TREATMENT OF TEXTILE EFFLUENT BY RADIATION FOR DYEING AND IRRIGATION PURPOSE

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DECLARATION

I, Muhammad Abdur Rahman Bhuiyan, declare that the contents of this thesis represent my own unaided work, and that the thesis has not previously been submitted for academic examination towards any qualification (except for publication).

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The Author

DEDICATION

For my mother, who supports and loves me unconditionally

ABSTRACT

This research demonstrated the scope of using high energy gamma radiation for textile wastewater treatment and studied the possibility of recycling the irradiated water for fabric processing and reusing in irrigation purposes. The treatment was carried out in Cobalt-60 gamma radiation source at different irradiation doses (3, 5, 8 and 12 kGy) with a dose rate of 13 kGy/h. The change of pH, decoloration percentage, reduction of total suspended solids (TSS), total dissolved solids (TDS), biological oxygen demand (BOD_5) chemical oxygen demand (COD), variation of electrical conductivity (EC) and heavy metal content of irradiated wastewater were extensively investigated. It was observed that, colored wastewater become almost colorless due to the breakage of the chromophoric groups of the dye molecules by gamma irradiation. Smaller organic compounds (mainly acidic) were formed due to the fragmentation of large dye molecules that results the reduction of pH of the irradiated wastewater. Total suspended solids (TSS), COD and BOD_5 were also decreased significantly because of the degradation of the organic solid particles. However, the change of TDS, EC and metal content were found less for treated wastewater after application of gamma irradiation. The irradiated wastewater was recycled to the pretreatment (chemical singeing, scouring and bleaching) and dyeing of cotton knit fabric with reactive dyes. The detailed experimental results demonstrated that, the irradiated water performed perfectly as an alternative to the fresh water in the pretreatment of cotton knit fabric samples. The chemical singeing, scouring and bleaching performance i.e. weight loss, visual appearance, absorbency and whiteness of fabric was found almost similar to the fabric treated with fresh water. The performance of the fabric dyed with treated wastewater was also compared with the fabric dyed with fresh water by analyzing the depth of shades of both types of dyed fabrics from the measurement of absorption spectrum (K/S value versus

wavelength). The absorption curves of fabric dyed by irradiated wastewater at light, medium and deep shade of three different colors have shown close match to their corresponding fresh water dyed fabric. Variation of shade between the dyed fabrics, representing by ΔE values, were also found within the maximum acceptable limit as it ranges from 0.1 to 0.75. The color fastness of dyed fabric was also assessed with respect to perspiration, rubbing and washing. In case of color fastness, both types of fabrics have shown similar rating (4 to 5) which lies between ‘good’ to ‘excellent’. Furthermore, the absence of carcinogenic azo dyes and formaldehyde in the cotton fabric dyed with irradiated water signifies the nontoxicity of the fabric for human health. The irradiated wastewater was also used for irrigation of Malabar spinach plant and its growth was compared with controlled plant that uses normal underground water. Remarkable results have been noticed for the plant growth, leaves count and root length of plant irrigated with irradiated wastewater. This unusual enhancement of various growth factors of Malabar spinach indicated that, gamma radiation degrades the textile dyes and create nitrogeneous compounds that may supply the various nutrients to the plant and acts as a biofertilizer. The mineral content of the plant was also analyzed by using a Tandem accelerator and the results showed significant increase of minerals content for the plants irrigated with treated wastewater than the plants irrigated with fresh water.

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LIST OF ABBREVIATIONS

AEC	Atomic Energy Commission
AERE	Atomic Energy Research Establishment
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
DAS	Days After Sowing
DO	Dissolved Oxygen
DOE	Department of Environment
EC	Electrical Conductivity
ETP	Effluent Treatment Plant
mgL^{-1}	Milligrams per Liter
owf	On the Weight of Fabric
ppm	Parts per Million
TDS	Total Dissolved Solids
TSS	Total Suspended Solids

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CHAPTER ONE

INTRODUCTION

1.1 Background

Textile industries have great significance in terms of economic contribution as well as employment generation in Bangladesh. The textile industry of Bangladesh, which includes knitwear and ready-made garments along with specialized textile products, is the nation's number one export earner. There are 1821 small and large knit dyeing industries in Bangladesh (BKMEA, 2012). Apart from this, there are also many printing, garments washing and woven dyeing factories for the processing of textile materials.

The dyeing and finishing of textiles covers a wide range of treatments and processes used for altering the appearance and properties of textile products. The most basic of these are desizing, scouring, bleaching, washing, dyeing and drying and the textile may be in the form of a yarn, woven or knitted fabric or even in the complicated garments (Broadbent, 2001). Huge amount of water is consumed in several stages to get finished products in a textile processing plant.Nearly 70 to 150L water is required for the processing of 1 kg cotton fabric (Allègre et al., 2006). Textile processing generates various types of waste streams, including water-based effluent as well as air emissions, solid wastes and hazardous wastes. The nature of the waste generated depends on the types of fibers and the chemicals used, the type of textile facility, and the processes and technologies being operated.

1.1.1 Water Consumption in Textile Industry

Textile processing industry is characterized not only by the large volume of water required for various unit operations but also by the variety of chemicals used for various processes (Cooper, 1995). There is a long sequence of wet processing stages requiring inputs of water, chemical and energy and generating wastes at each stage. The other feature of this industry, which is a backbone of fashion garment, is large variation in demand of type, pattern and color combination of fabric resulting into significant fluctuation in waste generation volume and load. The large volume of generated wastewater also contains a wide variety of chemicals used throughout the processing and discharge into sewers and drains without any kind of treatment As a result, textile industries are creating agonizing problems by polluting the existing water bodies and depleting the groundwater level.

Table 1.1: Water requirements for cotton textile wet finishing operations

Process	Requirements in liters/kg of product
Singeing	0.5-8.2
Desizing	2.5-21
Scouring	20-45
Bleaching	2.5-25
Mercerizing	17-32
Dyeing	10-60
Printing	8-16

Amount of water consumed in textile wet processing depends to a large extent on machine design and complexity of process. Different machines have their own characteristic features that set lower limits to the amount of water required e.g. machines such as winch or hank dyeing machine work at material to liquor ratio of at least 1:10-15 while jigger works at 1:3 (Broadbent, 2001).

Table 1.2: Percentage of water usage in textile mills (Shaikh and Ayaz, 2009)

Purpose	Percentage of Water Use	
	Cotton Textile	Synthetic Textile
Steam generation	5.3	8.2
Cooling water	6.4	9.5
Demineralization for specific purpose	7.8	30.6
Process water	72.3	28.3
Sanitary use	7.6	4.9
Miscellaneous and fire fighting	0.6	28.0

Many detailed surveys reveal remarkably wide variations in quantities of water used, Average consumption in the scouring and bleaching of cotton fabrics was found to be in the range of 10-80 lit/kg and 10-130 lit/kg respectively depending on the machine and process employed. In another survey carried out at wool processing mills the average consumption of water for various unit processes showed marked variation and the average consumption appeared to be higher than necessary for efficient scouring, milling and dyeing. In case of consumption of water by various types of washing machine, some information has been published. The cost determining factors in this case are water hardness, level control, spray devices, water pressure and washing temperature.

1.1.2 Nature of Textile Wastewater

The textile industries have been condemned as being one of the world's worst offenders in terms of pollution because these industries discharge millions of gallons of effluent each year, full of perilous chemicals, heavy metals and others (cooper, 1995), which are significant causes of environmental degradation and human illnesses. The mill effluent is also often of a high temperature and pH, both of which are extremely damaging. The nature of the pollution that accompanies the dyeing industries is primarily due to the non biodegradable nature of the dyes along with the strong presence of significant amounts of toxic trace metals, acids, alkalis and carcinogenic aromatic amines in the effluents (Correia et al., 1994). The main pollutants are organic matters which come from the pretreatment processes i.e. desizing, scouring and bleaching of cellulosic fibers as well as dyes and auxiliaries used in dyeing and printing process.

Figure 1.1: Highly colored wastewater discharged from the dyeing industry

The world production of colorants is 1 million tonnes per year, of which 50% are textile dyes (Nousiainen, 1997). During the dyeing of textile materials, not all the dye is fixed to the fiber during the dyeing process. A considerable amount (10-40%) of unfixed hydrolyzed dyes remains in textile wastewater causing highly colored effluent discharge (Cooper, 1993). The problems associated with the discharge of color from dye houses has concerned both industrial and academic scientist for at least four decades in most industrialized countries. The reactive dyes used for cotton have the poorest fixation rate, and since 52% of the textile-fiber market is cotton (Bashar & Khan, 2012), most colored effluent problems arise from dyeing cotton with reactive dyes. Heavy metals are associated with the effluents from wool dyeing (Broadbent, 2001).

Table 1.3: Estimated degree of fixation of different dye/fiber combination (Cooper, 1995)

Dye class	**Fiber**	**Degree of fixation %**	**Loss to effluent %**
Acid	Polyamide	80-95	5-20
Basic	Acrylic	95-100	0-5
Direct	Cellulose	70-95	5-30
Disperse	Polyester	90-100	0-10
Metal complex	Wool	90-98	2-10
Reactive	Cellulose	50-90	10-50
Sulphur	Cellulose	60-90	10-40
Vat	Cellulose	80-95	5-20

Many textile manufacturers use dyes that release aromatic amines (e.g., benzidine, toluidine). Dyebath effluents may contain heavy metals, ammonia, alkali salts, toxic solids and large amounts of pigments-many of which are toxic. About 40 percent of globally used colorants contain organically bound chlorine, a known carcinogen. Natural dyes are rarely low-impact, depending on the specific dye and mordant used. Mordants (the substance used to "fix" the color onto the fabric) such as chromium are very toxic and high impact. The large quantities of natural dyestuffs required for dyeing, typically equal to or double that of the fiber's own weight, make natural dyes prepared from wild plants and lichens very high impact.

1.1.3 Ecological Problems due to Textile Wastewater

Water usage in textile processing plants are produced millions gallons of colored wastewater and extensively contaminated the rivers, canals and surface waters due to the direct discharge of effluent by the industries. The variety and massive quantities of fibers used in textile manufacturing, even trace contaminants associated with them can accumulate into amounts, which may cause large scale pollution. At the same time, the usage of water as a vehicle for wet processes and a number of intermittent washing operations have the effect of diluting the pollutant concentrations. This makes the recovery of pollutants or discharged useful chemicals either impossible or uneconomical. The sequences in the manufacture of textile apparel, as far as wet processing is concerned, are slashing and sizing of yarn followed by fabric formation, desizing, preparation, dyeing, printing and finishing. In addition to the air and water pollutants released due to the chemical entities used, a considerable amount of packaging waste, yarn waste in spinning, fabric waste from weaving, preparation and dyeing is also generated.

Figure 1.2: Pollution of surface water by textile processing industry

Discharged wastewater by some industries under uncontrolled and unsuitable conditions is causing significant environmental problems. The importance of the pollution control and treatment is undoubtedly the key factor of the human future. High values of COD and BOD, presence particulate matter, sediments, oil and grease in the effluents causes depletion of dissolved oxygen, which has an adverse effect on aquatic ecological system (Wang et al., 2006). Industrial pollution is known to bring the changes in the abiotic and biotic components of the ecosystem. Textile and dyeing industrial effluents may cause alteration of the physical, chemical and biological properties of the aquatic environment by continuous change in temperature, odor, noise, turbidity etc. that is harmful to public health, live stock, wildlife, fish and other biodiversity (Haque et al., 2002). Effluents from textile mills also contain chromium, which has a cumulative effect and has higher possibilities to enter into the food chain.

Some auxiliary chemicals used during dyeing may have an adverse environmental impact. Although their function is to assist effectively the adsorption and fixation of the dyes into the fibers, they are unlikely to be consumed completely during the dyeing process and hence, may lead to pollution load on rinsing the dyed material using large amounts of water. The spent dye bath contains varieties of such auxiliary chemicals including salt with each one having a different environmental impact (Christie, 2007). Formaldehyde, which is widely used in the synthesis of auxiliaries, such as dye-fixing agents in direct and reactive dyeing and printing or dispersing agents for disperse and vat dyeing, is a respiratory sensitizer and skin irritator (Shenai, 2001). The dyeing of cotton with sulphur dyes by using the toxic sodium sulphide, which is hazardous to health and environment (Chavan et al., 2002).

The presence of dyes in surface and subsurface water is making them not only aesthetically objectionable but also causes many water borne diseases, viz. mucus membrane, dermatitis, perforation of nasal septum and severe irritation of respiratory tract (Lima et al., 2007). Traditionally produced fabrics contain residuals of chemicals used during their manufacture-chemicals that evaporate into the air we breathe or are absorbed through our skin. Some of the chemicals are carcinogenic or may cause harm to children even before birth (Robinson et al., 2001), while others may trigger allergic reactions in some people.

1.1.4 Textile WastewaterTreatment

Textile wastewater containing varying concentrations of both organic and inorganic compounds (Libra &Sosath, 2003). Treating industrial textile wastewater is complicated due to the high levels of biological oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS) and nonbiodegradable nature of the organic dyes present in the wastewater (Badani et al., 2005; Kim et al., 2002). The color of the textile wastewater is not removed efficiently by ordinary treatment technology. Typical techniques for treatment of wastewater include the classical methods such as adsorption (Qada et al., 2008; Hameed et al., 2007; Rauf et al., 2007), coagulation (Ahmad & Puasa, 2007; Shi et al., 2007), filtration (Mo et al., 2008) and sedimentation (Bagyo et al., 1997). All these techniques have some degree of effectiveness but all of them generate secondary waste which needs to be tackled further (Rauf& Ashaf, 2009). On the contrary, biological treatment based on activated sludge can efficiently reduce the COD but complete color removal is not possible with this technique (Bes-Piá et al., 2002). Because dyes are required to show a high degree of chemical and photolytic stability in order to fulfill the fastness requirements of both retailers and consumers. One consequence of this stability is that they are not readily degraded under the aerobic conditions prevailing in the biological treatment plant at a sewage treatment works. Moreover, huge space is required to set up a biological plant. In addition, applications of membrane technologies in textile industries are not yet very common (Bes-Piá et al., 2002). Again the ultra-filtration techniques prove its success mainly for the recovery of size materials from desizing effluent and indigo dye particles from the discharged dye liquor(Şolpan & Güven, 2002).

