
TEXTILE DYEING

Edited by Peter J. Hauser

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Preface

Nearly all textile materials are colored after fabrication and before final finishing. The coloration of fibers and fabrics through dyeing is an integral part of textile manufacturing. This book discusses in detail several emerging topics on textile dyeing.

The pretreatment of textiles prior to dyeing is addressed by several authors. Menezes and Choudhari present chemical alternatives to traditional pretreatment, while Tavcer discusses enzyme pretreatment procedures. Bendak and Raslan review pretreatment methods of protein and synthetic fibers, and Bhatti et al. introduce the concept of radiation induced pretreatment. Control of the dyeing process is discussed by Günay and enhancing the dyeability of fibers is reviewed by Gashti et al. Details for dyeing specific fiber types are given by Gupta et al (polypropylene), Suesat and Suwanruji (polylactic acid), and Giménez-Martín et al (acrylic). Individual dyestuff classes are addressed by Koh (disperse dyes), Rippon et al (vat dyes). The use of cyclodextrins as dye leveling agents is reviewed by Voncina while Durasevic et al. suggest that photochromic dyes can function as useful sensors. The interaction of plasma with textile material prior to dyeing is well represented with chapters by Durasevic et al, Souto et al, Deshmukh and Bhat, and Mokbul and Dirk.

"Textile Dyeing" will serve as an excellent addition to the libraries of both the novice and expert.

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Contents

Preface IX

- Chapter 1 **Effect of Radiation on Textile Dyeing 1**
Ijaz Ahmad Bhatti, Shahid Adeel and Muhammad Abbas
- Chapter 2 **Dyeing Wool with Metal-free Dyes – The Use of Sodium Borohydride for the Application of Vat Dyes to Wool 17**
John A. Rippon, Jackie Y. Cai and Shaun M. Smith
- Chapter 3 **Pretreatments of Textiles Prior to Dyeing: Plasma Processing 33**
R. R. Deshmukh and N. V. Bhat
- Chapter 4 **From Murex Purpura to Sensory Photochromic Textiles 57**
Vedran Durasevic, Durdica Parac Osterman and Ana Sutlovic
- Chapter 5 **Dyeing of Environmentally Friendly Pretreated Cotton Fabric 77**
Petra Forte Tavčer
- Chapter 6 **Improvement in Acrylic Fibres Dyeing 89**
E. Giménez-Martín, A. Ontiveros-Ortega and M. Espinosa-Jiménez
- Chapter 7 **The Future of Dye House Quality Control with the Introduction of Right-First Dyeing Technologies 119**
Melih Günay
- Chapter 8 **Commercially Adaptable Coloration Processes for Generic Polypropylene Fiber 155**
Murari L. Gupta, Fred L. Cook and J. Nolan Etters
- Chapter 9 **Substrate Independent Dyeing of Synthetic Textiles Treated with Low-Pressure Plasmas 173**
Hossain Mohammad Mokbul and Hegemann Dirk

- Chapter 10 **Dyeing with Disperse Dyes** 195
Joonseok Koh
- Chapter 11 **Pre-treatment of Textiles Prior to Dyeing** 221
Edward Menezes and Mrinal Choudhari
- Chapter 12 **Polyamide 6.6 Modified by
DBD Plasma Treatment for Anionic Dyeing Processes** 241
António Pedro Souto,
Fernando Ribeiro Oliveira and Noémia Carneiro
- Chapter 13 **Surface and Bulk Modification of
Synthetic Textiles to Improve Dyeability** 261
Mazeyar Parvinzadeh Gashti, Julie Willoughby and Pramod Agrawal
- Chapter 14 **Pretreatment of Proteinic and
Synthetic Fibres Prior to Dyeing** 299
A. Bendak and W. M. Raslan
- Chapter 15 **Effect of Plasma on Dyeability of Fabrics** 327
Sheila Shahidi and Mahmood Ghoranneviss
- Chapter 16 **Dyeing and Fastness
Properties of Disperse Dyes on Poly(Lactic Acid) Fiber** 351
Jantip Suesat and Potjanart Suwanruji
- Chapter 17 **Application of Cyclodextrins in Textile Dyeing** 373
Bojana Voncina

Effect of Radiation on Textile Dyeing

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1. Introduction

Love for colours is a natural instinct and every individual has his own choice and liking for colour. The icy appearance of Hamaliyan ranges or lush green forests or fields of agriculture or trees laden with colorful fruits or butterflies moving from flower to flower presents the beauty of nature, generation after generations are being attracted. The choice of beautiful fascinating colours reflects the aesthetic sense of humans that varies.

