor light fastness. Alum as mordant only brightened the shade but could not improve the light fastness.

An exhibition of light fastness performance was also available from the application of marigold flower extracts on cotton with the use of pre- mordanting by aluminium sulphate (6 Blue Wool Standard). Pre- mordanting through copper sulphate and both pre and post- mordanting with ferric chloride produced samples with light fastness equivalent to standard 5. All other samples obtained from dye formulation of mordanting exposed greater light fastness than control sample.

The light fastness of Turkey red dyed cotton was also identical to standard number 5 which is considered as good performance. This was presented by the pre-mordanting of all the metallic mordants utilized in the current project and the post-mordanting of aluminium sulphate. However, the general light fastness of Turkey red dyed cotton was only fair confirming 3 Blue Wool Standard.

4.1.5 Cumulative colour fastness of cotton samples

Cumulative colour fastness of alkanet dyed cotton was the maximum from the post- mordanting of ferric chloride. Where alum (pre- padding) presented the lowest cumulative colour fastness among all the dyeing formulas applied on cotton while colouring it with natural extracts of alkanet. In case of cutch dyed samples with various due formulations, maximum cumulative colour fastness was available from the post-mordanting of alum. Madder presented its highest cumulative colour fastness from the dye formulation of post- mordanting with ferric chloride. Post- padded copper sulphate in the dyeing recipe produced the lowest performance of madder. However, the same mordant proved the best (both applied as pre and post- padding of dye) when employed with marigold flower extracts. Turkey red dyed cotton showed its best cumulative colour fastness with the assistance of post- mordanting of aluminium sulphate in the dyeing formula.

The good fastness properties of cutch dye on cotton suggest that the dye mordant complex was firmly attached to the substrate which resulted into a better colour yield. The fastness of cutch dye on cotton with the utilization of metallic mordants confirms the earlier works (Patel et al., 2003; Ratnapandian et al., 2012). The results of colour fastness presented by cutch dyed cotton in the present study also agreed well with the hypothesis of Gupta (1999 b) that the characteristics of mordants has greater impact on the fastness properties as compared to the dyes themselves.

In an earlier study on natural dyes, Jothi (2008) presented the photographs (exhibits) of cotton and silk fabric samples dyed by marigold flower extracts with the aid of alum, copper sulphate and some other mordants. Most of these samples had different shades from each other. The same author also reported good results of light fastness form marigold flower extracts with the use of iron and copper sulphate as mordants. The present findings from the cotton dyeing with marigold flower extracts support this report, as very good light fastness (6 Blue Wool Standard) was also available from the dyed samples.

The structure of marigold flower extracts has two hydroxyl groups. According to Jothi (2008), the good fastness of this dye may be attributed to these -OH groups. Moreover, wash fastness of this natural dye on cotton was also good. It was particularly improved due to the use of CuSO_4 both as pre- mordant as well as post- mordant. Although the molecular weight of this natural product is low which is not in accordance with the good fastness properties, yet they can form aggregate inside the fibre polymer system thereby increasing the size of molecule. Such a large sized particle cannot be easily removed from the fibre polymer system through water or washing.

The good light and wash fastness of marigold flower extracts with CuSO_4 suggest the formation of stronger complex formed between the dye and mordant which is used to protect the coloured part of the dye molecule (chromophore) from photolytic degradation. According to Jothi (2008), the chromophores sorbed the photons which resonate within the six number ring, dissipating their energy, thereby protecting the dye molecule. Cristea and Vilarem (2006) in their research work on the improvement of light fastness of natural dyes on cotton have related the light fastness of textiles to the physical characteristics and chemical structure of the fibres themselves. They have also referred to the earlier work of researchers and stated that the type mordant and the method mordanting are dependable factors for dyes. Correspondingly, Crews (1982) have also emphasized on the importance of mordant and concluded that role of mordant is usually more vital for the light fastness properties than the dye itself.

Mordants have played their useful role in improving the light fastness properties of the cotton samples with natural dyes. In an earlier work (Mongkhlorattanasit et al., 2011), it was reported that dyed fabrics without metal mordant had poor resistance to the UV rays. Further, the increase in UPF value was related with the increase in K/S value. Due to the higher value of light fastness of the cotton dyed with natural dyes with the aid of various mordants in the present study it can be said that metal mordants can protect the skin effectively from the solar UVR if they are used for the dyeing of cotton with natural dyes.

4.1.6 The role of mordants in colour coordinates

For the textile dyes to be applied on fabrics, intensive and bright colours with acceptable fastness properties are needed to be identified. Otherwise the whole practice of extraction and dyeing etc. will be useless. In the current study all the natural dyes displayed better C^* , h° and K/S values from most of the dyeing formulas having pre or post-mordants. In case of Alkanet dyed cotton remarkable increase in the relative colour strength (in comparison to untreated sample) was exhibited by the samples the one which was post-mordanted with copper sulphate and the other pre-padded with ferric chloride. The two dyeing formulas also yielded greater chroma and hue values from the Alkanet dyed cotton sample. Yusuf et al. (2012) studied the dyeing of henna and madder and found the values of a^* and b^* from madder roots extracts in the red yellow zone. They found darker shades (L^*) of madder from the high dye concentration and reported that the colour strength (K/S) of mordanted samples was significantly higher than the unmordanted samples.

In the present study also, Madder exhibited high colour strength values. Bhattacharya and Shah (2000) reported about the use of copper and iron as mordants which exhibited high K/S values. While working on the optimization of colour fastness of henna, Ali et al. (2009) studied the effect of pre and post-mordanting on colour coordinates of dyed fabric. They have mentioned about huge change in hue from both the methods of mordanting. They have also found a great deal of decrease in chroma value in case of iron as mordant. In the present study, iron ($FeCl_3$) produced similar results with madder, cutch, marigold and Turkey red dyeing and the chroma (C^*) value was greatly decreased as compared to their corresponding control samples. However, applying Alkanet with $FeCl_3$ as mordant, the chroma values of produced samples were larger.