In this regard ionization radiation technology is the promising technique to decolorize and decompose the textile wastewater (Getoff, 1999) with no further generation of secondary waste. The radiation technology methods normally utilize a strong oxidizing species such as $^{\bullet}OH$ radicals which have high electrochemical oxidation potential and cause a sequence of reactions thereafter to breakdown the macromolecules of dye into smaller and less harmful substances (Bagyo et al., 2001). High energy radiation produces instantaneous radiolytic transformation through energy transfer from high energy accelerated electrons to the orbital electrons of water molecules. Absorbed energy disturbs the electron system of the molecule resulting in the breakage of interatomic bonds and ionizing the water molecules forming H_2O^+. Various active species are generated due to the radiation interaction between gamma rays and water. Generally these species are hydroxyl radical ($^{\bullet}OH$), hydrogen radical ($H^{\bullet}$), hydrated electron (e^-_{aq}), and hydrogen peroxide (H_2O_2) and so on (Rauf et al., 2007). Among these products, the most reactive species are hydroxyl radical, hydrated electron. Hydroxyl radical attacks the conjugated double bond of the dye particle and breaks it (Rauf et al., 2007). Thus the colored dye molecules produce colorless smaller molecules which results in the decoloration of the effluent.

1.1.5 Reuse and Recycle of Textile Wastewater

The textile industry is a water intensive industry (Brik et al., 2006; Badani et al., 2005; Chakraborty et al., 2003) because water is used as medium for the processing of textile materials. In Bangladesh knit dyeing industries have grown rapidly, where reactive dyes are used extensively. Again among the textile fibers about 48% cotton fibers consumed as clothing materials all over the globe (Bashar & Khan, 2012; Broadbent, 2001) and 20% of those are dyed with reactive dyes (Broadbent, 2001). They are water soluble anionic dyes exhibit one or more functional group capable of forming covalent bond with cellulose and are not suitable for recycling (Erswell et al., 1988). A considerable amount (10-40%) of unfixed hydrolyzed dyes remains in textile wastewater causing highly colored effluent discharge (Cooper, 1993). Thus reactive dye is the main culprit as the pollution source in the textile industry of Bangladesh. The wastewater generated in textile processing plants is contaminated with toxic synthetic colorants and various perilous chemicals such as heavy metals, surfactants, inorganic salts, organic helogens (AOX), acids, alkalis and carcinogenic aromatic amines.

The rivers, canals and streams of Bangladesh are extensively contaminated with textile wastewater due to the direct discharge of effluent by the industries. As a result, textile industries in Bangladesh are creating agonizing problems by polluting the existing water bodies and depleting the groundwater level. These conditions will make the life unsafe and will not support the sustainable development of textile industries in Bangladesh. Likewise, due to increasing population, the industries have to face the pressure to recover and reuse some of its wastewater, or face the danger of being shutdown (Tang & Chen, 2002). This is due to the combined pressure of increasing water demand and wastewater treatment costs. As a result, the reuse and recycle of wastewater has drawn a great attention to the researchers around the globe (Bruggen et al., 2001; Koyuncu et al., 2001; Gaeta et al., 1991; Ciardelli et al., 2001; Koyuncu, 2003).

The reuse of wastewater for agricultural irrigation has practiced in many countries of the world (Ajmal et al., 1981). The effluent contains organic and inorganic nutrients and may have a beneficial effect on the crops yield. The effluent can input greater amount of minerals for the better growth of crops due to the presence of micronutrients in wastewater higher than those of natural water (Jolly et al., 2008). The use of industrial wastewater for irrigation purpose can eliminate the surface water pollution and dependency on groundwater for irrigation. In addition, the recycling of treated colored wastewater can be an effective way to reduce the stream of effluent load. Wastewater can be recycled after removing the color by treatment, which leads the reduction of pollution of the existing water bodies and depletion the groundwater level.The main objectives of this study is to degradation of dye molecules and organic pollutants of textile wastewater by using gamma irradiation, investigation of physicochemical parameters of irradiated water, and analysis the scope of using treated wastewater for irrigation and dyeing purposes.

1.2 Objectives of the Research

With the rapid industrialization, the number of textile industries in Bangladesh is increasing day by. These industries carry out wet processing during finished fabric production and generate large volume of wastewater. This wastewater is extensively contaminated the rivers, canals and streams due to the direct discharge of effluent by the industries and create problems by polluting the existing water bodies and depleting the groundwater level. Due to increasing population of Bangladesh and raising the scarcity of fresh water, textile industries are facing the pressure to recover and reuse of its wastewater. The main objectives of this study is to treat the dyeing wastewater by gamma radiation and analysis the scope of using irradiated wastewater for reuse in irrigation and dyeing purposes. The research project has been initiatedto accomplish the following objectives:

- To treat colored dyeing wastewater by gamma irradiation.
- To determinethe physicochemical properties of textile wastewater after gamma irradiation such as pH value, Biochemical Oxygen Demand(BOD_5), Chemical Oxygen Demand(COD), Total Dissolved Solid(TDS), Total Suspended Solid(TSS), Electrical Conductivity (EC), heavy metal content and other parameters.
- To analyze the scope of treated effluent for irrigation and compare the growth, yield and nutritional value of plants grown with treated water and fresh water.
- To evaluate the application of gamma irradiated wastewater in fabric processing and compares the performance of the fabric processed with treated wastewater to that of the fabric with fresh water.

1.3 Organization of the Thesis

In pursuit of fulfilling the objectives of the research, five chapters are required to present and comprehend all the research writings and ultimate results.

Chapter one appears with background and present status of the problem, objectives and finishes with the organization of the thesis.

Chapter twodeals with the literature review-treatment of textile wastewater and also narrates the present wastewater treatment system and their limitation with the prospect and scope of using gamma irradiation for the treatment of textile wastewater.

Chapter three illustrates the methodology of the study and comprises with wastewater collection analysis, treatment of wastewater with gamma irradiation and investigation of required parameters. It also narrates the procedure and conditions of recycling and reuse of treated wastewater in dyeing and irrigation purpose. Detailed description of the experimental setup embrace is given, followed by experimental results and their analysis.

Chapter four titled ‘results and discussions’ show the analysis of physiochemical parameters of dyeing wastewater after treated with gamma irradiation, investigation of the performance of irradiated water used in dyeing purpose and comparison of yield and food value of vegetables irrigated with fresh water and gamma irradiated wastewater.

Chapter Five concludes the thesis by the summary of the findings and their discussion in the context of recycling and reuse of gamma irradiated wastewater and also recommendations of future study.

CHAPTER TWO

LITERATURE REVIEW

2.1 Treatment of Textile Wastewater

Industrial effluents have usually been discharged into municipal sewagesystems in developed countries since the 1920s. Previously, the majority ofsewage was discharged to tidal waters without any treatment. Little attentionwas paid to the color of wastewater until the 1980s and, even then, theobjections were on aesthetic grounds, since it was known that modern dyestuffsare relatively non-toxic.

At the beginning of the 1970s, only physical treatment methods such as sedimentation and equalization were applied to maintain the pH, total dissolved solids (TDS) and total suspended solids (TSS) of the discharged water. There were no obligatory discharge limits for the color of the effluent at that time. Secondary treatments such as the use of filter beds for biodegradation and, more recently, the introduction of the activated sludge process (aerobic biodegradation) have reduced the toxicity of sewage water considerably. As a result, much of the water is now discharged to local rivers. However, sewage treatment works have often been unable to remove the color from dyehouse effluent completely, especially when reactive dyes are included, and this causes the receiving river water to become colored. As a result, there have been complaints by the public, who are becoming increasingly aware of environmental issues.

Treatment of large volumes of effluent is a very costly process and investment in effluent treatment is often considered a waste of money as it makes no contribution to profit for an industrial company. However, textile wet processing is now under threat in many countries because of the tightening of discharge limits for effluents by environmental agencies. The problems associated with the discharge of color from dye houses has concerned both industrial and academic scientist for at least four decades in most industrialized countries. Studies of thirty different techniques under the heading such as coagulation, flocculation and precipitation, oxidation, adsorption, electrolysis, biological treatments and membranes were carried out for the treatment of dyeing wastewater.

2.1.1 Coagulation, Flocculation and Precipitation

Coagulation and flocculation of the inorganic coagulants such as lime, aluminum, magnesium and iron salts have been used for coagulation in the treatment of wastewater (Aguilar et. al., 2005). The technology is simple and a wide variety of products are on the market to accomplish this purpose. Coagulation methods are useful in reducing the amount of color in textile waste, but give only partial color removal and reduction in COD (Christie, 2007). The principle of this process is the addition of a coagulant followed by a general rapid association between the coagulant and pollutants. Finally they form coagulate or flock and subsequently precipitate. The precipitate is then removed by flotation, settling, filtration or other physical techniques to generate a sludge that is normally further treated to reduce its toxicity (Golob&Ojstršek, 2005). In general terms, the technique requires pH control and the addition of either an inorganic or an organic species that will generate a precipitate. Organic anionic, cationic or non-ionic coagulant polymers have been developed in the last few years for color removal treatments and in general they offer advantages over inorganic: such as lower sludge production, lower toxicity and improved color removal ability (Zouboulis, et. al., 2004).

At least three major difficulties present themselves for coagulation. The first is that the process can be expensive. The user is paying for chemicals whose only purpose is to be thrown away. The solids created add to the solidwaste burden of the textile plant or to the municipal waste treatment facility. Secondly, dyes with high water solubility resist coagulation and larger additions of the coagulant may be required in order to achieve reasonable removal of color from the effluent. Naturally, this increases the cost and solid wasteload, as well as sometimes having a detrimental effect on oxidation of ammonia to nitrite and nitrates (nitrification) in the biological treatment plant.

Thirdly, the solid waste production requires that a suitable means of removing and disposing of coagulated dye waste must be added to what other solid waste is generated by the textile dyeing and finishing operation. Increasingly, the pressure from environmental regulators is to decrease solidwaste load, and any process that adds to solid waste load will cause additionalheadaches for the environmental manager of the textile plant.

2.1.2 Adsorbents and Adsorption

Dyes that are recalcitrant to biological breakdown can often be removed by using adsorbents. The adsorbents most investigated for various types of effluent treatment are dead plants and animal residues, known as biomass, which include charcoals, activated carbons, activated sludge, compost and various plants (Christie, 2007).

The most widely used adsorbent is activated sludge. Important factors affecting the optimum adsorption of color with activated sludge are its quality and concentration, the hardness of the water and the duration of the treatment. Although activated sludge is suitable for removal of various textile dyes, it alone cannot satisfy modern day's tight consent limits (Christie, 2007). Another adsorbent is activated carbon, but it is very expensive and, for reuse, needs to be treated with solvent. However, the solvent is also expensive and alternative treatments, such as thermal and homogeneous advanced oxidation treatments (UV/H_2O_2 and H_2O_2/O_3) have been investigated for this purpose (Mourand et. al., 1995). Activated carbon adsorbents are applicable within a wide range of pH, but color removal is mainly effective for non-ionic and cationic dyes (Christie, 2007). Unfortunately, most of the dyes used in the textile industry are anionic in their soluble form (Broadbent, 2001).

Since most of dyes are chemically either anionic (reactive dyes, acid dyes, direct dyes etc.) or cationic (basic dyes) they could be removed on ion exchange resins. Various ion-exchange resins derived from sugar cane bagasse, waste paper, polyamide wastes, chitin, etc., were applied as adsorbents for removal of color and other organics (Laszlo, 1996;Huang & Chen, 1993). Color-removal efficiency with these ion-exchange resins was comparable with that achieved using activated carbon. Most ion-exchange resins have poor hydrodynamic properties compared with activated carbon, and it is difficult for them to tolerate the high pressures required to force large volumes of wastewater through the bed at a high flow rate.The demerits of adsorbents are not only the added cost for making them reusable, but also the production of large volumes of sludge. This requires further treatment, such as incineration or dumping. Incineration causes air pollution and in some countries where land availability is not abundant, dumping will be expensive (Christie, 2007).

The color removal of textile wastewater can also be carried out by chitin (McKay, 1979) which is a by-product of the shellfish industry. Chitin contains ^-OH and $^-NH_2$ groups and has affinity for dyes. Investigation showed that chitin is only suitable for those dyes that are strongly anionic or weakly anionic in nature, but, even then, the dye separation is too low (only fractions of a mill equivalent per gram of chitin used (Smith et. al., 1993). It works as a weak-base anion-exchanger, but there is a problem of instability at low pH. Although this can be overcome by forming cross-links within the polymeric structure (chitin), this, in turn, results in a lowering of its dye binding capacity. Moreover, mixing of different classes of dyes and addition of surfactants reduces the color removal efficiency.

2.1.3 Separation Techniques

Various separation techniques including microfiltration, nanofiltration, ultrafiltration and reverse osmosis have been applied in the textile industry for the recovery of sizing agent from effluent (Cooper, 1995) and some of these methods have also been investigated for color removal. Among them, microfiltration is no use for wastewater treatment because of its large pore size, and the other separation systems have very limited use for textile effluent treatment (Cooper, 1995). Microfiltration can be used as a pretreatment for nanofiltration or reverse osmosis.