Colour is visual perceptual property corresponding in humans to the categories called red, yellow, blue and others. It is a sensation that arises from the activity of retina of the eye and its attached nervous mechanism, and results in a specific response to the radiate energy of certain wavelength and intensity. Thus it is a quality of an object with respect to light (Mizzarini *et al.*, 2002). Colorants may be either pigment or a dye which are characterized by their ability to absorb or emit light in the visible range 400-700nm. They may be organic or inorganic depending upon their structure and method of production.

Dyes are the coloured substances which are capable of imparting their colours to the matrix which may be fiber, paper or any object. They must have fixing tendency on a fabric that is impregnated with their solution and the coloured fixed dyes must be fast to light as well as resistant to action of water, dilute acids, alkalies, various organic solvents used in dry cleaning, soap solutions, detergent, etc (Shukla, 1992). A pigment generally is a substance which is insoluble in the medium in contrast to dye in which it is applied and has to be attached to a substrate by additional compounds e.g. polymer in paints and plastics (Taylor and Nonfiction, 2006)

A compound looks coloured because it has absorbed certain electromagnetic radiation from the visible region. The moieties, present in colouring substance, responsible for the absorption of electromagnetic radiation and reflect in the visible region are called chromophores (Younas, 2006). Ultraviolet radiation constitutes to 5% of the total incident sunlight on earth surface (visible light 50% and IR radiation 45%). Even though, its proportion is quite less, it has the highest quantum energy compared to other radiations. Light is electromagnetic in nature. Within the electromagnetic spectrum, human eye captures visible light in the range between about 380 nm and 700 nm (Mizzarini *et al.*, 2002). Dyes absorb electromagnetic radiation of varying wavelength in the visible range of

spectrum. Human eyes detect the visible radiations only for the respective complementary colours.

Fig.1 shows the different regions of spectrum with their wavelengths.