Samanta and Agarwal (2009) stated that most of the natural dyes pose poor light stability particularly those which are extracted from the petals have poor to medium light fastness. Marigold flower dyed samples in their case faded significantly more than any other yellow dyes. More fading was observed from the use of Alum on Marigold dye as compared to the use of copper, chrome or iron. They reported that Marigold dye has good rubbing fastness on cotton jute fabrics.

Deveoglu et al. (2012) while dyeing cotton and silk with madder related the K/S value of the dye to the concentration of the dye and reported high K/S values from madder dyeing. They have also reported decreased wash fastness, however, fastness to light of mordanted sample was moderate (grade 3) as compared to grade 2 that is very poor fastness to light from unmordanted samples. Moreover, Zarkogianni et al. (2010) studied the colour and fastness of natural dyes on cotton and wool. They have also found the process of mordanting as playing significant role in increasing K/S for cotton samples. In case of unmordanted cotton samples they have reported a value of 1.4 of K/S from Madder and 1.5 from Alkanna (*Alkana tinctoria*). In the present study the K/S value from Alkanet dyed cotton sample was 1.92 whereas, that of Madder dyed cotton was 6.62. Their data regarding K/S value of pre-mordanted Madder dyed samples was 2.8 from Alum, 2.7 from potassium dichromate, 2.2 from copper sulphate and 3.3 from ferric chloride. In the present study, the data in Table 3.6 clearly depicts high K/S values of cotton samples obtained from pre-mordanting. The values of post-mordanting are even higher. Similarly, the K/S values of cotton dyed samples with Alkanet in the present study are also considerably higher than the earlier work using pre-mordanting, exhaustion dyeing.

Employing similar natural dye and mordant, the comparatively higher values of K/S in the present study clearly indicate that dyeing procedure was the only factor (step) responsible for this greater colour yield. As pad steam dyeing procedure was adopted in the current study, which boosted the dye uptake and resulted in greater colour yield (K/S). It is very important not only to select proper mordants but the adoption of suitable dyeing procedure is also a crucial step in optimizing the fastness properties of natural dyes. The present findings also support the postulates of Mongkholrattanasit et al., (2009) who mentioned that both natural dyeing and mordant dyeing can coexist if padding technologies are utilized for natural dyes which will particularly be advantageous for those products of dyeing which have low affinity.

4.1.7 Effect of mordants on the tensile strength of cotton

Natural dyeing of cotton with the aid of various mordants had greater impact on the tensile strength and elongation of the resulted dyed specimen. In case of Alkanet dyed

samples, the application of mordants prior to dye padding, generally showed greater loss in the tensile strength of cotton fabric. However, some of the dyeing formulas were able not only to maintain the original tensile strength of the cotton but also improved it to a considerable limit. Maximum increase in tensile in case of alkanet dyed cotton was brought about by the post- mordanting of potassium dichromate while the pre- treatment of the same mordant lowered the tensile strength at the maximum. The use of alum with Alkanet dye had adverse effect in this regard as its performance was equal to the control sample. The role of alum in the tensile strength of dyed cotton was consistent irrespective of the type of natural dye and method of mordanting.

In case of dyeing cotton with cutch, mordanting with copper sulphate proved better as it was capable of producing stronger fabric as compared to control sample. The use of CuSO_4 as mordant resulted in high dye uptake which means that the copper complex formed with the natural dye was strong resulting in a stronger dye- mordant- fabric interaction. The increase in tensile strength of Cutch dyed cotton using copper sulphate both as pre and post- mordant as compared to the control sample might also be due to these strong Catechu-copper sulphate - cellulose complexes, formed as a result of pre or post- padding of mordant and dye.

Maximum damage in the tensile strength of cutch and marigold flower extracts dyed cotton was recorded from the use of ferric chloride as mordant both pre and post- padding. Similarly, its use with madder as pre- mordanting was also extremely damaging and decreased the tensile strength of madder dyed cotton up to 60%. The mordant potassium dichromate proved harmless for the tensile strength in the case of madder and marigold flower extracts dyed cotton fabric and played extremely damaging role in the dyeing cotton with Turkey red.

Most of the natural dyes cannot be combined directly with the material intended to colour. They require fixing agents or mordants not only to bind the dye molecules with the fibre polymer system but also to prevent colour fading or bleeding. These compounds are of three type viz., metallic mordants (such as metal salts of tin, copper, iron, chromium or aluminium), tannins (e.g. myrobalan) and oil mordants (vankar, 2000). Metal mordants of aluminium, chromium, copper and iron were used in the present study

and each one played its role in the improving of wash, crocking and light fastness as well as colour strength and tensile strength on one natural dye or another. The type and nature of mordant applied to assist the natural dyes had a significant effect not only on the intensity and shade of colour but they also had great impact on the fastness and tensile properties of the dyed articles.

4.2 EFFECT OF CATIONIZATION ON THE DYEING OF COTTON

In order to increase the dye affinity and dyeability of cotton fabric, fixative/cationic agent (Albafix WFF) was used both as pre and post-treatment in the dyeing of cotton with five natural dyes. It is a quaternary ammonium compound, cationic in nature with a pH value about 6 and specific gravity about 1.0 (at 20°C).

Cationization of cotton before and after the padding of alkanet and cutch, slightly improved its wash and light fastness but could not change or enhance its rubbing fastness as compared to the control sample. Contrary to these results, dyeing cotton with madder extracts, the Albafix lowered the wash and light fastness of the dyed samples as compared to untreated specimen and showed some improvement only in the crock fastness. Likewise, when applied this cationizing agent with marigold flower extracts, it could not play any role at all in the fastness and tensile properties of the cotton. In case of Turkey red dyed cotton, very good wash fast samples resulted from the padding of Albafix. These samples possessed good dry rubbing fastness also. Though the light fastness was impaired and the samples could not be graded due to change in shade.