However, ultrafiltration and nanofiltration techniques were effective for the removal of all classes of dyestuffs (Marmagne&Coste, 1996) but allow water and some small molecule salts and organics to pass through. A combination of adsorption and nanofiltration can be adopted for the treatment of textile dye effluents. The adsorption step precedes nanofiltration, because this sequence decreases concentration of ions during the filtration process, which improve the process output (Chakraborty et. al., 2003). Nanofiltration membranes retain low molecular weight organic compounds, monovalent ions, divalent ions, hydrolyzed reactive dyes and dyeing auxiliaries. However, the dye molecules inside the membrane cause frequent clogging of the membrane pores. High working pressures, significant energy consumption, high cost of membrane and a relatively short membrane life have limited the use of these techniques for dye house effluent treatment (Christie, 2007).

Again reverse osmosis membranes have a retention rate of 90% or more for most types of ionic compounds and produce a high quality of permeate (Sadrghayeni et. al., 1998). Decoloration and elimination of chemical auxiliaries in dyehouse wastewater can be carried out in a single step by reverse osmosis. Reverse osmosis permits the removal of all mineral salts, hydrolyzed reactive dyes and chemical auxiliaries. It must be noted that, higher the concentration of dissolved salt, the more important the osmotic pressure becomes; therefore, the greater the energy required for the separation process. But reverse osmosis units are associated with high capital cost and relatively high running cost. The membranes in this unit have to be cleaned on a regular basis and may be attacked by the dye materials or other constituents of the effluents (Cooper, 1995). This may change the surface characteristic of the membrane, resulting in either a poorer quality permeate or premature membrane failure.

2.1.4 Biological Treatments

Biological treatments have been investigated for the treatment and color removal from wastewater by many researchers. Most biotreatment systems are based on living micro-organisms.Like most organic materials of animal andvegetable origin, dyes can be degraded into simpler compounds and arefinally mineralized to water and carbon dioxide by a wide variety of aerobicor anaerobic organisms (McMullan et. al., 2001). Thetreatments can be aerobic or anaerobic, i.e. with or without the presence of oxygen. In aerobic conditions, enzymes secreted by bacteria present in the wastewater breakdown the organic compounds. Various micro-organisms including the wood-rotting fungus and other micro-organisms have been investigated for color removal from textile and pulp bleaching effluents (Zhang et. al., 1999; Banat et. al., 1996).

Biological treatment can be carried out directly at the site of an industrialplant or in a communal sewage treatment plant. In both cases, living wholecell systems are typically used in mixed cultures of various types of microorganisms. In order to yield successful biotreatment, some requirements must be met.The micro-organisms must be kept healthy and active. It is important to keeptype and concentration of potentially toxic substances at a level that does notcause any serious damage to the micro-organism population (Beydilli et. al., 2000). Since dyedegradation is attributed to secondary metabolic pathways, appropriate growthconditions have to be accomplished by addition of a nutritional supply.Sufficient amounts of nitrogen- and phosphorus-containing nutrients mustbe present in the effluent.

Many factors such as concentration of pollutants, e.g. dyestuff concentration, initial pH and temperature of the effluent are persuaded the decolorization process (Lee et. al., 2006). After the fungal treatment, an improvement in the treatability of the effluent by other micro-organisms was observed. It was found that the aerobic or anaerobic degradation of effluent is not efficient for color removal (Cooper, 1995). Because dyes are required to show a high degree of chemical and photolytic stability in order to fulfill the fastness requirements of both retailers and consumers. The consequence of this stability is that they are not readily degraded under the aerobic conditions.Although biological treatments are suitable for some dyes but some of them are recalcitrant to biological breakdown (Crips et. al., 1990).Moreover, there is some concern that the presence of sulphates in the dye waste may give rise to hydrogen sulphide under anaerobic conditions (Cooper, 1995).

Pavlosthasis and co-workers investigated color removal from simulatedreactive dye wastewater by biological treatment. They found that more than 83% color removal was achieved for CI Reactive Yellows 3 and 17, Black 5, Blue 19 and Red 120, but only marginal color removal was achieved with Blue 4, Blue 7 and Red 2. Again no information is available about the stability of bacteria in the presence of high concentrations of salt, which might affect the decolorizationprocess, as high amounts of salt could be toxic to bacteria.

The effect of structural parameters of the dye on bioelimination is generallylinked to the mechanism of the treatment process. Since, in this case, poor solubility is of advantage, functional groups that confer high water solubility, such as, for example, sulfonic acid groups, are unfavorable. On the other hand, for biodegradation processes involving bacteria where intracellular digestion takes place, solubility and suitable polarity seem to be of advantage. Furthermore, it is important that the dye molecule is able to penetrate the cell wall and thus it should be of relatively smaller size. Large functional groups such as, for example, sulfonic acid groups may again prove unfavorable if too many are present. In general, sufficient bioavailability must be guaranteedin order to efficiently eliminate dye molecules.

2.1.5 Oxidation Treatments

Oxidation treatments are the most commonly used decolorization processes as they require low quantities and short reaction times. In the oxidation process, dyestuff molecules are oxidized and decomposed to lower molecular weight species such as aldehydes, carboxylates, sulphates and nitrogen, the ultimate goal being to degrade them to carbon dioxide and water. Various types of oxidant including chlorine, hydrogen peroxide, ozone and chlorine dioxide are used for color removal from wastewater.

Chlorine in the form of sodium hypochlorite has long been used for bleaching of textile materials. Water-soluble dyes such as reactive, acid, direct and metal complex dyes are decolorized readily by hypochlorite, but water-insoluble disperse and vat dyes are resistant to decolorization in this process (Namboodri et. al., 1994). If a dye is somewhat resistant to biological degradation, then pre-treatment with hypochlorite can improve the total mineralization. Decolorization of reactive dyes require long reaction times, while metal complex dye solution remains partially colored even after an extended period of treatment.

A major reason for not using sodium hypochlorite is the concern about producingchlorinated organic compounds, generally a much undesired scenario. In recent years, the emphasis on the elimination of chlorinated compounds from waste effluents has increased, and it is unlikely that the risk of creating more toxic compounds would be deemed worth the effectiveness that chlorination represents (Slokar et. al., 1997).

Again hydrogen peroxide by itself can be used for decolorization of colored dyeing wastewater. It is readily available, easily mixed with water, and is not expensive. It can be used todecolorize dyes and will generally lower the COD. Because it does not persist, it does not have a negative effect on any bacterial process. The disadvantages of using hydrogen peroxide include the long reaction timeneeded for effectiveness and the cost of equipment needed for storage. Withoutactivation, it is not a viable choice.

Hydrogen peroxide alone is not effective fordecolorization of dye effluent at normal conditions, even at boil (Namboodri et. al., 1995). However, incorporation with ferroussulphate (known as Fenton's reagent), peroxomonosulphuric acid, manganese dioxide, ferrous sulphate, ferric sulphate, ferric chloride or cupric nitrate, generates hydroxyl radicals, which are many times stronger than hydrogen peroxide. In acidic conditions, hydrogen peroxide generateshydroxyl radicals OHin the presence of ferrous ions. The OH radicals generated in the reaction attack organic molecules (hereunsaturated dye molecules) and thus render the dye colorless.In a study,five different types of simulated dye wastewaterwere treated with Fenton's reagent and it was found that decolorization was greatly affected by pH, the type of dye treated, the auxiliaries present in the wastewater, the temperature and the specific structure of the dyes themselves (Kuo, 1992).

The oxidation of disperse dyes by ozone, hypochlorite and Fenton's Reagent was performed (Szpyrkowicz et. al., 2001). The results by hypochlorite were not impressive, but ozone reduced colorby 90%, though the COD after ozone treatment was still quite high. This probably meant that the azo bond was broken (thus breaking up the chromophoric system) but with little further effect. Again more than 98% color removal was achieved with an 81% reduction in COD after the oxidation of methylene blue using Fenton's Reagent in controlled conditions (Dutta et. al., 2001).

Some decolorization systems such as adsorption, Fenton's reagent and electrochemical oxidation are effective as phase transfer processes in transferring toxic pollutants from liquid phase to solid phase, but they produce a large volume of sludge, which needs either incineration or dumping. Chlorine treatment increases toxicity by generating trihalomethane in the wastewater, as mentioned earlier. Biological treatment takes months for color removal and some dyes are recalcitrant to biological breakdown. In these respects, ozone seems to be the most convenient alternative because it does not produce any sludge or toxic byproducts. In the ozonation process, the half-life of ozone is very short, only minutes, and it then decomposes to produceenvironmentally friendly oxygen. For this reason, research over recent years has focused on this system.

Color removal by ozone is influenced by many parameters, including temperature, pH, dye bath admixtures, chemical structure of the dyestuff, gas sparging systems (as it affects ozone mass transfer from gaseous phase to liquid phase) and initial concentration of the organic matter in the wastewater. Some classes of dyestuffs decompose more easily in the ozonation process than in the other oxidation processes. Reactive dyesdecolorized more readily in the ozonation process than other classes of dye, but water-insoluble disperse and vat dyes were very difficult to decolorize by this process (Horning, 1978).

2.1.6 Electro-Coagulation Processes

Electro-coagulation processes have been used in several industries for removal of color from waste effluent. These include pulp and paper, leather treatments, and textiles. The processes utilize an electric current that passes through sacrificial electrodes creating chemical reactions that then produce the desired effect with the dye molecules in solution. The results can be coagulation, flotation, reduction or oxidation. The cathodes and anodes involved can vary but the most common reactions are ones where the anode is a metal that becomes solubilized with the metal ions created serving as coagulating agents (Hemphill & Rogers, 1973).

In removing color from waste streams, regular coagulation has the disadvantage of over-feeding of chemicals to the waste stream, with the result that the excess of chemicals added may add to the chemical pollution in the decolorized effluent. This excessive addition of coagulants can be avoided by the use of electro-coagulation. Electro coagulation uses simple equipment, has an operation that is easy to control, and usually results in less sludge than conventional coagulation creates (Do & Chen, 1994; Ogutveren&Kaparal, 1994).

A number of factors affect the efficiency of electrochemical coagulation. These include the intensity of the current (which factors into the comparative cost of the process), the engineering design of the equipment used and the types of electrodes used as well as their physical characteristics, the pH and temperature of the process, the solution characteristics and the properties of the dyes in the mixtures being treated themselves (Hao et. al., 2000).

The color removals of three dyes, reactive, disperse and acid, with aluminium and ferric anodes as coagulant generators was investigated (Yang and McGarrahan, 2005) and the process was successful in removal of color from the dyebath. Again over 95% decolorization was obtained by using an aluminium sacrificial anode to treat a Levafix orange dye solution (Kobya et. al., 2006). Moreover, the decolorization of disperse and reactive dyes was also carried out by electro-coagulation method (Kim et. al., 2002). Their study concentrated on examining the operating parameters such as current density, electrode number, electrolyte concentration, electrode gap, dyestuff concentration, and pH of the solution on the decolorization rates and efficiencies.

2.1.7 Radiation Treatment

Radiation is a process in which electromagnetic waves travel through a vacuum or through matter-containing media. These electromagnetic waves combined with a class of energetic subatomic particles with very high kinetic energies, are called ionizingradiation, and the particles are termed particle radiation. The spectrum of radiant energy can be divided into ionizing and non-ionizing, according to whether it ionizes or does not ionize the atoms in ordinary chemical matter. Ionizingradiation is composed of subatomic particles, ions or atoms moving at electromagnetic waves on the short wavelength end of the electromagnetic spectrum, that carry enough energy to liberate electrons from atoms or molecules, thereby ionizing them. Gamma rays and X-rays are the example of ionizing radiation and the word radiation is often used in reference to ionizing radiation.

Two radioactive sources, the electron beam irradiation and gamma irradiation are used as a source of high energy ionizing radiation. The electron beam irradiation carried out under an electron accelerator and gamma irradiation mostly performed using a Cobalt-60 or Caesium-137 source, are presently available (Wang and Wang, 2007b). It should be noted that the pulse radiolysis technique is generally employed to study the formation and decay of reactive transients underradiolytic conditions (Rauf and Ashraf, 2009). Under electron beam or gamma irradiation, hydroxyl radical ($^{\bullet}OH$), hydrogen atom ($^{\bullet}H$), hydrated electron (e_{aq}^{-}), H_2, H_2O_2, H_{aq}^{+} and OH_{aq}^{-} are formed in dilute aqueous solutions. The energy required to do this varies with the kinds of atoms and their physical state, such as temperature, chemical binding and so on. Both ionizing and non-ionizing radiation can be harmful to organisms and can result in changes to the natural environment. In general, however, ionizing radiation is far more harmful to living organisms per unit of energy deposited than non-ionizing radiation.

Though ionizing radiation is harmful to living organism but radiation technology has been applied to a variety of environmental problems and wastewater treatment. This technology has been shown to be useful for the decoloration of dyeing wastewater and degradation of textile dyes (Chen et al., 2008; Ma et al., 2007), the processing of sewage sludge (Park et al., 2009), the destruction and oxidization of organic pollutants in aqueous media (Al-Sheikhly et al., 2006), and the removal of pesticides (Basfar et al., 2007). It is an effective technique for disinfecting wastewater sludge and is an excellent remover of low solute concentrations. Ionizing radiation may be promising for the treatment of textile dye waste effluents, because the effect of radiation can be intensified in aqueous solution in which the dye molecules are degraded effectively by the primary products formed from the radiolysis of water. The irradiation dose necessary for complete decomposition of a dye depends principally on its molecular structure and reactivity towards the primary water radiolysis products, the presence of oxygen or oxidizing agents, temperature and pH and concentration of the solution (Şolpan et. al., 2002).