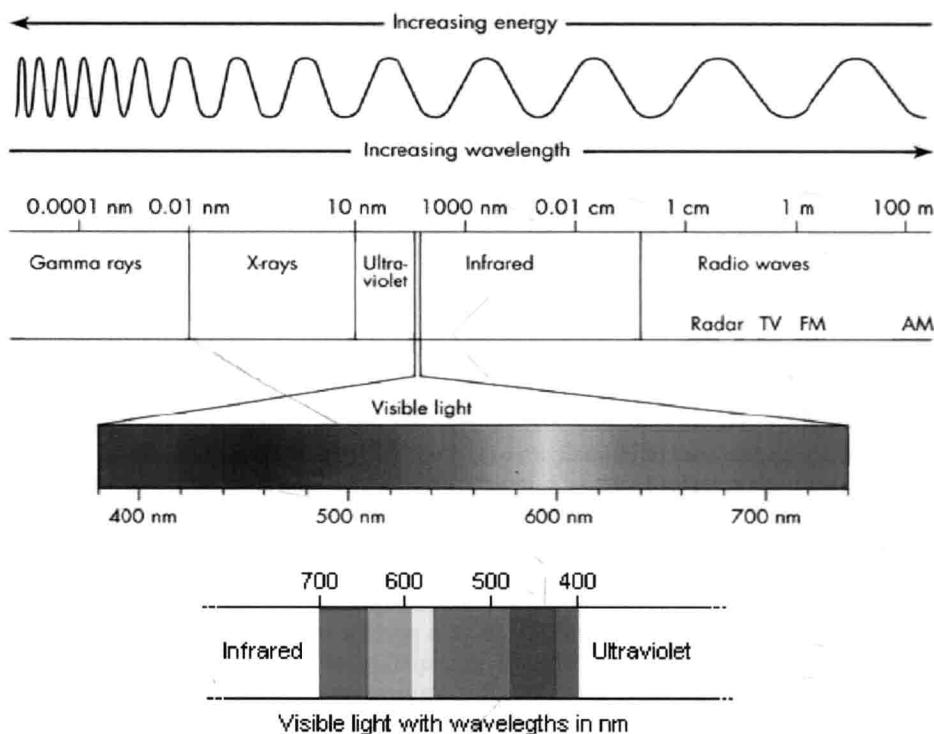


Fig. 1. Regions of electromagnetic spectrum

2. Classification of dyes: Natural & synthetic dyes

All colourants obtained from animals, plants and minerals without any chemical processing are called natural dyes. e.g. Alizarin a pigment extracted from madder, tyrian purple from snail and ochre which is a mineral of Fe_2O_3 (Gulrajani, 1992). Natural dyes may be vat dyes, substantive or mordant dyes as they require the inclusions of one or more metallic salts of tin, chromium, iron, copper, aluminum and other for ensuring reasonable fastness of the colours to sun light and washing. The natural dyes have several advantages such as: these dyes need no special care, wonderful and rich in tones, act as health cure, have no disposal problems, have no carcinogenic effect, easily biodegradable, require simple dye house to apply on matrix and mild reactions conditions are involved in their extraction and application (Sachan and Kapoor, 2004). There are some limitations of natural dyes which includes, lesser availability of colours, poor colour yield, complex dyeing processing, poor fastness properties and difficulty in blending dyes (Pan *et al.*, 2003). Table 1 given below, shows the classification of dyes based upon both colours and structures.

Colours	Chemical Classification	Common Names
Yellow and Brown	Flavone Dyes	Quercitron, Tesu
Yellow	Iso-quinoline Dyes	Barberry
Orange- Yellow	Chromene Dyes	Kamala
Brown	Naphthoquinone Dyes	Henna , Alkanet
Black	Benzophyrone Dyes	Cochineal , Madder
Blue	Indigoid Dyes	Logwood
Red	Anthraquinone Dyes	Indigo
Neutrals	Tannins	Pomegranate, Eucalyptus

Table 1.

Commercialization of natural dyes can be done successfully by a systematic and scientific approach to extraction, purification and use. Optimization of extraction condition is a must to minimize the investment cost and to avoid discrepancy in the dye shade quality. Natural dyes occur in many plant parts in small quantities and as complex mixtures with many chemical compounds of similar or different structures. These compounds vary considerably with change in general, same genus but different species and ecological conditions of the plant source. So when natural dyes extracted from these sources are used for dyeing and printing, variation in shade, depth and tone, among others, may arise. Further, chemical components of plants change with age and maturity of the parts. Extraction may include drying, pounding, soaking, skimming, crystallizing, condensing, caking and liquidifying, among others, depending on the quality and species of the dye yielding plant, mineral and insect (Shrivastava and Dedhia, 2006; Vankar *et al.*, 2000).

Synthetic dyes are a class of highly coloured organic substances, primarily utilized tinting textiles that attach themselves through chemical bonding between the molecules of dye and that of fiber. The use of natural dyes in textiles was eliminated since synthetic dyes give variety of reproducible shades and colours (Deo and Desai, 1999). Synthetic dyes are classified on the basis of chemical structure or on the basis of methods of application to the material. Dyes are synthesized in many ways by using different chemicals. On the basis of methods of application dyes are categorized as:-

Acid dyes: These dyes are anionic and form ionic bonds with fibers that are cationic in acid solutions. These dyes are applied onto the acrylic, wool, nylon and nylon/cotton blends. These are called acidic because they are normally applied to nitrogenous fibers in inorganic or organic acid solutions.

Azoic dyes: These dyes contain azo component ($-N=N-$), used for dyeing of cotton fabrics. In the dyeing process fiber is first treated with coupler followed by application of azo dye. This type of dye is extremely fast to light.

Basic dye: These dyes are cationic and form ionic bonds with anionic fibers such as acrylic, cationic dyeable polyester and cationic dyeable nylon. These are amino derivatives used mainly used for application on paper

Disperse dyes: These dyes are colloidal and are soluble in hydrophobic fibers. Mostly these dyes are used for coloring polyester, nylon, and acetate and triacetate fibers. They are usually applied from a dye bath as dispersion by direct colloidal absorption method

Direct dyes: These are also azo dyes applied generally on cotton-silk combination from neutral or slightly alkaline baths containing additional electrolyte. These dyes predominantly interact and attach themselves with the Matrix (wool , polyamide fabric) through electrostatic interactions. These dyes are used to color cellulose, wool, nylon, silk etc.

Reactive dyes: Reactive dyes are the best choice and other cellulose fiber at home or in the art studio. Fixation of dye occur onto the fiber under alkaline conditions by forming a covalent bond between reactive group of dye molecule and OH, NH, SH etc groups present in the fibers (Cotton, wool, silk, nylon etc).