Cotton fibres are cationized by introducing quaternary ammonium groups or amine groups via hydroxyl groups of cellulose (Seong & Ko, 1998). They have reported the cationization of cotton with epoxy quaternary ammonium compounds to improve dyeing properties. They have investigated that the light fastness of cationized cotton was slightly better, regardless of the kind of cationizing agent used. They have further stated that light fastness generally increased as the depth of shade increased.

The relative colour strength of alkanet dyed cotton with the pre- padding of Albafix was much higher than the untreated cotton. In the same way, marigold flower extracts and Turkey red dyed fabrics also displayed improvement due to the use of

Albafix. Whereas, the K/S value of cationized samples dyed with cutch and madder was almost equal to the untreated samples. This increase in K/S value of cationized cotton dyed with natural dyes was all due to the pre- padding of the fixative rather than post-treatment. The post- padding of fixative Albafix on the natural dyed cotton samples failed to make any improvement in K/S values.

The present findings confirm the earlier opinion of Mughal et al. (2008) who stated that cationization before dyeing can prove more beneficial method for improving the affinity of dye by the fibre. Eom et al. (2001) worked on Red wood and Cochineal (natural dyes) on cotton with cationization and concluded that there was drastic increase in the K/S values and dyeing was also more uniform as compared to the untreated cotton. They have used commercial products as well with chemical constitutions quaternary ammonium compounds for the cationization of cotton Marie et al. (2014) have worked on the dyeing of cationized cotton with natural dyes and utilized Tanafix SR cationic agent for the enhancement of the dyeability of cotton. They have found increased K/S value of the dyed samples which kept on increasing with the increase in concentration of the cationic agent.

Cotton is believed to make anionic appearance in aqueous medium. When it is treated with cationizing agent, the increase in dyeability (higher K/S, colour yield etc.) would mean that ionic attraction may have been established between the dye anion and cationized cotton. Enhanced colour strength from the cationization and low light fastness has also been reported (Mugal et al., 2008; Fang et al., 2005). In comparison to other conventional dyeing, cationizing agent displayed improved rate of dyeing particularly the pre-treated cotton exhibited good properties. Furthermore, Lewis and McIlroy (1997) and Kamel et al. (1998) also made cotton fabric cationized and reported enhanced dyeing properties.

Some known cationic dye fixing agents are CTAB, cetrimide on Sandofix- HCF to improve wash fastness properties of synthetic dyes (Samanta et al. 2009 a). These are cationic quaternary ammonium compounds of different molecular sizes and weights. As far as the mechanism of these fixing agents is concerned, it seemed that the dye might from anions in the presence of Alkali (Samanta et al. 2009 b) and the cationic group of

the fixative or cationizing agent and dye anion might combined to form insoluble complex compound of bigger size for improving wash fastness. It is very pleasing that textile chemical and auxiliaries' manufacturers produce readymade cationizing agents with various names and trademarks for the improving of dyeing properties of various classes of dyes on cotton fabrics.

4.3 POLYURETHANE FINISH (DICRYLAN) WITH NATURAL DYES

Cumulative colour fastness achieved by using polyurethane emulsion, Dicrylan was higher with all the five natural dyes in the present project when it was compared with the control (untreated) samples of corresponding dyes. The change in shade of samples dyed with alkanet and post padding with Dicrylan was particularly good. In case of cutch dye on cotton, the performance of Dicrylan was nearly equal to the cationized cotton. However, this durable finish could not work well with madder dye on cotton. Whereas, employment of this soft polyurethane finish with marigold dye proved considerably good, as the colour fastness of samples coloured with combination of Dicrylan and marigold dye was far better than the control sample. The fastness properties of Turkey red dyed cotton samples were also improved due to the padding of this finish.

The fastness performance donated by this ionic easy care finish was comparable to most of the metallic mordants as well as crosslinkers utilized in this study. Regarding the effect of Dicrylan on the tensile strength of dyed cotton samples, this additive has not only protected this mechanical property of dyed samples but also made sizable improvement in some cases. The only loss in strength due to the application of this auxiliary was produced from its padding prior to the padding of alkanet. Generally, it stayed harmless and brought no change in the tensile strength with all the natural dyes when it was applied as pre-treatment while the post-padding of this soft polyurethane finish increased the tensile strength of dyed samples (e. g. 16% increase in the case of cutch dyed sample). Dicrylan managed to enhance the K/S value of dyed samples as compared to the control sample. This increase was more obvious from the data of post-treated cotton samples.

4.4 EFFECT OF UV ABSORBERS

Natural dyes are believed to pose poor light fastness as compared to synthetic dyes. Numerous studies have been carried out (Gupta & Gulrajani, 1996; Lee et al., 2001; Oda, 2001 b; Gupta et al., 2004 b; Fang et al., 2005; Cristea & Vilarem, 2006; Iqbal et al., 2008; Samanta, 2009 b; Mongkholrattanasit et al., 2011) to improve the light fastness of natural dyes. In the present investigation about the effect of natural dyes on cotton fabric, two types of UV absorbers (UV-SUN, reactive UV absorber based on oxalanilide and Rayosan C, a heterocyclic compound) were utilized with all the five natural dyes which were selected for the present research project. Both the UV absorbers led to improvement in the light fastness of alkanet, cutch, marigold flower extracts and Turkey red dyed cotton, whereas, madder could not exhibit any improvement in the light fastness of cotton with the use of these UV absorbers. Relative colour strength or K/S value of alkanet dyed cotton improved and that of cutch dyed cotton decreased with the post-treatment of UV-SUN.

The K/S of madder dyed cotton resulted in improvement with UV-SUN but no change was found with Rayosan. Dyeing with marigold flower extracts produced cotton with good K/S values which were slightly improved with Rayosan and more improved with UV-SUN in the dye formulations. Turkey red dyed cotton showed decrease in K/S value with the pre-treatment of UV-SUN. Most of the dyeing formulas with the pre of post- padding of UV absorbers were able to increase the tensile strength of the dyed samples to some extent as compared to the untreated sample.