Gamma irradiation is considered to be an alternate technology for decomposing recalcitrant organic pollutants in industrial waste waters (Uygur, 1997) with no further generation of secondary waste. The radiation technology methods normally utilize a strong oxidizing species such as $^{\bullet}OH$ radicals which have high electrochemical oxidation potential and cause a sequence of reactions thereafter to break down the macromolecules of dye into smaller and less harmful substances (Bagyo et. al., 2001). High energy radiation produces instantaneous radiolytic transformation through energy transfer from high energy accelerated electrons to the orbital electrons of water molecules. Absorbed energy disturbs the electron system of the molecule resulting in the breakage of interatomic bonds and ionizing the water molecules forming H_2O^+.Various active species are generated due to the radiation interaction between gamma rays and water as shown in the equations given below.

$H_2O^+ + e^- \longrightarrow {}^{\bullet}OH + {}^{\bullet}H$

$H^+ + H_2O + e^- \longrightarrow H_3O^+ + e^- \longrightarrow 2H^{\bullet} + {}^{\bullet}OH$

$OH^+ + H_2O + e^- \longrightarrow {}^{\bullet}H + 2{}^{\bullet}OH$

In the presence of dissolved air or oxygen, a radical known as perhydroxyl radical i.e. $^{\bullet}HO_2$ is also formed:

$^{\bullet}H + O_2 \longrightarrow {}^{\bullet}HO_2$

One of the consequences ofradiolysis in aqueous solutions is that the charged species becomehydrated within a very short interval of time (10^{-11} seconds).Generally these species are hydroxyl radical ($^{\bullet}OH$), hydrogen radical ($H^{\bullet}$), hydrated electron (e^{-}_{aq}) and hydrogen peroxide (H_2O_2) and so on (Rauf et. al., 2007). Among these products, the most reactive species are hydroxyl radical, hydrated electron. Hydroxyl radical attacks the conjugated double bond of the dye particle and breaks it (Rauf et. al., 2007).

In the field of radiation chemistry, the investigation of radiation induced decomposition of dyes and their derivatives due to their environmental hazard is a popular topic and many papers have been published regarding this matter. The changes of a dye solution due to the radiation can be achieved either by steady state radiolysis or pulse radiolysis(Rauf and Ashraf, 2009) and it causes to undergo a step-wise degradation or conversion the dye macromolecules to smaller species. Steady state radiolysis is relatively simple in its use and has been used by many workers to investigate radiation induced dye degradation. For example, the radiolysis of two different reactive dyes (Reactive Blue 15 and Reactive Black 5) in aqueous solutions at different dose rates has been reported(Şolpan et. al., 2002). The change of absorption spectra and the degree of decoloration were examined in the presence of air and H_2O_2.Hydrogenperoxide reacts rapidly with hydrated electron formed in the radiolysis of water, leading to the formation of$^{\bullet}OH$ radical. Therefore,the increase in the degree of decoloration by the addition of hydrogen peroxidewould bemainly due to an increase in the $^{\bullet}OH$ radical. This finding suggested that the $^{\bullet}OH$ radical destroyed the dye chromophore more efficiently than the hydrated electron.The effect of radiation on the degradation of a specified chemical depends on the property of chemical itself and the amount of energy deposited in the material exposed to a radiation field.

In the case of electron and gamma radiation, the lower ionizationenergy allows for greaterdiffusion of the primary species thereby resulting in other reactions. In very dilute aqueous solutions, practically all the radiation is absorbed bywatermolecule. Thus any change in solute compositionwould result fromthe secondary reactions of radiation inducedspecies fromwater and solutemolecule rather than the direct effect of radiation on the solute molecules. These secondary reactionsarise from the reactions of solutes with the oxidizing and reducingspecies initially produced during water radiolysis. Thus the linear energy transfer value of radiation is the determining factor of the radiation effect besides the dose rate of the radiation. It is possible to reduce the types and amount of primary reacting radicals by selecting appropriate experimental conditions.

CHAPTER THREE

EXPERIMENTAL

3.1 Materials

The wastewater samples of this study were collected directly from the equalization tank (mixture of chemical singeing, scouring, bleaching, dyeing, washing, rinsing, finishing and printing wastewater) of Effluent Treatment Plant (ETP) of Divine Textiles Mills Ltd, Gazipur, Bangladesh. 500 ml plastic bottle was brought together from the local market to collect wastewater samples. The test of chemical oxygen demand (COD) of wastewater was performed by using higher range COD (HR COD) vials having range 0-1500 mgL^{-1} was supplied from HACH, USA. The reagents used for the digestion of wastewater for the determination of heavy metals were collected from Merck, India and standard stock solutions of known concentrations of different heavy metals were supplied from ScharlauChemi, Spain.

For the recycling of irradiated wastewater 100% cotton knit fabric of 120 GSM (grams per square meter) was used to perform the pretreatment and dyeing operation. The fabric was knitted in single jersey structure and 26^{S}combed yarn was used to manufacture the fabric. The enzyme treatment of fabric was carried out by using a neutral enzyme (Cellzymefrom Dysin, Bangladesh). The scouring and bleaching treatment of fabric was performed by adding a mix of the chemical agents: wetting agent (Imeron PCLF) and peroxide stabilizer (Stabilizer SOF liquid) from Clariant, Bangladesh.Hydrogen Peroxide (H_2O_2), acetic acid (CH_3COOH), and caustic soda (NaOH) from Merck, India and sequestering agent from Dysin, Bangladesh. All the chemicals were of analytical grade and used as received.

Three commercial reactive dyes namely Novacron Yellow FN2R, Novacron Red FN2BL and Novacron Blue FNR were used to dye the cotton fabric in laboratory dyeing machine. Dyestuffs were collected from Swiss Colours Ltd. Bangladesh.Auxiliary chemicals like detergent (Imeron PCLF) and leveling agent (Drimagen E3R) were collected from Clariant, Bangladesh. Glauber salt ($Na_2SO_4.10H_2O$), sodium acetate (CH_3COONa), soda ash (Na_2CO_3) and acetic acid (CH_3COOH) were brought from Merck, India and all of them were of analytical grades.

3.2 Methods

3.2.1 Study Area

The wastewater samples of this study were collected from the Divine Textiles Mills Ltd, Gazipur, Bangladesh. This factory is located 30 kilometer away from the Dhaka city at PolliBiddut in Kaliakoir, Gazipur. It is a knit composite factory having dyeing and printing capacity 14 tons per day. The source of wastewater of this industry is the dyeing and printing unit, where mainly cotton, polyester, viscose and blended fabrics are dyed and printed. The present study was carried out exclusively on the effluent of this factory. The wastewater samples collected from the factory was irradiated to Cobalt-60 gamma radiation source in the Institute of Radiation and Polymer Technology (IRPT), Bangladesh Atomic Energy Research Establishment, Savar, Dhaka. Then the physico chemical parameters of raw and irradiated wastewater were carried out in the laboratory of the department of Civil Engineering, Dhaka University of Engineering and Technology (DUET), Gazipur. The use of irradiated wastewater in cotton fabric processing was performed in the dyeing laboratory of the department of Textile Engineering, Dhaka University of Engineering and Technology (DUET), Gazipur. The application of treated wastewater in the irrigation of Malabar spinach plant was conducted at the field of Institute of Radiation and Polymer Technology, Atomic Energy Research Establishment (AERE), Savar, Dhaka.

3.2.2 Sample Collection

The wastewater samples of this study were obtained directly from the equalization tank of Effluent Treatment Plant (ETP) of the factory. Wastewater samples were collected in 500 ml plastic bottles. Before collecting the wastewater sample, the plastic bottleswere washed thoroughly using distilled water. The bottles were almost completely filled with sample water and for the ease of identification each bottle was marked by the permanent marker.

3.2.3 Irradiation of Wastewater

Collected wastewater samples were irradiated in a 500 ml plastic bottle at four different radiation doses (3, 5, 8 and 12 kGy) at room temperature at a dose rate of 13 kGy/h without any further treatment or dilution. The plastic bottles containing wastewater were packed in polyethylene bags and sealed for the safety before submission for gamma irradiation. The wastewater samples were submitted to Cobalt-60 gamma radiation source provided in the Institute of Radiation and Polymer Technology (IRPT), Atomic Energy Research Establishment,Savar, Dhaka.

3.2.4 Characterization of Irradiated Wastewater

3.2.4.1 Measurement of pH

The pH of the raw wastewater and irradiated samples was measured directly by digital pH meter (Ecoscen, 1161795) from Eutech Instruments, Singapore.

3.2.4.2 Measurement of Color Reduction

The color absorbance of raw and irradiated wastewater was measured by UV-Vis spectrophotometer (T60, PG Instrument from UK). The degree of decoloration was then calculated from the decrease of absorbance at maximum absorption wavelength after irradiation as follows (Rauf et al. 2009).

$$\text{Decoloration (\%)} = \frac{A_0 - A_1}{A_0} \times 100 - - - - - - - - (3.1)$$

Where, A_0 and A_1 are the maximum absorbance in visible area of the textile wastewater before and after irradiation.

3.2.4.3 Determination of Chemical Oxygen Demand (COD)

The chemical oxygen demand (COD) is commonly used to indirectly measure the amount of organic compounds in water. The test was carried out by dichromate digestion method (Dedkov et al., 2000). 2 ml of wastewater sample was added to the COD vials containing a solution of a strong oxidizing agent, potassium dichromate ($K_2Cr_2O_7$) in a strongly acidic medium (H_2SO_4) including a silver sulfate (Ag_2SO_4) catalyst. The sample was refluxed at 150°C for 2-3 hours for the digestion. The COD values were measured directly by HACH spectrophotometer (Model no-DR 2800, USA) and the test results are expressed as milligrams of oxygen consumed per liter of sample (mg/L COD).

3.2.4.4 Determination of Biological Oxygen Demand (BOD_5)

Biological oxygen demand (BOD_5) was measured by dilution method. The method consists of filling with sample to an airtight bottle of 300 ml size and incubating it at 20°C for 5 days. Dissolved oxygen (DO) of wastewater was measured by DO meter (HQ40d portable DO meter, HACH, USA) initially and after incubation, and the BOD_5 was computed from the difference between initial and final DO. Then BOD_5 was calculated as follows:

$$SeededBOD_5 = \frac{(D_0 - D_5) - (B_0 - B_5)f}{P} \quad (3.2)$$

Where, D_0 is the dissolved oxygen (DO) of the diluted solution after preparation (mg/l), D_5 is the DO of the diluted solution after 5 day incubation (mgL^{-1}), P is the decimal dilution factor, B_0 is the DO of diluted seed sample after preparation (mgL^{-1}), B_5 is the DO of diluted seed sample after 5 day incubation (mgL^{-1}) and f is the ratio of seed volume in dilution solution to seed volume in BOD test on seed.

3.2.4.5 Measurement of Total Suspended Solids (TSS) and Total Dissolved Solids (TDS)

The term total suspended solids can be referred to materials which are not dissolved in water and are non filterable in nature. It is defined as residue upon evaporation of non filterable sample on a filter paper. The test TSS was performed by filtering the wastewater through a fiber pad filterand then measuring the dry weight (obtained by drying the filter and its content at 103-105ºC for 1 hour) of the material. After drying the filter paper was cooled for 30 minutes in an oven at room temperature. The increase in weight of the filter represents the total suspended solids in wastewater. The term total dissolved solids referred to the materials that are completely dissolved in water. These solids are filterable in nature. It is defined as residue upon of non filterable sample on a filter paper. The determination of TDS of raw and irradiated wastewater was carried out directly by the TDS meter HQ40d from HACH, USA.

3.2.4.6 Measurement of Electrical Conductivity (EC)

Electrical conductivity is defined as a measure of the ability of a water sample to convey an electric current and itis a useful parameter for assessing the concentration of solid substances present in any sample of waste water. The determination of electrical conductivity of raw and irradiated wastewater was carried out directly by electrical conductivity tester EC 150, from HACH, USA.

3.2.4.7 Determination of Heavy Metals in Wastewater

The determination of heavy metals such as chromium (Cr), copper (Cu) and cadmium (Cd), lead (Pb) and Nickel (Ni) in raw and irradiated wastewater was analyzed by Atomic Absorption Spectrophotometer (Model AA-7000, from Shimadzu Corporation, Japan). The test was carried out after digestion of wastewater with a mixture of concentrated acids HNO_3 and HCL solution. The solution of wastewater was carefully heated in sandbath nearly to dryness in fumhood. After cooling the crucible at room temperature, deionized water was added to the sample and was filtrated through a filter paper. The filtrate was collected in the measuring flask and was preserved for the determination of Pb, Cd, Cu, Cr and Ni. The Atomic Absorption Spectrophotometer was calibrated for all the metals by running different concentrations of standard solutions. Average values of three replicates were taken for each determination. The detection limits for the selected heavy metals were 1.00 ppm.

Figure 3.1: Atomic absorption spectrophotometer for the measurement of heavy metals in wastewater

3.2.5 Recycling of Irradiated Wastewater

3.2.5.1 Pretreatment of Cotton Fabrics

Pretreatment is the process of preparing the textile materials for dyeing, printing and finishing operation. The pretreatment of cotton includes chemical singeing, scouring and bleaching of fabric. The chemical singeing also known as enzyme treatment or biopolishing is the process of removing the loose hairy fibers protruding from the surface of the cloth, thereby giving it a smooth, even and clean look appearance. The treatment was carried out by using a neutral enzyme applied to the fabric in neutral medium (pH 6.5-7.0) at a temperature 70°C for 50 minutes maintaining material liquor ratio 1:10.

The scouring of cotton is carried out to improve absorbency by removing the impurities like fat and wax and the bleaching action destroy the natural pigments present in cotton to impart a permanent whiteness. The scouring and bleaching of fabric was done in the same bath for irradiated and fresh water using 5.0g grey fabric samples according to the recipe given in Table-3.1.