Mordant dyes: Applied in conjunction with chelating salts of Al, Cr and Fe. Metallic salts or lake formed directly on the fiber by the use Al, Cr or Fe salts which cause precipitation in situ.

Sulfur dyes: These dyes are used for dyeing cotton and rayon. The application of this dye requires careful process due to its water-soluble reduced form and insoluble oxidized form. These dyes are fast to washing but poorly fast to chlorine and give dark and dull colors.

Vat dyes: These dyes are insoluble in water and cannot be directly applied to textiles. These dyes require oxidation as well as reduction step for its application onto matrix.

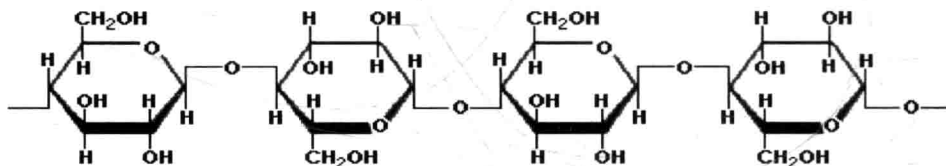
Acetate rayon dyes: Developed for cellulose acetate and some synthetic fibers (Kim *et al.*, 2005; Shenai, 1992).

Dyes are synthesized in a reactor, filtered, dried, and blended with other additives to produce the final product. The synthesis step involves reactions such as sulfonation, halogenation, amination, diazotization, and coupling, followed by separation processes that may include distillation, precipitation, and crystallization. In general, organic compounds such as naphthalene are reacted with an acid or an alkali along with an intermediate (a nitrating or a sulfonation compound) and a solvent to form a dye mixture. The dye is then separated from the mixture and purified. On completion of the manufacture of actual colour, finishing operations, including drying, grinding, and standardization, are performed. These steps are important for maintaining consistent product quality.

3. Chemistry of fibers

Cotton the most abundant of all naturally occurring substrates and is widely used. For the fabric strength, absorbency quality, capacity to be washed and dyed, cotton has become the principal clothing fabric of the world. The materials characteristically exhibit excellent physical and chemical properties in terms of water absorbency, dye ability and stability and can not be entirely substituted by artificial polymer fibers (Jun *et al.*, 2001).

The cellulose consists of glucose units linked together through oxygen atoms, 30 to several hundred chains from micro fibrils (Foldvary *et al.*, 2003). By dry weight 94% of cotton is made up of cellulose. The remaining constituents include 1.3% protein, 1.2% pectic substances, 0.6% waxes, 1.2% ash, and 4% of other components. Of three hydroxyl groups on the cellulose ring, two are secondary, and one is primary. Most of the reactions with cellulose occur at the primary hydroxyl groups.

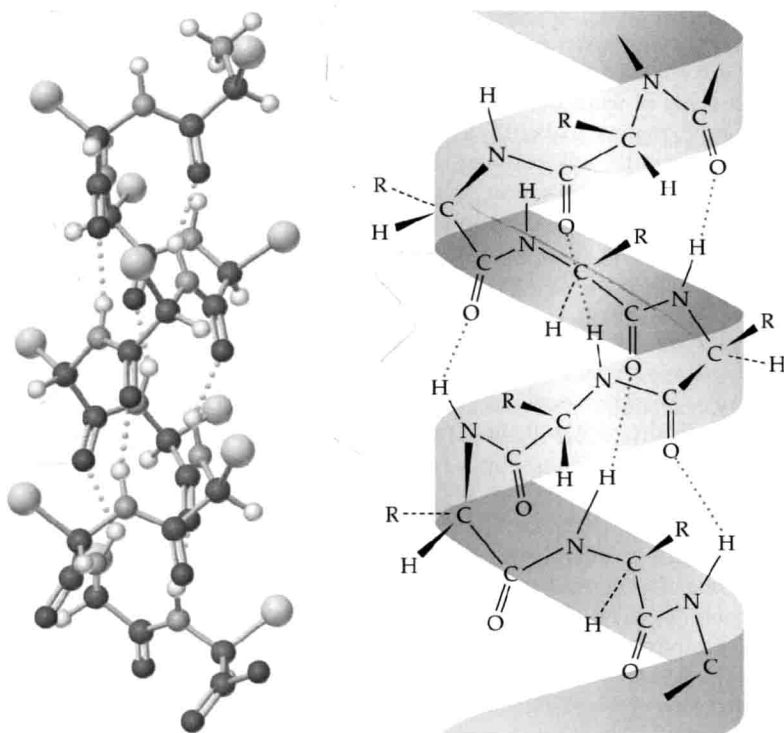


When cellulose is chemically modified with the compounds containing cationic and anionic groups, the molecular chains are modified. In the modified fiber surface, the chemical and