There are many possibilities that the light fastness of a material is either high or low. Besides the additives or after treatments, some internal factors such as the nature of fibre, the type of dyeing auxiliary, the physical state and chemical nature of dye etc. also have a role in the lightfastness of coloured fabrics. The use of UV absorbers can prevent the photo degradation of the material. These compounds have absorption capacity of radiation between 290 nm and 400 nm (Cristea & Vilarem, 2006). They can provide stability to light exposure for longer duration and molecular dispersion for screening activity. They stay chemically inert to the other substances and additives in the substrate

during dyeing. It is of great interest to investigate various UV absorbers for attempting to improve the light fastness of natural dyes on cotton.

A variety of UV absorbers are available for protecting dyes on cotton as they have the function of absorbing radiation (Crew, 1987; Oda, 1989; Oda, 2002; Oda, 2012 a; Oda, 2012 b). However, only four of them (Oda, 2001 a) have found significance commercial important. In an earlier work (Lee et al, 2001) utilized sulphonated hydroxy benzohiazole UV absorber, sulphonated hydroxyl benzophenone UV absorber and Uninul of BASF and reported that considerable improvements were made in the light fastness with the use of these UV absorbers. However, they resulted in the decreased K/S values as compared to the untreated fabric dyed without mordant. Their findings are in conformity with the present findings, where K/S values were decreased by the UV absorber based on oxalanilide in some cases and by the Rayosan C (Clariant) in few samples. To impart increased UV absorptiveness of cotton cloth, Todorova and Vassileva (2003) applied Rayosan C (UV absorber) and the degree of photo degradation of a dye was evaluated by K/S value. They reported a considerable increase in the absorption of UV rays due to this compound.

In a related study, Merdan et al. (2012) applied Rayosan C to cotton fabric by exhaust method. They found a general improvement in the light fastness from the treatment of this UV absorber without changing the colour of fabric and reported better results of light fastness from the pre-dyeing process of this UV absorber. In the current study also, Rayosan C did not adversely affect the original shade of the dyed samples as the shades yielded by this compound with various natural dyes were comparable to the shade of corresponding control sample. This property is particularly advantageous in forecasting and matching of the shade of dyed materials. In the present research work, the most outstanding performance of 6 Blue Wool Standard light fastness was exhibited by the post- padding of Rayosan C on cutch dyed cotton. This performance is comparable with any good synthetic dye on cotton.

4.5 ROLE OF CROSSLINKING AGENTS

Cellulose crosslinking is one of the important chemical processes in textile. Crosslink is a covalent or valence bond which occurs not only within fibre polymers but also between the polymers at selected points (Gohl & Vilensky 1987). Crosslinking agents contain two or more reactive ends which are capable of attaching to functional groups of other molecules (Trotman, 1984). The process of this chemically joining or linking of one polymer to another by a covalent bond is called crosslinking. Functional treatments given to fabrics to fulfill consumer desire of having some particular characteristic in a material (which is not the inherent part of the fibre or fabric) are all based on reactants or resins. The original chemical finish in this regard was urea formaldehyde, but there are resins which release no formaldehyde (Corbman, 1985) and the most widely used crosslinking agents is dimethyloldihydroxyethyleneurea (DMDHEU). In the current study, three types of crosslinkers were utilized to investigate the possibilities of optimization of colour fastness of natural dyes on cotton. All the three crosslinkers i.e. Fixapret CPF (methylolation products based on glyoxalmonourein), Fixapret F-ECO (DMDHEU) and knittex RCT (DHEU) were employed with natural dyes both as pre and post- padding. They generally made improvement in the wash and light fastness (as well as cumulative colour fastness) of alkanet, cutch and marigold flower extracts dyed cotton samples. However, in case of rubbing fastness there was no improvement or even slight decrease in the fastness (as compared to untreated sample) of samples dyed with the aid of crosslinkers. Regarding dyeing with madder root extracts, there was no improvement in the colour fastness of cotton samples dyed with combinations of this dye and crosslinkers. While in case of Turkey red dyed cotton, the light fastness of dyed samples treated with Knittex (DHEU) displayed improvement.

Crosslinkers are intended to improve dye uptake as well as fastness properties. Although their main function is to make a chemical link between the dye and cellulose, however, they must form crosslinked net work which can block the passage or entrance of fibre pores for dye molecule which have already been penetrated (Yang, 2003). This property of crosslinker will prevent staining of the fabric during washing.

The samples dyed with the natural dyes by the use of crosslinkers were also judged for change in tensile strength due to dyeing. In most of the cases, the samples padded with crosslinkers prior to dyeing resulted in considerable loss in tensile strength as compared to the untreated sample. The most obvious among them was the pre-treatment of Fixapret CPF employed with cutch and marigold flower extracts dye on cotton. Knittex was able to improve the tensile strength of cotton dyed with marigold flower extracts but on the other hand it severely damaged the tensile strength of madder dyed cotton. Joshi et al. (2007) worked on the natural dyes by using crosslinker (glyoxal/glycol) and reported a marginal decrease in the tensile property of fabric, although, most other properties of the fabric were improved. The same behavior of crosslinkers was also reported in by Corbman (1985) where 30-50 per cent of loss in tensile strength has been associated with the use of crosslinkers during cotton finishing. Sheth et al. (2003) while studying the effect of various crosslinkers on cotton fabric with natural dyes reported that although the colour depths of the dyed and crosslinked fabrics were comparable, the tear and tensile strength retentions of crosslinked and dyed cotton were only 51-100 percent.

The present findings also confirm the earlier investigation of Kamaluddin et al. (2007) who applied the Fixapret CPN and Fixapret ECO of BASF with reactive dyes and reported a decrease in strength of all kinds of crosslinked dyed fabrics. In the present study, the cotton samples treated with Knittex were cured at 120°C whereas, the samples dyed with the dye formulations having Fixapret type of crosslinkers were cured at 130°C. The decrease in tensile strength of the cotton samples dyed in the presence of crosslinkers might be due to the embrittlement of cellulose during curing at very high temperatures.