Table 3.1: Single bath scouring and bleaching recipe for all test samples

Ingredients	**Wetting agent**	**Caustic soda**	**Hydrogen peroxide**	**Stabilizer**	**Peroxide killer**	**Acetic acid**	***M:L**
Amount	1 gL^{-1}	4 gL^{-1}	2.5 gL^{-1}	1 gL^{-1}	0.4 gL^{-1}	0.5 gL^{-1}	1:10

*Material Liquor ratio

The scouring and bleaching of fabric samples was performed by exhaust method at 98°C temperature for 40 minutes and was carried out in Sandolab infrared lab dyeing machine from Copower Technology Ltd Taiwan. The single bath scouring and bleaching procedure is shown in Figure-3.2.

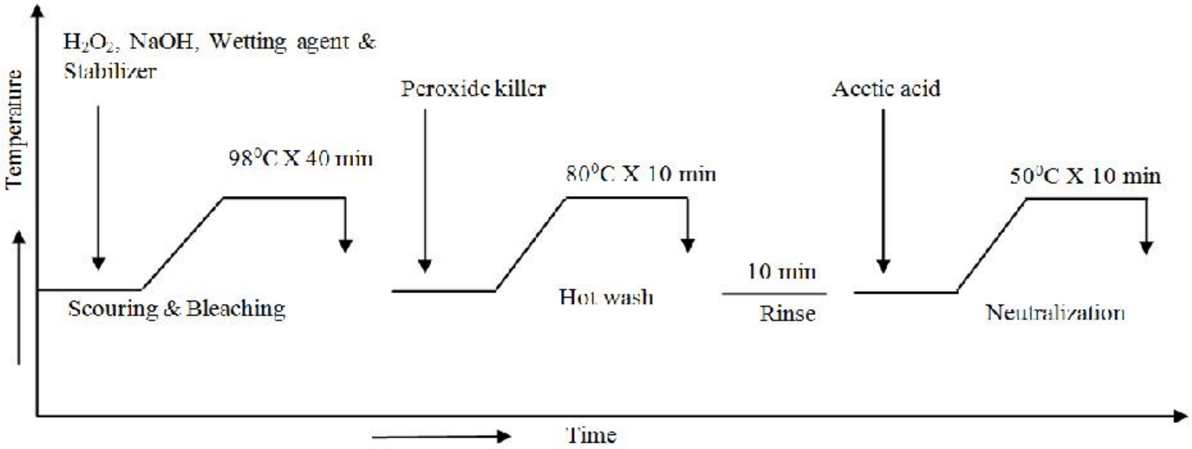


Figure 3.2: Schematic of the scouring and bleaching sequence applied to cotton fabric

3.2.5.2 Analysis of Fabric after Enzyme Treatment

After enzyme treatment or chemical singeing, the weight loss of fabric due to the removal of hairy fibers from the fabric surface was measured by digital electronic balance, Model AV-412 from Transcat, USA. The weight loss was determined on atmospherically conditioned (25±2°C temperature, 65±2% relative humidity for 4 hours) knit fabric after enzyme treatments. The weight-loss percentage (W_i) was calculated from the differences in weight, using the following equation (Jevšnik et al. 2012):

$$W_i = \frac{W_{pre} - W_{after}}{W_{pre}} \times 100 ---------- (3.3)$$

Where W_{pre} is the weight of the conditioned fibers prior to treatment and W_{after} is the weight after the performed treatment.

3.2.5.3 Analysis of Scouring & Bleaching Performance

The scouring and bleaching performance was analyzed in terms of their weight loss and whiteness. The whiteness index of different bleached cotton fabric samples was measured according to AATCC test method 110-1995.The determination of whiteness index of the bleached fabric samples was performed by color measurement spectrophotometer (Data color 650 from USA) with the settings: illuminant D65, large area view and CIE 10° standard observer. Each sample was folded twice to give an opaque view and whiteness was measured four times at different parts of fabric surface. The deviation of whiteness was calculated by determining ΔE values between fresh water treated and wastewater treated fabric samples. The weight loss of fabric as a result of scouring was measured by digital electronic balance, Model AV-412 from Transcat, USA and expressed in percentage to identify the removal of fat and wax from the fabric due to scouring and bleaching process.

3.2.5.4 Dyeing of Fabric Samples

Dyeing is the process of coloring the textile materials by immersing them in an aqueous solution of dye. The dyeing of scoured, bleached and enzyme treated 100% cotton plain knit fabric was carried out by using three commercial reactive dyes namely Novacron Yellow FN2R, Novacron Red FN2BL and Novacron Blue FNR in a laboratory dyeing machine (Sandolab infrared lab dyeing machine from Copower Technology Ltd., Taiwan).

Figure 3.3: Sandolab Infrared lab dyeing machine for the pretreatment and dyeing of cotton fabric.

Fabric samples were dyed with each of the above mentioned dyes at three different shade percentages (5%, 1.5% and 0.5% on the weight of fabric) by using fresh and irradiated wastewater. General recipe is given in Table-3.2.

Table: 3.2: General dyeing recipe for all test samples

Shade % → Ingredients ↓	**Deep shade (5%)**	**Medium shade (1.5%)**	**Light shade (0.5%)**
Wetting Agent	1 gL^{-1}	1 gL^{-1}	1 gL^{-1}
Leveling Agen	1 gL^{-1}	1 gL^{-1}	1 gL^{-1}
Dyes	5.0 % (owf)	1.5 % (owf)	0.5 % (owf)
Glauber Salt	40 gL^{-1}	30 gL^{-1}	15 gL^{-1}
Soda ash	10 gL^{-1}	8 gL^{-1}	4 gL^{-1}
*ML Ratio	1:10	1:10	1:10

*Material Liquor ratio

5.0 g fabric samples were dyed for each color in threedifferent shades by exhaust dyeing method in 250ml stainless steel pot at a temperature 60°C for 60 minutes. The dyeing procedure is shown in Figure 3.4.

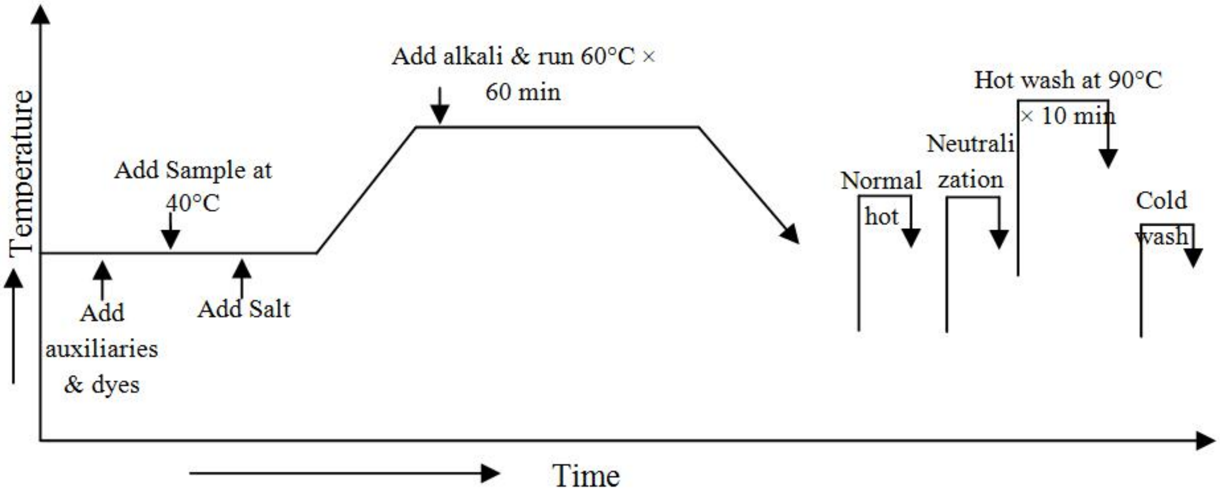


Figure 3.4: Dyeing curve of cotton fabric with reactive dye

3.2.5.5 Dyeing performance Test

The performance of dyed fabric regarding the depth of color and small color difference for acceptability was analyzed by using color measurement spectrophotometer (Data Color 650 from USA). The depth of color of the dyed fabric was determined by the K/S value (Broadbent, 2001) and color differences for acceptability i.e. CMC ΔE color difference value was evaluated according to AATCC test method 173-2006. The color of the fabric was measured on Data Color with the setting: illuminant D65, large area view and CIE 10° standard observer. Each sample was folded twice to give an opaque view and color reflectance was measured four times at different parts of fabric surface.

Figure 3.5: Spectrophotometer (Data Color 650) for the measurement of color and whiteness of fabric.

Colorfastness to washing was performed according to ISO 105 C03 by wash fastness tester (Gyrowash model no: 415/8 from James H. Heal & Co, UK) of fabric sample size 10cmx4cm. The test was carried out at 50: 1 liquor ratio in a 2.0 liter wash wheel vessel that was rotated at constant speed 40±2 rpm and at constant temperature. The change of color was assessed by comparing the untreated fabric with the treated fabric samples with respect to the ratings of color change grey scale.

Figure 3.6: Wash fastness tester (Gyrowash) for the assessment of color fastness to washing of dyed fabric.

Color fastness to rubbing was measured according to ISO 105 X 12: 1993 by rubbing fastness tester (Crock meter, model no: 670 from James H. Heal & Co, UK). The dyed specimens were rubbed 10 times using a Crockmeter which has a weighted finger covered with piece of undyed cotton cloth 5cm X 5cm. For wet rubbing the cotton cloth was wetted out before being rubbed on the dyed sample. The cotton rubbing cloth was then examined for dye which may have been removed and assessed using the grey scales for staining.

Figure 3.7: Color change grey scale for the evaluation of color fastness properties of dyed fabric

Color fastness to perspiration was measured according to ISO 105 E04 by perspiration fastness tester (Perspirometer model: HX-30 from James H. Heal & Co, UK). The test was performed at a liquor ratio of 50:1 and allows the fabric to remain in the solution for 30 minutes at room temperature. The excess liquid was removed from the specimen and placed the specimen between two plates of the perspirometer under a pressure of 12.5 kPa at 37^0C for 4h.

3.2.5.6 Presence of Banned Amines and Formaldehyde in the Dyed fabric

The existence of carcinogenic azo dyes in the fabric dyed in irradiated wastewater was determined by Gas chromatography–mass spectrometry (GC-MS) from Modern Testing Service Ltd., Bangladesh, according to EN 14362-1:2012. The presence of formaldehyde in the dyed fabric was performed by wetting the fabric with phenyl hydrazine and ferric chloride solution was added on the sample. The change of the fabric color to pink indicates positive result or the presence of formaldehyde in the fabric. Negative result specifies the absence of formaldehyde in the dyed sample by indicating no change of the color after adding the ferric chloride solution to the dyed fabric.

3.2.6 Use of Irradiated Wastewater in Irrigation

3.2.6.1 Cultivation of Vegetable

For the cultivation of vegetable by using irradiated wastewater, Malabar spinach plant was selected for the experiment. This plant is popular leafy vegetable in Bangladesh having good nutritional value and taste. The experiment was conducted at the field of Institute of Radiation and Polymer Technology, Atomic Energy Research Establishment (AERE), Savar, Dhaka. Shade was prepared by using plastic for controlling the environmental condition during cultivation period.

Table 3.3: Various names of Malabar spinach plant

Bengali Name	English Name	Scientific Name
PuiShak	Malabar Spinach	Basella alba

3.2.6.2 Plantation

Twelve plots have prepared where, the plants were successively nourished by water, untreated effluents and the irradiated wastewater. Each plot was identified and the soil of plots was moistured by respective raw wastewater, irradiated wastewater and fresh water containing plastic drums. Generally irrigation was done every alternative day and required amount of manure and fertilizers were applied to the plant. After rising of plants, thinning and weeding were done accordingly.

3.2.6.3 Harvesting

To evaluate the yield, food value and plant nutrient harvesting was done for 55 days after seed sowing. Generally the recommended time for the harvesting ofMalabar spinach plant is 60-80 days. The plants were collected randomly from each replication of treatment to analysis the yield and other physico chemical parameters of the vegetables.

3.2.6.4 Growth and Yield Analysis

3.2.6.4.1 Plant Height

Plant height was measured by measuring tape from the root to the tip of the leaves of the plants. Measurement was taken five times randomly selected plants from each replication and average value were calculated by statistical analysis.

3.2.6.4.2 Root Length

After uprooted the plants, the length of roots were measured from the soil surface to the tip of the root with the help of measuring scale. Measurement was taken five times randomly selected plants from each replication and average value were calculated.

3.2.6.4.3 Number of Leaves per Plant

Number of leaves per plant was counted from each replication of control (fresh water), raw and irradiated wastewater applied plants.

3.2.6.4.4 Mineral Content of Plant

The mineral content (Mn, Zn, K and Ca) of the plant after harvesting was analyzed by Tandem Accelerator at Atomic Energy Research Establishment, Dhaka, Bangladesh. The sample was prepared by grounding the different parts of plants (root, stem and leaves) after oven drying at 60°C. The powdered samples were pressed using hydraulic press to make pellet of 13 mm diameter and around 1 mm thickness.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

PART ONE

Treatment of Textile Wastewater

4.1.1 Analysis of Raw Wastewater

The wastewater collected from the equalization tank of ETP was the combination of water, discharged from different processing steps of dyeing and printing operation. As a result, the parameters of wastewater samples were not fixed. The parameters were varied depending on the step of fabric processing. For instance, the wastewater from scouring and bleaching includes high alkalinity and BOD where as dyeing wastewater comprises high salinity, pH, color and COD (Broadbent, 2001; Cooper 1995). Again the wastewater from washing and rinsing is almost neutral and contains low amount of contaminants. As a result, the physicochemical parameters of wastewater were changed after combination of water of different processing steps. The resultant parameters of wastewater after mixing are tabulated in Table-4.1.1.