physical properties of cellulose fiber are changed. Through chemical modification, the reactivity of the cellulose fiber is enhanced. And several classes of dyes such as direct, azo, reactive etc can be successfully applied. The application of the cationic dyes has not gained widespread success. Our study comprises of the treatment method such as high energy radiation treatment which may create the anionic centre in the fabric to transfer the cationic dye onto the physically or chemically modified fabric. The reports of modified cellulose with the compounds containing multifiber cationic and anionic groups are scarce (Kim *et al.*, 2005).

Wool is different to other fibers because of its chemical structure that influences its texture, elasticity, staple and crimp formation. It is composed of keratin-type protein having more than 20 amino acids and very small amount of fat, calcium and sodium. The amino acids in wool linked together in ladder-like polypeptide chain to form a protein/polymer type structure.

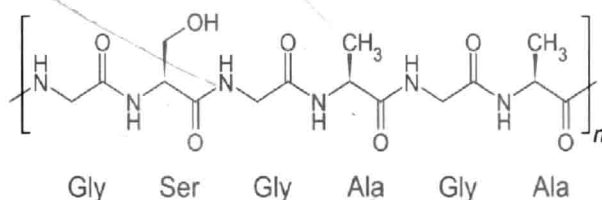
Wool polymer contains some important chemical groups that able to form inter-polymer forces of attraction. These groups are: the polar peptide groups (i.e. $-\text{CO}-\text{NH}-$) and the carbonyl groups ($-\text{CO}-$), which forms hydrogen bonds with the slightly positively charged hydrogen of the amino groups ($-\text{NH}-$) of another peptide groups. There are also carboxylate groups ($-\text{COO}-$), and amino groups ($-\text{NH}_3^+$) present in wool as side groups, between these two groups salt linkages or ionic bonds may be formed. Finally, the existence of the above mentioned inter-polymer forces tends to make the van der Waals' forces rather significant (Tamada, 2004).



Wool is easy to dye since the surface of the wool fiber diffuses light giving less reflection and a softer colour. The proteins in the core of the fiber absorb and combine with a wide variety of dyes and allow the wool to hold its colour (Michael and El-Zaher, 2005).

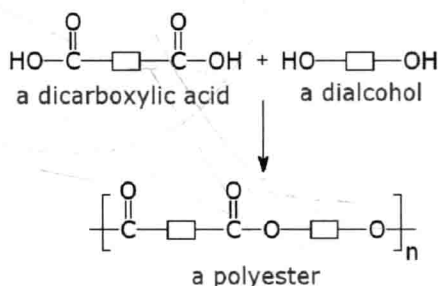
Silk is an insect fiber comes from the silkworm that spins around itself to form its cocoon. A single filament from a cocoon can be as long as 1600 meters. It is considered an animal fiber because it has a protein structure. Like other animal fibers silk does not conduct heat, and acts as an excellent insulator to keep our bodies warm in the cold weather and cool in the hot weather. The flat surfaces of the fibrils reflect light at many angles, giving silk a natural shine.

Natural and synthetic silk is known to manifest piezoelectric properties in proteins, probably due to its molecular structure. Silk emitted by the silkworm consists of two main proteins, sericin and fibroin, fibroin being the structural center of the silk, and sericin being the sticky material surrounding it. Fibroin is made up of the amino acids Gly-Ser-Gly-Ala-Gly-Ala and forms beta pleated sheets. Hydrogen bonds form between chains, and side chains form above and below the plane of the hydrogen bond network (Ellison, 2003).



Silk polymer is composed of sixteen different amino acids where as wool polymer contains twenty amino acids of wool polymer. Three of these sixteen amino acids namely, alanine, glycine and serine, make up about four-fifth of the complete polymer chain. The important chemical groupings of the silk polymer are the peptide groups which give rise to hydrogen bonds, the carboxyl and amine groups give rise to the salt linkages. The high proportion (50%) of glycine, which is a small amino acid, allows tight packing and the fibers are strong and resistant to breaking. The tensile strength is due to the many interceded hydrogen bonds, and when stretched the force is applied to these numerous bonds and they do not break (Jun and Chen, 2006)

Polyester was first introduced to the American public in 1951 by W.H. Carothers Laboratory. It was advertised as a miracle fiber that could be worn for 68 days without ironing and still look presentable. Polyester was once hailed as a magic fiber capable of being washed, scrunched and pulled on without showing any signs of water or wrinkles.