CONCLUSIONS

This study was conducted to appraise the fastness properties of some natural dyes from plant origin on cotton fabric, without significantly decreasing its tensile strength. For this purpose some of the dyes were produced by solvent extraction from the roots of plants namely alkanet, cutch and madder. While marigold flower dye (Sun yellow) and Turkey red dyes were obtained from natural dyes suppliers (India). Dyeing was carried out through 2-bath-2-stage; pad steam procedure by utilizing metallic mordants, fixative,

wash fastness finishes, UV-absorbers and crosslinking agents, applied by pre and post-treatments. Alkanet produced a range of green shade which varied in hue and intensity with the use of different mordants. Some of the dye formulations resulted in a good colour fast dyed samples with maximum or no loss in tensile strength. The most outstanding result regarding wash fastness was introduced by dye formulation of pre-mordanting with FeCl_3 . The dry rubbing and light fastness from this recipe was also appreciable and its K/S and C^* values were highest as well among the mordant treatments. However, this dye formulation led to about 25 percent loss in tensile strength of the fabric.

Cationized cotton with the aid of Albafix (aqueous preparation of a polymeric, quaternary ammonium compound) and coloured with extracts of alkanet presented good wash fastness, very good dry rubbing along with light fastness, enhance colour strength and increased the tensile strength of the fabric as compared to the control as well as original (white, bleached, desized) fabric. The use of soft polyurethane finish (Dicrylan) proved useful in producing articles with good fastness properties and relative colour strength. However, it was responsible for lowering the chroma (C^*) along with about 6% of tensile strength from its pre-treatment.

Reactive UV absorber based on oxalanilide (UV-SUN) donated good light fastness to cotton sample in additions to good wash fastness and good dry rubbing fastness and at the same time slightly added to tensile strength. However, the K/S and C^* values were not satisfactorily improved by this UV absorber. On the other hand, Rayosan a heterocyclic compound was successful in enhancing all the fastness properties of the cotton samples dyed with alkanet, although, it could not maintain the colour strength and chroma values as well as the tensile strength of the fabric. Crosslinkers Fixapret CPF, Fixapret F-ECO and Knittex showed almost identical behavior towards the dyeing of cotton with Alkanet. They managed to take the wash and light fastness little forward, maintained the rubbing fastness (as compared to control sample) but the K/S and colour purity (C^*) were greatly reduced. The tensile strength of samples was also lowered due to pre-treatment of these crosslinkers, yet this decrease was negligible and much reduced as compared to the loss of strength due to metallic mordants. The analysis of overall

cumulative colour fastness of Alkanet dyed cotton through paired sample t-test presented significant result between the means of pre-treatment and post-treatment.

The extract of cutch root created a range of brown shade with a soft, smooth and attractive appearance. All the mordants utilized in this study yielded colour fast cotton samples (with exceptions of wet rubbing). Pre-mordanting with CuSO_4 exhibited good wash fastness on cotton dyed with cutch extracts. Rubbing fastness was enhanced by post-mordanting with alum. Improvement in light fastness was available from almost all the dye formulation of mordanting. Some of the post-mordanting (copper sulphate, potassium dichromate and hydrated potassium aluminium sulphate) improved it up to 6 Blue Wool Standard. CuSO_4 also made the fabric stronger by increasing 18 percent tensile strength of the dyed sample as compared to the strength of control sample. Alum proved harmless and did not bring any change in the tensile strength, while all other recipes of mordanting decreased the tensile strength of cotton fabric. The most damaging role has been played by FeSO_4 used as pre-mordant (22% loss in tensile strength). On the other hand, this was the only mordant which increased the K/S value of the dyed samples.

All the finishes and UV absorbers utilized in this study increased the wash and light fastness of cutch dye on cotton. However, the post padding of polyurethane emulsion and post-treatment of reactive UV absorber (UV-SUN) made slight enhancement in the rubbing fastness as well. Pre-cationized sample could provide rubbing fastness similar to control only. Post-padding of heterocyclic compound (Rayosan C) decreased the crocking fastness of dyed sample. These finishes protected the tensile strength of cotton and produced samples with acceptable colour strength also. Post-treatment of Dicrylan and Rayosan yielded higher values of chroma from the cutch dyed samples. The overall analysis of colour fastness suggests significant difference between the mean values of pre-treatments and post-treatments of all the dyeing auxiliaries employed with the dyeing of cutch root extracts.

Solvent extraction of natural dye from madder root and its padding on cotton was optimized. The extracts yielded red to violet and orange shades. Post-mordanting with ferric chloride led to improvement in fastness properties, tensile strength as well as colour strength of the cotton dyed with madder. Generally, the wash fastness of madder dyed

cotton samples was not good. Except the slight improvement made by a UV absorber Rayosan, none of the finishing agent could enhance the wash fastness of cotton coloured with madder in terms of change in shade, although, staining on the adjacent white cloth was negligible (4-5 GS). Dry rubbing fastness of the samples dyed with madder was acceptable whereas, wet rubbing was poor and light fastness was not increased by any dye formulation (as compared to control sample). Most of these dyeing formulas brought positive change in the tensile strength of the samples. However, they could not bring any significant increase in the K/S values of dyed cotton. Application of madder on cotton was not very booming accomplishment. It seems that the dye could not manage to penetrate into the fibre polymer system, although, wetting agent and migration inhibitor were also incorporated in the dye formulation.

In comparison to metallic mordants, the post padding of crosslinkers Fixapret CPF and Fixapret F-ECO enhanced the fastness properties along with increasing the tensile strength of the dyed cotton samples. Crosslinkers, DMDHEU (Fixapret F-ECO) added about 27% tensile strength to the Madder dyed cotton as a result of both pre and post padding. On the other hand, DHEU (Knittex) decreased 19% of the tensile strength of the samples whether used as pre-treatment or post-treatment.