Table 4.1.1: Parameters of raw wastewater were collected from the equalization tank

Parameters	**pH**	**Color**	**COD**	**BOD$_5$**	**TSS**	**TDS**	**EC**
Amount	8.2-9.0	Purple/ Orange/ Dark etc.	272-295 mgL^{-1}	180-197 mgL^{-1}	305-335 mgL^{-1}	1000-1055 mgL^{-1}	1980-2060 µs/cm

The collected wastewater samples from the mixing tank having the parameters in the Table 4.1.1 were irradiated in gamma radiation source for the treatment. After irradiation the pH, color, COD, BOD_5, TSS, TDS, EC and other parameters of raw wastewater were observed. The change of wastewater quality due to gamma irradiation is discussed below.

4.1.2 Determination of pH of Irradiated Wastewater

The actual pH of the reactive dye bath normally lies between 10 to 11(Shore, 1995). However, as wastewaters from dyebath mixed with other wastewater from other processes, final pH of the wastewater in mixing tank have found to be in the range of 8 to 9. Again after irradiation the pH of wastewater was reduced. The percentage reduction of pH of wastewater after irradiation is shown in Figure- 4.1.1.

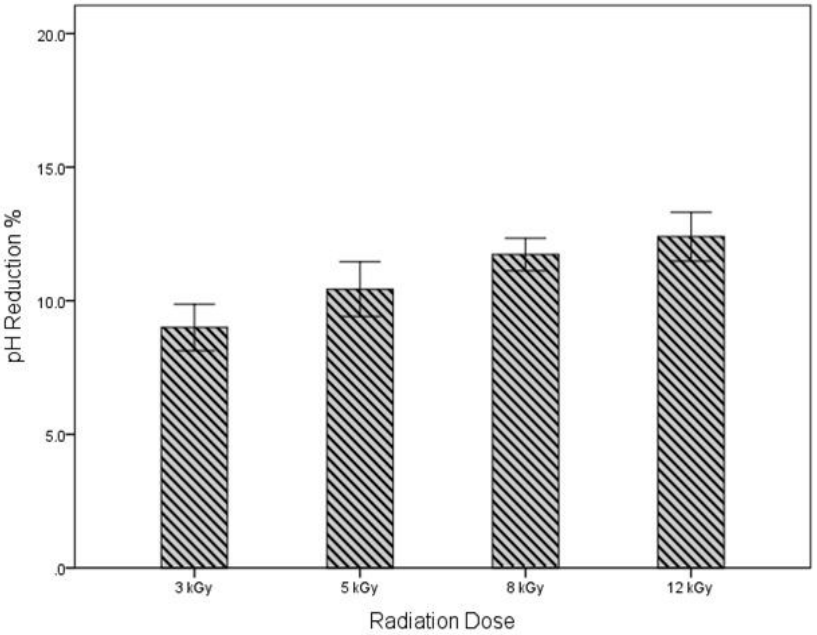


Figure- 4.1.1: Reduction of pH of wastewater after gamma irradiation at different radiation doses.

Figure 4.1.1 illustrates the reduction of pH of wastewater due to gamma irradiation. It was observed that, after irradiation the pH value of the wastewater was decreased to nearly neutral value (7-7.5) due to the formation of organic acids (such as dicarboxylic acids or monocarboxylic acids like acetic acid, and other acidic aromatic compounds or carbonic acid) due to the breakdown of aromatic rings (Bagyo et al., 2001). From the study it has been found that, though the pH of the final wastewater of a textile industry may vary depending on the nature of processing but after irradiation the pH has decreased with the radiation doses and the highest reduction percentage was obtained from the sample treated with 12 kGyradiation dose. But the rate of reduction was not significant with increasing radiation dose. The insignificant reduction of pH of wastewater with higher radiation dose is due to the organic acid resulted from the breakdown of benzene ring, is converted to further smaller components (Bagyo et al., 2001).

4.1.3 Analysis on Color Removal of Wastewater

Color removal efficiency was analyzed by measuring the presence of color in irradiated and un-irradiated wastewater through UV-Vis spectrophotometer. In thisresearch 3, 5, 8 and 12 kGy radiation dose was applied on collected textile wastewater samples. Then the color reduction percentages were measured. The color reduction percentages of collected wastewater at above mentioned four radiation doses are given in Figure– 4.1.2.

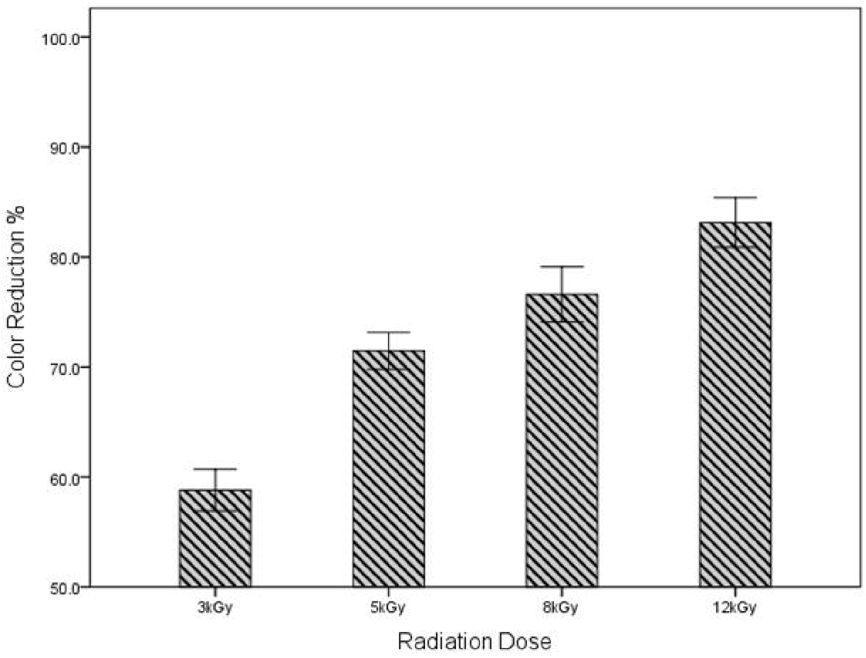


Figure- 4.1.2: Color reduction of textile wastewater at different radiation doses.

Figure 4.1.3: Appearance of raw and gamma irradiated (at 12 kGy radiation dose) wastewater with respect to the fresh water .

From the Figure-4.1.2, it was observed that, color reduction percentages were increased according to the gradual increment of radiation doses. The statistical analysis showed that there were fluctuations in color reduction at different radiation doses resulting longer error bar. The amount of color reduction of dyeing wastewater by gamma radiation depends on color and the structure of dye (Getoff et al., 1999). Since color of the textile wastewater differs significantly according to different textile processing, chemicals and dyes resulting the deviation in the reduction of color at different radiation doses.

4.1.4 Reduction of Chemical Oxygen Demand (COD)

The chemical oxygen demand (COD) is one of the most widely used parameters that is indicative of the characteristics of wastewater (Kang et al., 1999). The COD is the equivalent amount of oxygen required to chemically oxidize the organic matter contained in a known volume of wastewater using a standard test in which a strong oxidant (potassium dichromate) is used. The COD values of wastewater and irradiated water are shown in Figure- 4.1.4.

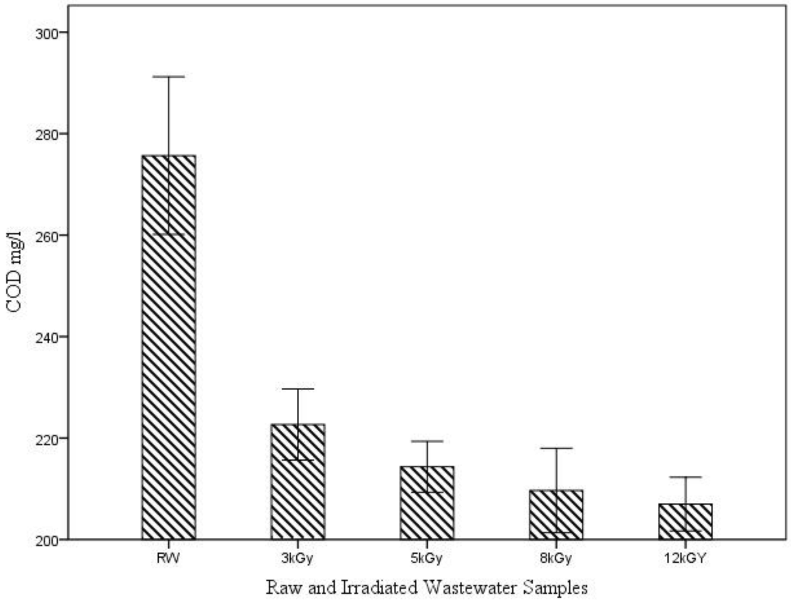


Figure- 4.1.4: Reduction of COD values of textile wastewater after gamma irradiation

From the Figure-4.1.4 it has been found that, the COD values of wastewater have reduced after irradiation which indicates the decomposition of organic pollutants in the water (Selambakkannu et. al., 2011). Again the COD values of wastewater were decreased as the dose of radiation increased. Water molecules undergo radiolysis process to produce ionized and excited water molecules and free electrons when exposed to ionizing irradiation. Reactions between pollutants and primary products of water radiolysis and secondary short lived species, which formed from the pollutants causes the removal of pollutant from the wastewater (Getoff et al., 2002). Hydroxyl radical is the main reactive species which leads to decomposition of pollutants due to its high potential as oxidizing agent to dehalogenation and cleavage of the chemical bonds. The quantity of water molecule which undergoes radiolysis associated with absorbed dose produce more hydroxyl radical at higher irradiation dose. Therefore, higher absorbed dose causes the decomposition of organic pollutants results in the lower COD values of irradiated wastewater.

4.1.5 Reduction of Biological Oxygen Demand (BOD_5)

The BOD_5 of a wastewater is defined as the amount of oxygen required by aerobic microorganisms to (partially) oxidize the organic matter in a known volume of wastewater according to a standardized test. BOD_5 is typically expressed in mg of oxygen/L of wastewater. The test was carried out of incubating the wastewater (appropriately diluted) samples for five days at 20^0c temperature, and measuring the amount of residual oxygen at the end of the test to determine the amount of oxygen consumed.

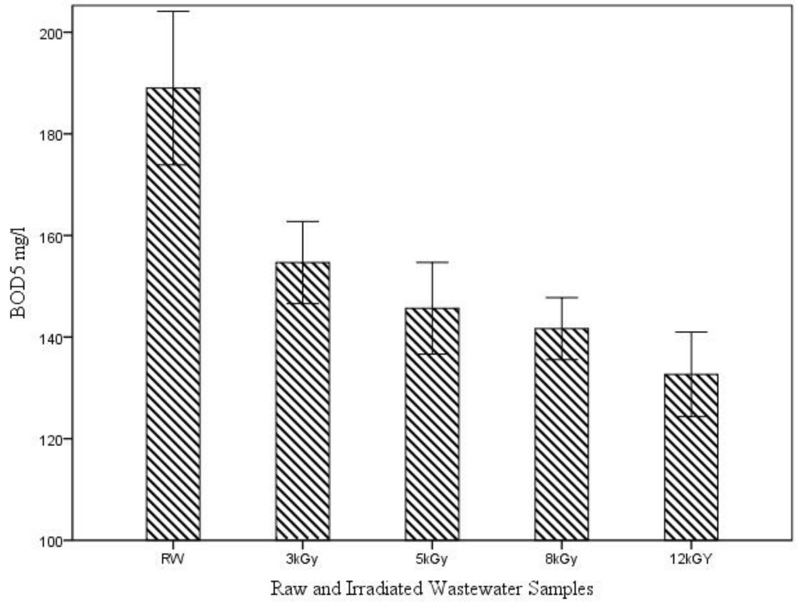


Figure- 4.1.5: Reduction of BOD_5 values of textile wastewater after gamma irradiation

Figure- 4.1.5 shows that, the average BOD_5 value of raw wastewater was reduced from 190 mg/l to 132 mg/l after irradiation at 12 kGy radiation dose. Again the reduction of average BOD_5 values was increased with the increment of radiation doses. The reason is that, gamma irradiation can effectively decompose the organic matter in wastewater. Due to the decomposition of organic pollutants in wastewater, the amount of biodegradable organic matter decreases which results in lower BOD_5 values of the irradiated water. Another reason is the microorganisms which are responsible for oxygen consumption from wastewater are destructed for their sensitivity to radiation pulses (Selambakkannu et al., 2011).

4.1.6 Effect of Gamma Irradiation on Suspended and Dissolved Solids of Wastewater

The solid contents in textile wastewater vary considerably, depending on the process involved. Typically, suspended solids carry a major portion of organic material, thus significantly contributing to the organic load of the wastewater. Again, suspended solids absorb heat from sunlight, which increases water temperature and subsequently decreases level of dissolved oxygen. Hence, effective solid removal can appreciably contribute to wastewater treatment.

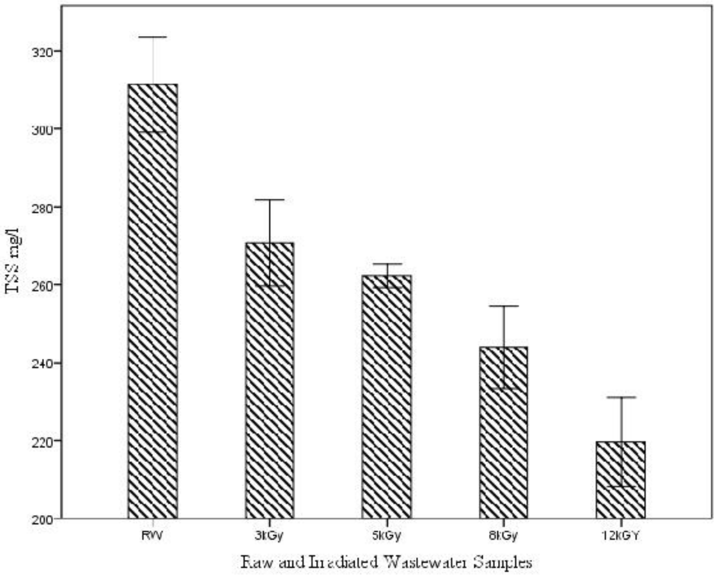


Figure- 4.1.6: Total suspended solids of raw wastewater and irradiated wastewater at different radiation doses.