Now it is remembered for its bright double knit fabrics and comfortable texture. The name "polyester" refers to the linkage of several monomers (esters) within the fiber. Polyester is long chain polymer chemically composed of at least 85% by weight of an ester and a dihydric alcohol and a terephthalic acid (Kiran, 2009).

Polyester Cotton (PC) is a blend of polyester and cotton in varied proportions. This particular fabric is well received by customers around the world. The yarn is available in single and twisted form. The polyester cotton (PC) fabric yarn commonly has a blend ratio of 50% polyester to 50% cotton. In polyester cotton fabric (PC), polyester provides wrinkle resistance and shape retention while cotton provides absorbency and consequent comfort (Hunger, 2003).

4. Irradiation in textiles

Irradiation processes have several commercial applications, in the coating of metals, plastics and glass, in printing, wood finishing, film and plastic cross linking and in the fields of adhesive and electrical insulations. The advantages of this technology are well known energy saving (low-temperature process), low environmental impact, simple, economical and high treatment speed. Despite these advantages, there have been few applications of radiation curing in the textile industry, such as non woven fabric bonding, fabric coating and pigment printing (Ferrero and Monica, 2011). Radiation treatment on fabric and garments can add value in colouration. Modification of the surface fiber can allow more dye uptake; its fixation at low temperature and increase wettability. Cotton knitwear pilling can be eliminated from the surface of the fabric by radiation treatment without affecting the strength of the fiber (Kim *et al.*, 2005). Effect of UV radiation in natural as well as synthetic dyeing using irradiated cotton fabric has given significant results.

4.1 Effect of UV and gamma radiation on the fabric dyed with natural dyes

There is a remarkable difference in colour strength when different extracts of irradiated and un-irradiated turmeric powder were used to dye the irradiated and un-irradiated fabric (Afifah *et al.*, 2011). The methanol solubilized extract gave more colour strength than aqueous (heat) solubilized and alkali solubilized extract as displayed in Fig. 2. The low colour strength using alkali solubilized extract is due to alkaline degradation of curcumin into products like vaniline, vanilic acid, feruloylmethane, ferulic acid and other fission products, which sorb on the fabric along with colourant and impart dull redder shades (Tonnesen and Karlsen, 1985a). While using (heat) aqueous solubilized extract, the colourant being insoluble in water may undergo hydrolytic degradation and the actual colourant concentration becomes low onto the fabric as a result low colour strength is observed (Tonnesen and Karlsen, 1985 b). By using methanol solubilized extract, the actual colourant gets significant chance to sorb onto fabric and impart yellow colour with dark shades.

The irradiation of fabric is also another factor which affects the colour strength of the fabric. Previous studies show that UV irradiation adds value to colouration and also increases the dye uptake ability of the cotton fabrics through oxidation of surface fibers of cellulose (Millington, 2000; Javed *et al.*, 2008). The colourants from Methanol solubilized extract reach the vicinities of fibres and upon investigation of colour strength using spectraflash SF 650, dark yellow shade was observed. In the case of un-irradiated fabric, the insoluble impurities get significant chance to sorb on the matrix along with colourant which showed the dull redder shades.