The padding of marigold flower on cotton samples with twenty four different dyeing formulas was a gratifying experience. Most of the dye formulations resulted in pretty yellow colour, with good colour fastness. Pre-mordanting with CuSO_4 can be considered as the best dye formulation with combination of marigold flower on cotton in terms of fastness properties good K/S value as well as slightly increasing the tensile strength of the sample. Considering the effect on tensile strength, the most damaging mordant was found to be FeCl_3 in both the pre and post procedures. Dyeing with alum seemed to have no effect on the fastness properties, tensile strength as well as relative colour strength (K/S) values. The performance of samples from both the pre and post-mordanting of alum was almost similar to control sample. Cationization of cotton with Albafix and finishing with Dicrylan generally produced sufficiently good colour fastness, with slightly increasing the tensile strength as well. However, colour strength was enhanced only by the cationization in this regard.

Ultraviolet absorbers have been found successful in defusing the destructive role of UV light. Best result in this context was achieved with the post- padding of reactive UV absorber based on oxalanilide (UV-SUN). However, it could neither enhance/maintain the K/S value nor the tensile strength of the dyed sample. For obtaining better results, crosslinkers were also employed with marigold dye on cotton. It was found that most of the dye formulations of crosslinkers enhanced the fastness properties to some extent. Their major role played was noticed in the improvement of light fastness. The pre-treatment of Fixapret CPF and Fixapret F-ECO seem to have directly attacked the cellulose polymer and decreased the tensile strength of the fabric by ruining the polymer structure. However, their post padding protected/ improved this mechanical property of the marigold flower dyed cotton samples. As far as, the K/S values are concerned, none of the crosslinker was able to enhance the colour strength of the marigold dyed cotton samples.

Regarding the application of Turkey red dye on cotton with five different metallic mordants produced range of shades from pastel violet to signal violet and red lilac etc. with slight improvement of the dye absorptions and an increase in the fastness properties and K/S values in some cases. Fastness to washing was highly improved by pre-mordanting with ferric chloride; crocking fastness was enhanced by the post-treatment of ferric chloride, whereas fastness to light was increased by post-mordanting with aluminium sulphate. Tensile strength of the cotton samples was generally protected/ improved by many of the dyeing formulas of mordanting. However, damaging of this property was also accompanied by few dyeing recipes. Maximum decrease in tensile strength of 40% was brought about by the pre-mordanting of cotton sample with potassium dichromate. In case of pre and post-mordanting with ferric chloride and only the post-mordanting of copper sulphate, the chroma values or purity of colour values were less than the chroma attained by the control sample.

Cationization of cotton sample prior to dye padding presented enhanced fastness properties, with improved K/S values while maintaining the tensile properties of the dyed cotton sample. Likewise the application of polyurethane emulsions also enhanced the fastness properties and colour coordinates values without harming the tensile strength of

the dyed samples. UV absorbers were able to increase the light fastness of coloured samples to some extent. Moreover, they also increased the tensile strength while maintaining the K/S value as compared to the control sample. Among the crosslinkers, the post padding with DHEU enhanced the colour fastness of the Turkey red dyed samples. All the dye formulations of crosslinkers greatly reduced the tensile strength of the dyed cotton sample. Analyzing the overall results, it looks like that Turkey red dye has exhibited improved fastness properties as compared to the solvent extracted Madder dye on cotton.

The fastness properties presented by alkanet cutch and marigold flower seemed sufficiently good for practical dyeing of cotton fabric. The beautiful and fast browns yielded by cutch on cotton are comparable with any high grade synthetic dye. Pad- steam dyeing producer have resulted in better colour yielded and fastness as compared to conventional (exhaust) dyeing reported in the earlier studies particularly when dyeing is to be carried out on long runs. Cationization and polyurethane emulsion have been satisfactorily successful in achieving the goal. Employment of UV absorbers with the application of natural dyes was a suitable option as they were found useful in the improvement of light fastness. The use of crosslinkers with natural dyes on cotton has been proved successful as, not only did they enhance the fastness properties but also maintained the shade yielded by the control sample. In this regard their use could be more practical in acquiring matching shades as compare to mordants which have produced their own district shade.

The results from this study are consistent with the initial hypothesis which indicated that natural dyes applied to cotton by pad-steam dyeing (continuous dyeing) process offer better fastness properties as well as economic benefits to the textile wet processing sector. The expected potential benefits comprises of saving water and energy. The revival of natural dyes will be useful in greatly eliminating the effluent load in the form of no added salt, reduction in environmental pollution and minimizing risks to human health.

RECOMMENDATION

Colour has always been important in fabrics. Colouration of textiles is a complicated procedure involving not only the material and dye but also many other auxiliaries and details concerning treatments and processes. Some significant recommendations from the current project on natural dyes are as below:

Alkanet-root extracts

If cotton is to be dyed in any shade of green, a solvent extracted dye from Alkanet root should be applied through pad-steam dyeing procedure. For acquiring better fastness to wash, light, rub (dry only); colour coordinates such as chroma, hue and colour strength; soft, smooth and leveled dyed fabric as well as maintained/improved tensile strength, it is recommended to employ copper sulphate with this dye through post-mordanting procedures. Cationization of cotton with quaternary ammonium compound (both pre-treatment and post-treatment) has improved the fastness properties, tensile strength as well as relative colour strength (K/S) of alkanet dye on cotton. Its use is proposed for yielding good colour and offering potential for environmental friendly dyeing operation. Reactive UV absorber based on oxalanilide (UV-SUN) and heterocyclic compound as UV absorber (Rayosan C) greatly increased the light fastness of alkanet dyed cotton. Their use should be made as post padding with Alkanet dye on cotton. Soft polyurethane emulsion (Dicrylan) is suggested as post-treatment for improving light and wash fastness as well as maintaining the tensile strength of cotton dyed with alkanet root extracts. Crosslinkers should not be applied with alkanet dye on cotton if greater K/S value of the dyed is article required. Likewise, the use of potassium dichromate is not recommended for the dyeing of cotton with alkanet as it has not only affected the shade of the dyed sample but its pre-mordanting has brutally damaged the fabric in terms of its tensile strength.