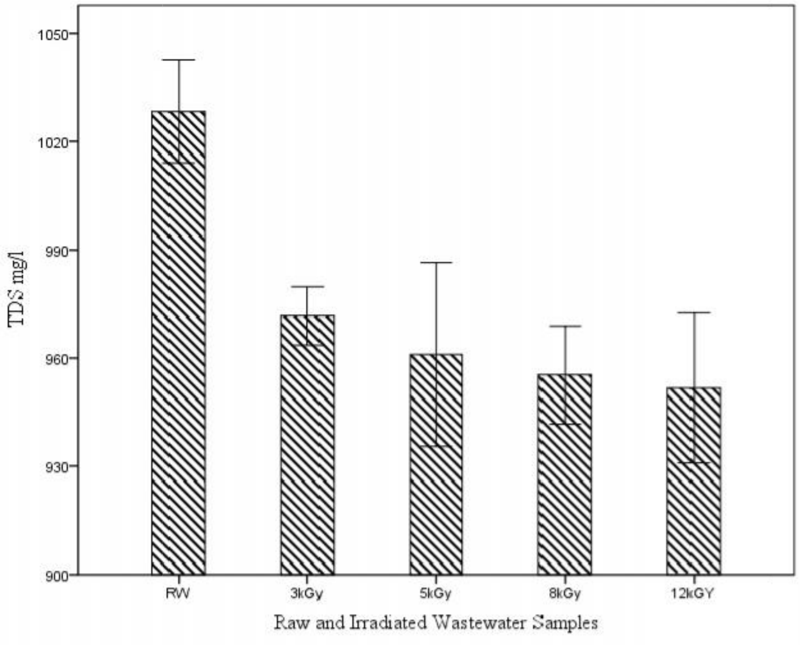


Figure- 4.1.7: Total dissolved solids of raw wastewater and irradiated wastewater at different radiation doses.

The degradation of total suspended solids (TSS) by gamma irradiation is shown in Figure- 4.1.6. The average TSS value of irradiated water at 12 kGy radiation dose was observed 218 mg/l whereas this value was 310 mg/l for raw wastewater (RW). The results signify that suspended solid materials of wastewater were decomposed effectively by gamma irradiation. The main reason is, free radicals that formed during water radiolysis are highly reactive. These radicals not only react with target pollutants but also with many other solutes contained in the water. In consequence, the reaction of free radicals with organic materials in wastewater leads the degradation of suspended matter of water after gamma irradiation.

Again in Figure-4.1.7, no significant change was observed in case of dissolved solids (minerals, salts, metals, cations or anions dissolved in water) of wastewater after gamma irradiation. Though hydroxyl radical and other reactive species that are formed due to the radiolysis of water, react with some inorganic ions like bicarbonate and nitrate (Sarla et al., 2004). But most of the dissolved matters are unaffected by gamma radiation resulting insignificant change in TDS value of irradiated wastewater.

4.1.7 Effect of Gamma Irradiation on Electrical Conductivity of Wastewater

Electrical conductivity (EC) is a useful parameter for assessing the concentration of solid substances present in any sample of waste water. It is also known as specific conductance and is defined as a measure of the ability of a water sample to convey an electric current (Uwidia1 et al., 2013). High values of electrical conductivity of industrial textile wastewater shows the presence of inorganic ions such as H^+, Na^+, K^+, $Mg^{2+,}$ Ca^{2+}, Cl^-, SO_4^{2-} which have major influence on the conductivity in water.

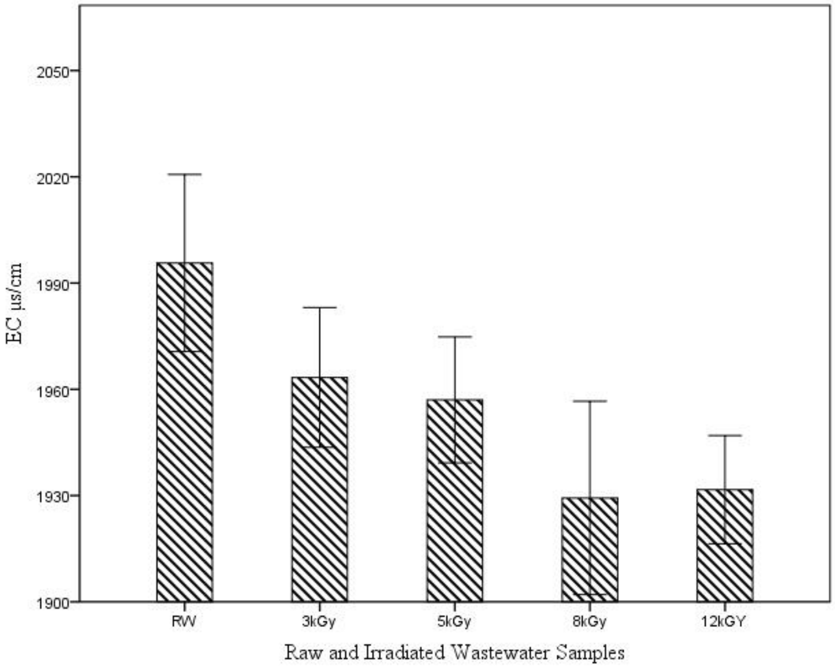


Figure- 4.1.8: Electrical conductivity of raw wastewater and irradiated wastewater at different radiation doses.

Figure-4.1.8 illustrates that, the average conductivity of raw wastewater is about 2000 µs/cm.The high value of EC of dyeing wastewater specifies the presence of inorganic dissolved solids or high salinity of the wastewater. The high salinity of the wastewater was due to the use of large amount inorganic salts such as sodium chloride (NaCl) orglauber's salt ($NaSO_4.10H_2O$) in dyeing of cotton fiber especially in case of reactive dyeing (Shore, 1995). Again the insignificant change of electrical conductivity of wastewater after gamma irradiation indicates no or less efficiency of gamma radiation to eradicate the inorganic dissolved solids from the wastewater.

4.1.8 Heavy Metals in Treated Wastewater

Metal complex dyes are the main source of heavy metals in textile wastewater. Heavy metals particularly chromium (Cr), copper (Cu) and cadmium (Cd) are widely used for the production of metal complex textile dyes (Halimoon et al., 2010). It has been reported that, the major problem associated with many textile wastewater is the presence of heavy metals which arise from material used in dyeing process or large amount of dyes containing metal (Correia, 1998).

Table- 4.1.2: The concentration of heavy metals in raw and irradiated wastewater

Heavy Metals	**Cu (ppm)**	**Cd (ppm)**	**Cr (ppm)**	**Pb (ppm)**	**Ni (ppm)**
Raw Wastewater	0.152	0.3090	0.0306	0.563	0.0237
Irradiated Wastewater	0.156	0.298	0.0305	0.432	0.0325

Table-4.1.2 shows the concentration of heavy metals in raw and irradiated wastewater samples. The amount of copper, cadmium, chromium, lead and nickel in untreated wastewater were 0.152, 0.309, 0.0306, 0.563 and 0.0237 ppm respectively. The variations of the heavy metals concentration in the wastewater were due to the different types of dyestuff and chemicals used in the processing of different types of fiber when the wastewater samples were taken from the mixing tank. Again the concentration of heavy metals in the wastewater was found lower and within the acceptable limit according to the Department of Environment, Bangladesh (except Pb 0.1 ppm) for irrigation standard. The lower concentrations of heavy metals in raw wastewater were due to the presence of reactive and disperse dyestuffs in waste liquor which were used for the coloration of cotton and polyester fabric (Broadbent, 2001). Since no metal complex groups are present in the structure of disperse dye (Shore, 2002) and only 12-15% reactive dye contains metal complex azo group (Cooper, 1995). This leads the lower level of heavy metals in the collected wastewater samples. However, no significant change was found in the concentration of heavy metals in wastewater after gamma irradiation. The unchanged metal concentration in irradiated wastewater signifies the ineffectiveness of gamma irradiation to remove the heavy metal from wastewater.

4.1.9 Summary of the Outcomes

The investigation of treated textile wastewater was performed after irradiated with gamma radiation. It was observed that, colored wastewater become almost colorless due to the breakage of the chromophoric groups of the dye molecules by gamma irradiation and pH of wastewater was decreased due to the formation of acidic compounds. Again total suspended solids (TSS), COD and BOD_5 were also decreased significantly because of the degradation of the organic solid particles. However, the change of TDS, EC and metal content were found less for treated wastewater after application of gamma irradiation.In this research work 3, 5, 8 and 12 kGy radiation dose was applied on textile wastewater and the physicochemical parameters of irradiated wastewater were investigated. Since textile wastewater differs significantly according to different textile processing, chemicals and dyes results the fluctuation in the reduction of various parameters of wastewater.So, considering the cost effectiveness, 8 kGy irradiated wastewater was selected for the current research work to analyze the performance in reusing purpose. The average parameters of irradiated wastewater at 8 kGy radiation dose are compared with the standard irrigation water and presented in Table 4.1.3.

Table-4.1.3: Parameters ofraw wastewater, gamma irradiated wastewater and irrigation standardwater.

Wastewater → **Parameters↓**	**Raw Wastewater**	**Irradiated Wastewater**	**Irrigation Standard***
pH	8.3	7.1	6-9
Color Reduction (%)		78.00	NA
COD (mg/l)	280	210	400
BOD_5(mg/l at 20^0C)	195	140	100
TSS (mg/l)	310	242	200
TDS (mg/l)	1050	960	2100
EC (µs/cm)	2000	1930	1200
Heavy Metals			
Copper (ppm)	0.152	0.156	3.0
Cadmium (ppm)	0.309	0.298	0.5
Chromium (ppm)	0.0306	0.0305	1.0
Lead (ppm)	0.563	0.432	0.1
Nickel (ppm)	0.0237	0.0325	1.0

* Department of Environment (DOE), Bangladesh

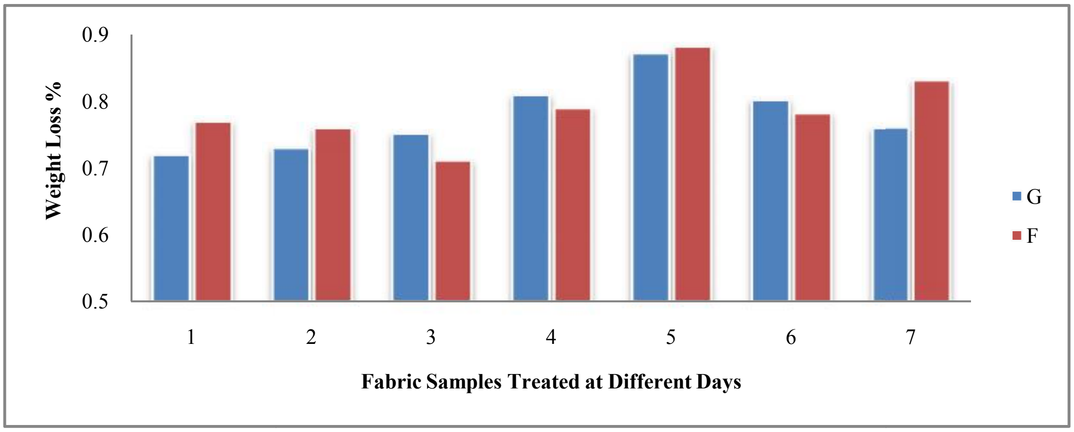
PART TWO

Recycling of Irradiated Wastewater for Cotton Fabric Processing

4.2.1 Analysis of Pretreatment Performance

4.2.1.1 Chemical Singeing (Enzyme Treatment)

The process of singeing is carried out for the purpose of removing the loose hairy fibers protruding from the surface of the cloth, thereby giving it a smooth, even and clean look appearance. Surface properties, which are important during the production process, are significant for the hand of a knitted fabric (Jevšnik et al., 2012). The chemical singeing or enzyme treatment of knitted fabric is gaining an increasingly important role in industrial textile applications to improve the quality and functionality of fabrics or to achieve the desired effect with low environmental impact. The effect of enzyme treatment on fabric was assessed in terms of weight loss and the visual appearance of the fabric surface. The percentage weight loss of cotton knit fabrics after the chemical singeing by using the irradiated and fresh water are presented in Figure-4.2.1.



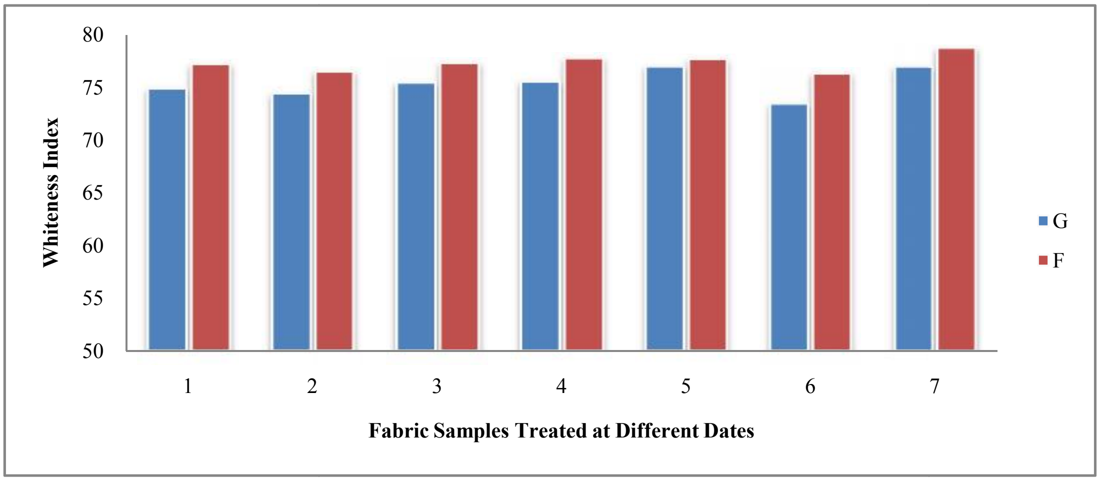
G=Gamma irradiated water and F= Fresh water

Figure 4.2.1: Weight loss of fabric samples after chemical singeing processed in irradiated and fresh water at different dates.