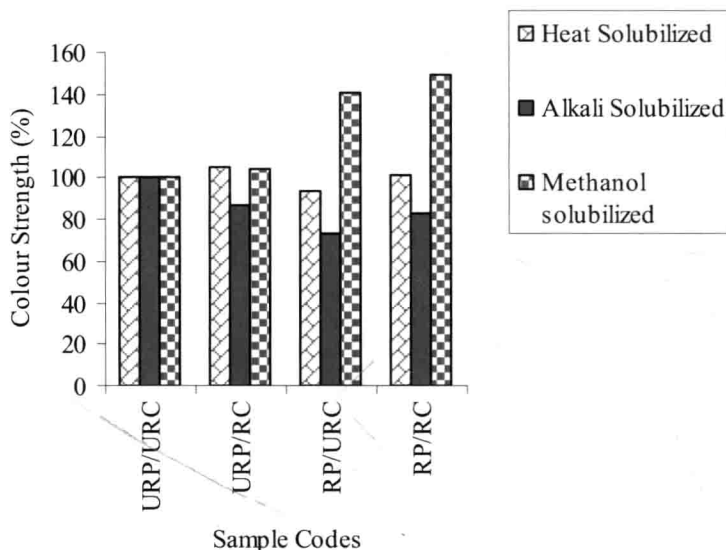


Fig. 2. Effect of UV radiation on the colour strength of the irradiated and un-irradiated cotton dyed with heat solubilized, alkali solubilized and methanol solubilized extract of irradiated and un-irradiated turmeric powder (Where URP-un-irradiated powder, RP – irradiated powder, RC- irradiated cotton fabric, URC-un-irradiated cotton fabric)

Gamma rays are ionizing radiations that interact with the material by colliding with the electrons in the shells of atoms. They lose their energy slowly in material being able to travel through significant distances before stopping. The free radicals formed are extremely reactive, and they will combine with the material in their vicinity. Upon irradiation the cross linking changes the crystal structure of the cellulose, which can add value in colouration process and causes photo modification of surface fibers. The irradiated modified fabrics can allow: more dye or pigment to become fixed, producing deeper shades, more rapid fixation of dyes at low temperature and increases wet ability of hydrophobic fibers to improve depth of shade in printing and dyeing (Millington, 2000).

The influence of gamma radiation on the colour strength values of the fabric dyed with natural dyes extracted from eucalyptus bark has been shown in Fig. 3. High colour strengths and dark brown shades of the fabric dyed in ethanolic extract were obtained as compared to aqueous extracts. The low colour strength and un-evenness in shade in aqueous extract is due to presence of insoluble impurities that might come on the fabric along with colourant. (Vankar *et al.*, 2000) The results shown in Fig. 3. demonstrate that irradiated fabric dyed using alcoholic extract gave more colour strength than un-irradiated fabric. Previous studies showed that gamma irradiation causes dislocation and fragmentation of fabric fibers (Foldvary *et al.*, 2003) however, only soluble colourant free from impurities get maximum chances to sorb on the fabric. But un-irradiated fabric contained less dye and yielded greener shade.

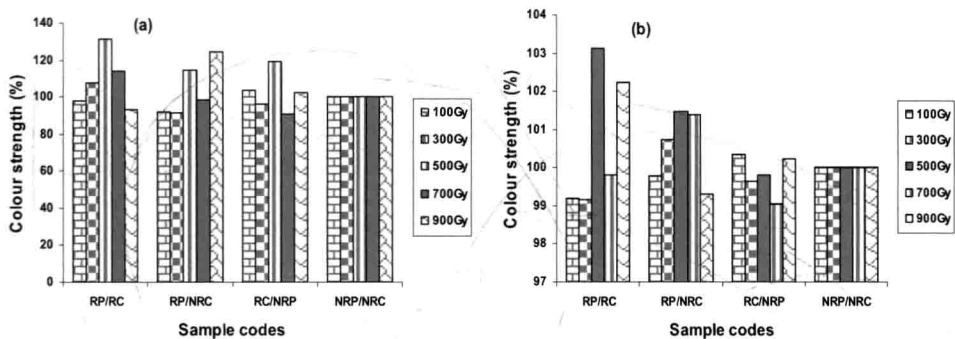


Fig. 3. Effect of gamma radiation on the colour strength of the cotton dyed with (a) ethanolic (b) aqueous extracts obtained form irradiated and un-irradiated Eucalyptus powder. NRP-un-irradiated powder, RP - irradiated powder, RC- irradiated cotton fabric, NRC-un-irradiated cotton fabric