Cutch root extracts

For any brown shade on cotton, cutch root extract is suggested to be the primary choice due to its excellent demonstration of fastness properties and tensile strength. Mordanting of cutch dye on cotton is proposed with the padding of CuSO_4 . Cationization

of cotton for dyeing with cutch should be carried out prior to dye padding. Post padding with soft polyurethane was a successful dye formulation and its use is therefore prescribed while dyeing cotton with cutch root extracts. The use of Rayosan C and UV-SUN (particularly the pre-treatment) is recommended to guarantee very good light fastness of cutch dyed sample. Likewise, the post padding of crosslinkers, DHEU (Knittex) on cutch dyed cotton fabric is advised for achieving enhanced fastness properties and improved tensile strength.

Madder root extracts

Among all the five natural dyes applied on cotton in this study, Indian madder was the least successful dye in terms of fastness and tensile properties. Due to its severe damaging role on cotton (loss in tensile strength up to 60%), it is not advisable to pad cotton with solvent extracted madder root dye.

Marigold flower dye

In order to exercise marigold flower dye on cotton, the use of copper sulphate mordant is suggested for achieving better fastness properties enhanced K/S value as well as increased tensile strength of the fabric. Cationization of cotton is recommended with this dye as it yielded good colour and fastness properties with enhanced tensile strength. Post padding soft polyurethane emulsion (Dicrylan) and post-treatment of UV-SUN are suggested for improved wash fastness and good light fastness respectively. Marigold flower dye should be used with the aid of various crosslinkers particularly the post padding glyoxalmonourein (Fixapret CPF) as it donates good fastness properties and adds tensile strength to the fabric. However, in order to get a dark yellow shade, the amount (concentration) of dye should be increased from 20g/l.

Turkey red dye

Pre-treatments of most of the metallic mordants have greatly decreased the tensile strength of Turkey red dyed cotton. It is therefore, recommended to apply this dye through post-mordanting method. Concerning the fastness properties aluminium sulphate should be utilized, whereas, from the point of view of colour strength, copper sulphate and ferric chloride should be used as mordants.

Future perspectives

In future, this study can be continued by further investigating all the successful dyeing formulas emerged as a result of this project by varying the amount of dye, concentration of various dyeing auxiliaries as well as conditions of treatment etc. Additional searching of various types of mordants, finishing agents, UV absorbers, anti-oxidants, crosslinkers, various dyeing procedures and conditions of treatments should be accomplished to optimize dye fixation levels and fabric strength resulted from natural dyes on cotton and other textile fibres. Furthermore, whilst working on natural dyes in future, the anti microbial and UV protection properties of fabrics also need to be investigated.

Large scale dye extraction and efficient suppliers of natural dyes are quite important which should provide dye houses with standardized and reproducible dyes of consistent quality. Information of technical/standard method of application with details of conditions of treatment specific to each method for every dye should be available for every textile fibre. Number of available natural dyes/colours with required fastness properties related to ultimate end use of the fabric should be increased. Technical knowledge related to testing the toxicity and data about the toxicity concerning human skin and other health issues should be available. Government should take policy measure to introduce and revive natural dyes on industrial scale.

Owing to the growing trend of going “green” throughout the world, environmentally friendly practices like colouration of textiles with natural dyes should be adopted for achieving this ecological goal. With consumers focused on an eco-friendly environment due to the huge awareness about issues on environmental pollution, human health, live earth, global warming etc., this is an ideal time for the textile industry to embrace this growing trend and focus on advertizing “green” products.

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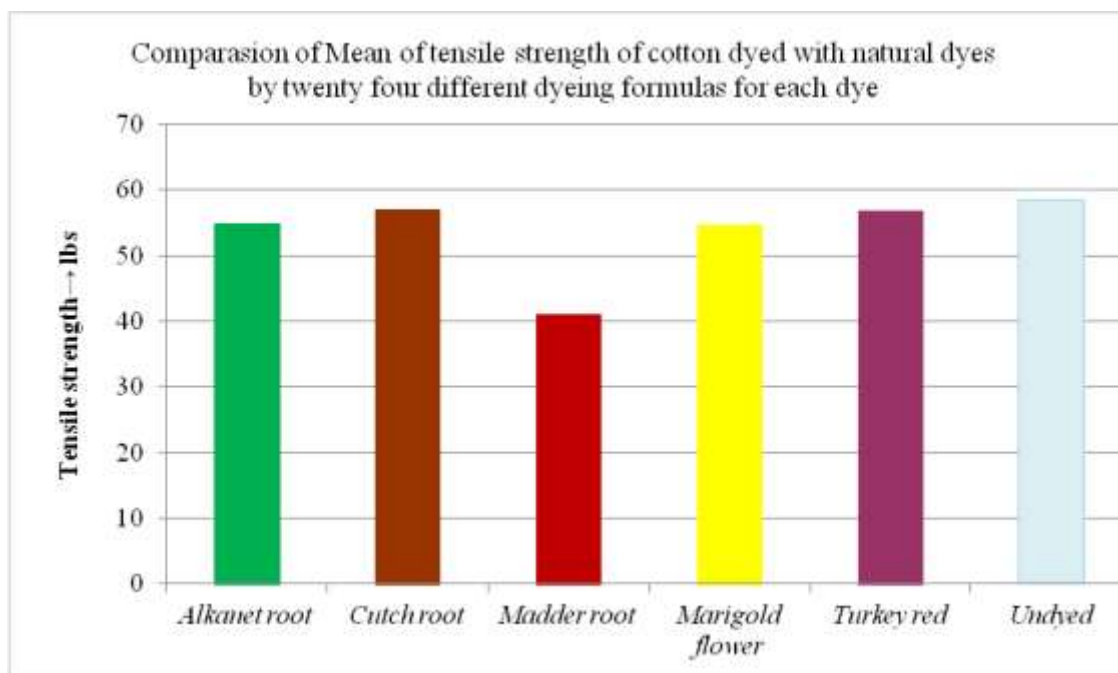


Figure 5.1: Over all tensile strength of natural dyed cotton fabric

fabric

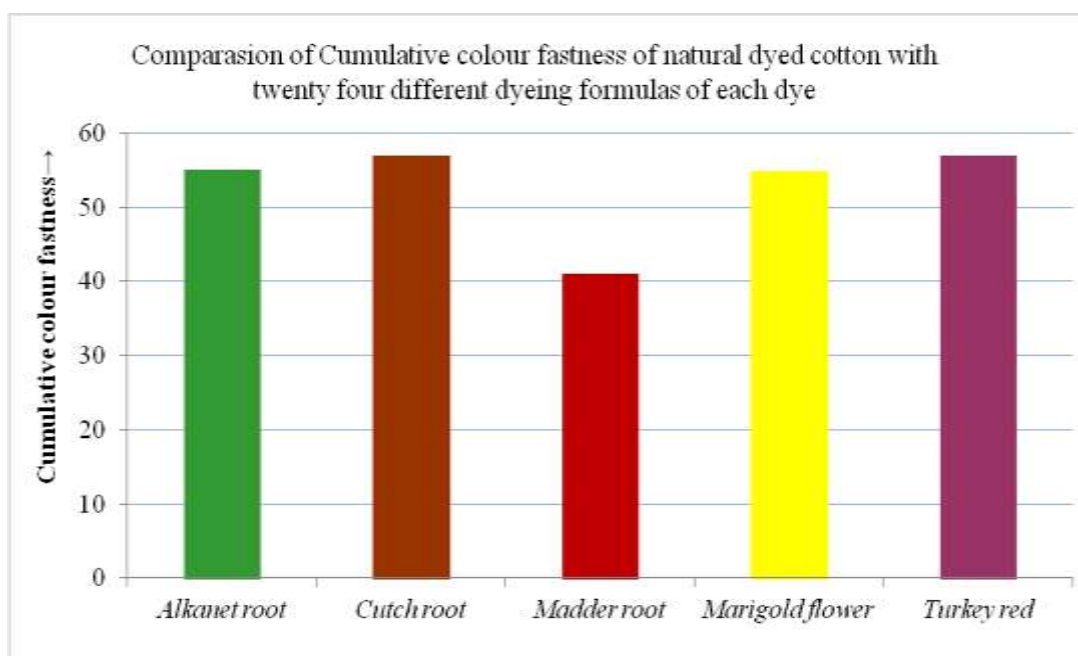


Figure 5.2: Over all cumulative colour fastness of natural dyed cotton

Table 5.1: Shades of cotton fabric obtained from dyeing with natural dyes using various dyeing auxiliaries.

Shade obtained	Dye recipe	
	Pre-treatment	Post-treatment
Alkanet root (<i>Alkana tinctoria</i>)		
Medium greyish green	Rayosan, Fixapret CPF, Knittex,	Aluminium sulfate, Rayosan
Dark greyish- green	Albafix	
Darker greyish- green (Reed green)		Alum
Most green		Potassium dichromate, Copper sulfate
Greenish-grey (pale green)	Dicrylan, Fixapret ECO, UV-SUN	Albafix, Dicrylan, Fixapret ECO, Fixapret CPF, Knittex, UV-SUN
Dark greenish-grey	Alum, Aluminium sulfate, Copper sulfate	
Greenish-brown	Potassium dichromate	
Yellowish-brown	Ferric chloride	Ferric chloride
Cutch root (<i>Acacia catechu</i>)		
Darkest brown (sepia brown)		Ferric chloride
Darker brown (mahogany brown)	Ferric chloride	
Medium brown (olive brown)	Alum, Fixapret CPF	
Light reddish brown (ochre brown)	Albafix , Dicrylan	Aluminium sulfate, Potassium dichromate Albafix

Reddish brown (nut brown)		Alum
Reddish medium brown	Copper sulfate	
Reddish dark brown	Potassium dichromate	
Light brown (clay brown)	Knittex, Fixapret ECO, UV-SUN Rayosan,	Albafix, Dicrylan, Knittex, Fixapret ECO, Fixapret CPF, UV-SUN, Rayosan
Madder root (<i>Rubia tinctorum</i>)		
Most reddish (brown red)		Copper sulfate
Reddish (light red)		Albafix
Reddish (pearl pink)		Potassium dichromate
Reddish (flame red)	Alum	
Orangish- red		Alum
Yellowish- orange		Knittex
Reddish- grey		Ferric chloride
Light reddish purple	Potassium dichromate	
Dull purple (pastel violet)	Aluminium sulfate	
Purple (signal violet)		Aluminium sulfate
Pinkish red (dark purl pink)	Copper sulfate	
Marigold flower (<i>Tagetes erecta</i> L)		
Dark yellow	Alum	
Medium yellow (traffic yellow)		Alum

Light yellow	Dicrylan, Fixapret CPF, Fixapret ECO, Knittex, UV-SUN, Rayosan	Albafix, Dicrylan, Fixapret CPF, Fixapret ECO, Knittex, UV-SUN, Rayosan
Dirty light yellow (zink yellow)	Copper sulfate	
Dirty light yellow (ivory)	Copper sulfate	
Greenish yellow (olive yellow)	Aluminium sulfate	Aluminium sulfate
Khaki (dark lemon yellow)	Potassium dichromate	Copper sulfate Potassium dichromate,
Dark greyish khaki		Ferric chloride
Darker greyish khaki	Ferric chloride	
Turkey red (<i>Rubia cordifolia</i>)		
Darkest purple (red lilac)	Potassium dichromate	
Darker purple	Ferric chloride	
Dark purple (pearl violet)	UV-SUN, Dicrylan, Fixapret CPF, Fixapret ECO, Knittex	Albafix, Potassium dichromate
Dull purple (pastel violet)	Albafix	
Reddish-purple (signal violet)	Alum, Copper sulfate	Copper sulfate
Reddish-purple (blue lilac)	Aluminium sulfate	
Maroonish		Aluminium sulfate
Reddish-orange (salmon pink)		Alum