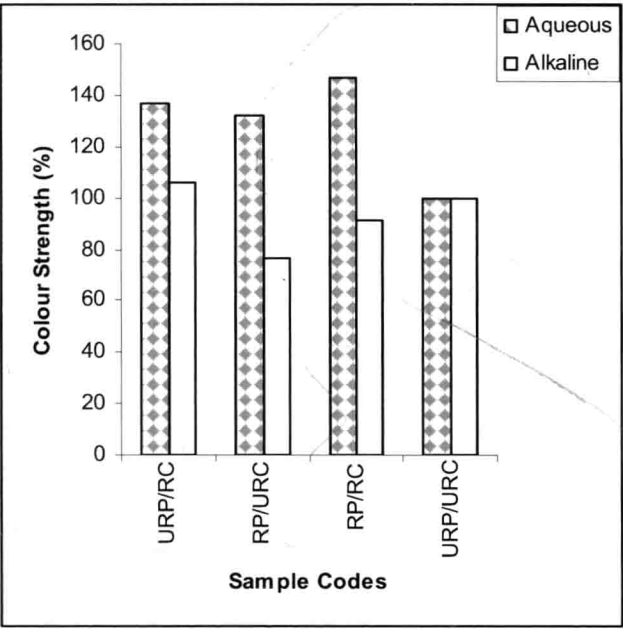


Fig. 4. Effect of gamma radiation on the colour strength of the cotton dyed with extracts obtained form irradiated and un-irradiated turmeric powder using aqueous and alkaline media (Where URP-un-irradiated powder, RP - irradiated powder, RC- irradiated cotton fabric, URC-un-irradiated cotton fabric)

The colour strength changes significantly in aqueous than in alkaline media. The fabrics dyed in aqueous extract of turmeric powder were darker yellow in shades than that of

fabrics dyed in alkaline extract. The low colour strength was due to alkaline degradation of curcumin into water-soluble products like vaniline, vanilic acid, feruloylmethane, ferulic acid and other fission products, which gave dull redder shades (Tonessen and Karlsen, 1985a). Tonessen and Karlsen reported that below pH 7, curcumin existed in yellow colour and is insoluble in water (Tonessen and Karlsen, 1985b). Due to insolubility, the colourant might have tendency to get absorbed completely on the fabric without passing through the medium and shows darker yellow shades. Hence irradiated fabrics dyed in aqueous media gave more colour strength than un-irradiated fabrics due to oxidative degradation of cellulose fibres. Treatment of fabric by high-energy radiation causes either dislocation and fragmentation or slight loss in mass of fabric (Foldvary *et al.*, 2003; Takacs *et al.*, 2000). However, only colourants get maximum chance to sorb on fabric than insoluble impurities. So more colour strength is obtained in case of irradiated fabric dyed using aqueous extract of irradiated turmeric powder. Thus it is found that if irradiated fabric dyed with aqueous extract of irradiated turmeric powder, maximum colour strength and darker yellow shade was obtained.

4.2 Effect of UV and gamma radiation on the fabric dyed with synthetic dyes

UV irradiation effects the colour strength values and shades of fabric dyed with synthetic dyes. Using suitable dye and fabric, the process of irradiation can produce large variation in shades.

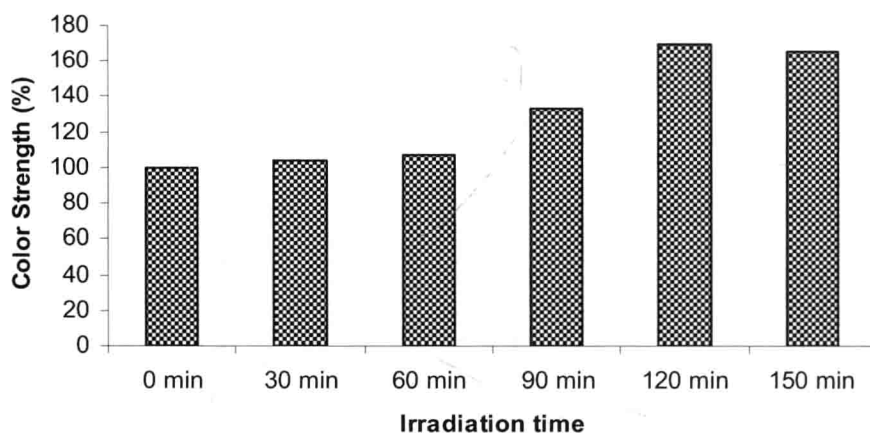


Fig. 5. Effect of UV irradiation time on the colour strength of the irradiated cotton fabric dyed with irradiated stilbene based reactive dye

The data displayed in Fig 5. shows that irradiated fabric for 120 min. gave maximum colour strength as compared to un-irradiated fabric. The fabric irradiated for 120 min. showed even shade with better colour strength. The reason might be the oxidation of cellulose upon exposure to UV radiation. Michael and EL-Zaher in 2005 reported that the UV treatment of cellulose fibre created spaces between fibres which imbibed more dye and as a result the interaction between dye and cellulose fabric becomes more significant. The dye molecules rush rapidly onto the fabric and as a result darker shades were obtained (Tayyba, 2010).