From Figure-4.2.1, it has been found that, the weight loss of cotton fabric due to the removal of loose hairy fibers from the fabric surface is almost same in case of samples treated with irradiated and fresh water. The average weight loss was found 0.79% and 0.78% for the fabrics treated in fresh and irradiated water respectively which specified the same amount of loose hairy fibers were removed from fabric surface. Again no significant change was observed of the surface properties of fabric during visual assessment. The results signified that, the enzymes can effectively perform the singeing action in irradiated wastewater and the performance was found to be similar to that of fresh water. The usual performance of enzymes in irradiated water indicated that, irradiated wastewater have no harmful or toxic action towards enzymes. So it can be concluded that, the gamma irradiated wastewater can be successfully use as an alternative of fresh water for the chemical singeing of cotton fabric in textile industry.

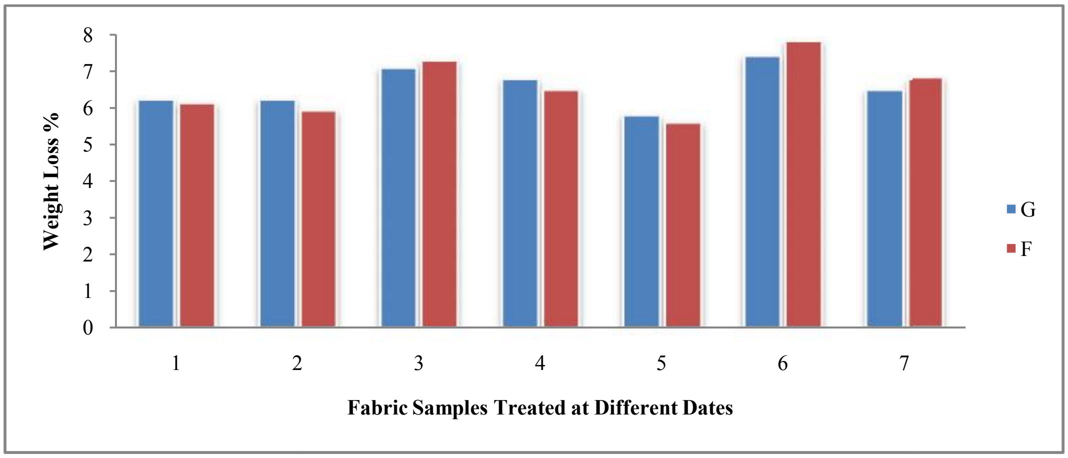
4.2.1.2 Scouring and Bleaching

The scouring action of cotton results improved absorbency by the removal of impurities and the bleaching action destroy the natural pigments present in cotton to impart a permanent whiteness. The efficiency of scouring can be measured by measuring the weight loss. Commercially the maximum acceptable limit of weight loss is 4 to 8 % where the value lower than 4% indicates improper scouring and the values higher than 8% is a sign of vigorous destruction of the fats and wax in the fiber (Karmakar, 1999). The bleaching performance was analyzed by measuring the whiteness index of the fabric samples by spectrophotometer. In general a bleached samples having whiteness index between 75 to 85is acceptable in commercial purpose (Tomasino, 1992). The average results of whiteness and weight loss ofscoured-bleached samples obtained from treated wastewater samples are plotted against corresponding fresh water samples which are shown in Figure-4.2.2 and 4.2.3.



G=Gamma irradiated water and F= Fresh water

Figure 4.2.2: Whiteness index of different white bleached fabric samples processed in irradiated and fresh water at different dates.



G=Gamma irradiated water and F= Fresh water

Figure 4.2.3: Weight loss of different scoured fabric samples processed in irradiated and fresh water at different dates.

In both scouring and bleaching operation, the irradiated wastewater have shown quite acceptable and almost similar performance to the samples which were processed with fresh water. The average weight loss due to scouring was found 6.57 % and 6.48 % for fresh water and gamma irradiated samples respectively whereas the average reflectance of white bleached samples was found to be 75.35 % for irradiated water samples and 77.31% for fresh water samples. Figure-4.2.2 illustrated that, whiteness index of all the bleached samples from irradiated wastewater have reflectance percentage well above the minimum acceptable limit and almost similar to the fresh water samples. Figure-4.2.3 demonstrated that, scouring with irradiated water does not impart more destruction of oil and wax of the fabric and the weight loss limit is within acceptable range. The weight loss was observed from 5.6% to 7.8% and 5.8% to 7.4% respectively for the fabric samples treated with irradiated and fresh water. Thus it can be summarized that the gamma irradiated wastewater can be used for the scouring and bleaching of cotton goods as an alternative of fresh water for the same purpose.

4.2.2 Analysis of Dyeing Performance

4.2.2.1 Shade Matching

In commercial dye house, textile materials are dyed to match the color of a produced shade against a given standard. This is known as shade matching. In case of shade matching, the variation of shade is expressed in terms of CMC ΔE value (Broadbent, 2001). The maximum acceptable value for ΔE is 1 (Broadbent, 2001) where lower value indicates that the reproduced color is closer to the original and vice versa. The ΔE values for all the selected shade percentages of each color are given in Figure-4.2.4.

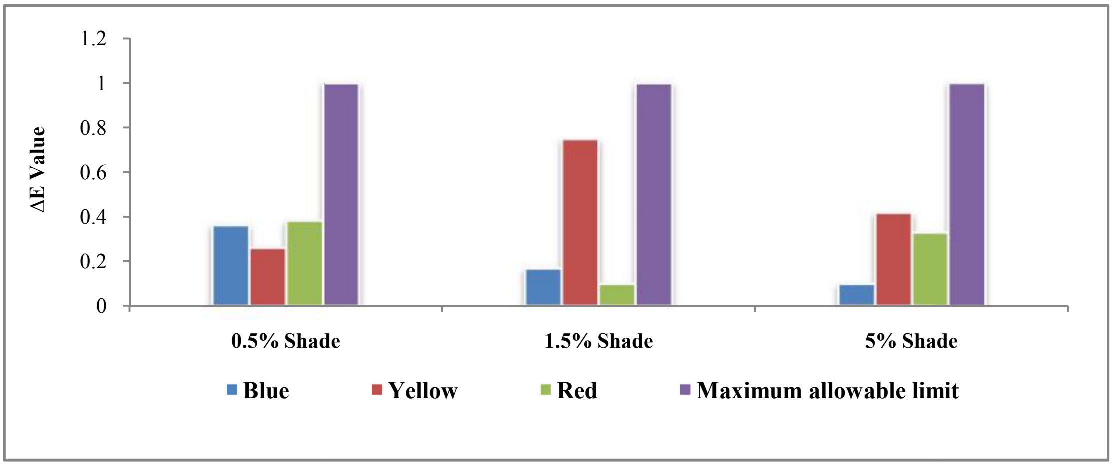


Figure 4.2.4: Color difference (ΔE values) of dyed cotton knit fabrics, dyeing in irradiated wastewater and fresh water at different shade percentages with respect to maximum allowable limit.

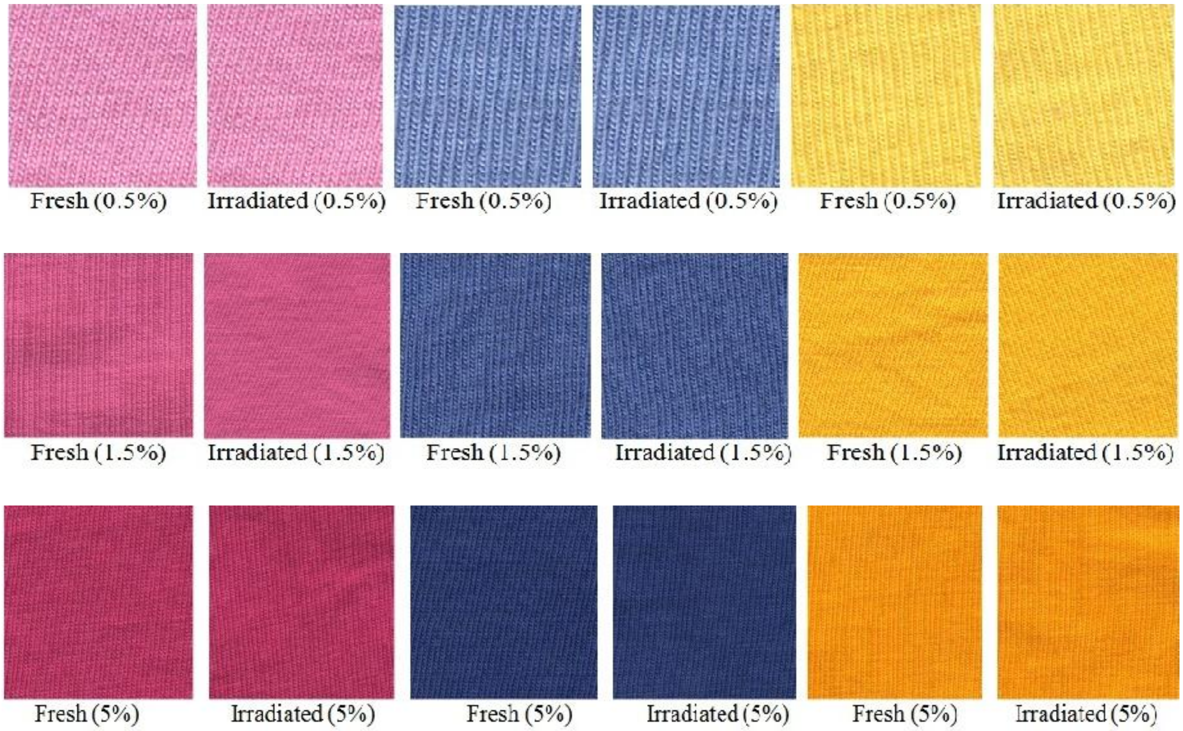


Figure 4.2.5: Cotton knit fabric samples dyed with Novacron Red FN 2BL, Novacron Blue FNR and Novacron Yellow FN2R in irradiated and fresh water at .05%, 1.5% & 5.0% shade.

Figure-4.2.4, illustrated that, all the ΔE values lies under the maximum allowable limit. These values signify that, both irradiated and fresh water have shown similar performance which act as a medium during dyeing. This performance leads to same exhaustion and fixation of dyestuffs in the fabric resulting negligible color differences between wastewater and fresh water treated dyed fabrics. Hence, it can be concluded that the irradiated wastewater has no negative influence for dyeing and color reproduction of fabrics.

4.2.2.2 Color Depth Analysis

Thedepth of color of dyed fabric was analyzed by K/S value. This value numerically represents the nature of the coloring material layer and an easy way to determine a color as a concentration. The color concentration decreases as the value for reflectance increases, and vice versa. The values found for all the fabrics of different color and depth of shade are shown in Figure-4.2.6-4.2.8.

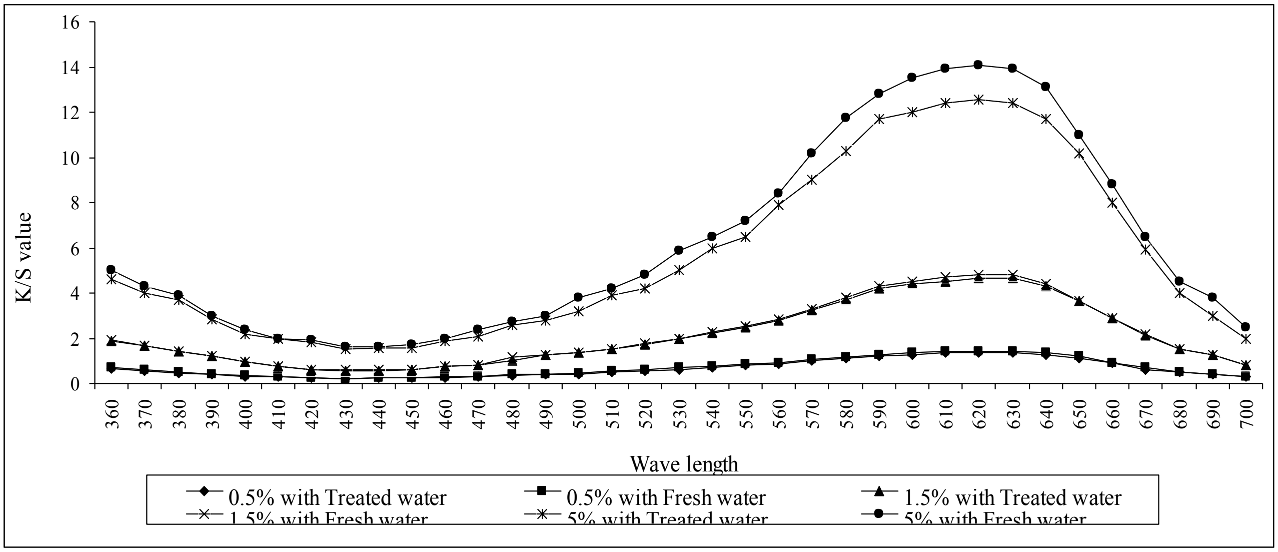


Figure 4.2.6: Dyeabsorption (K/S value versus wavelength) at λ_{max}=630nm of Novacron Blue FNR.

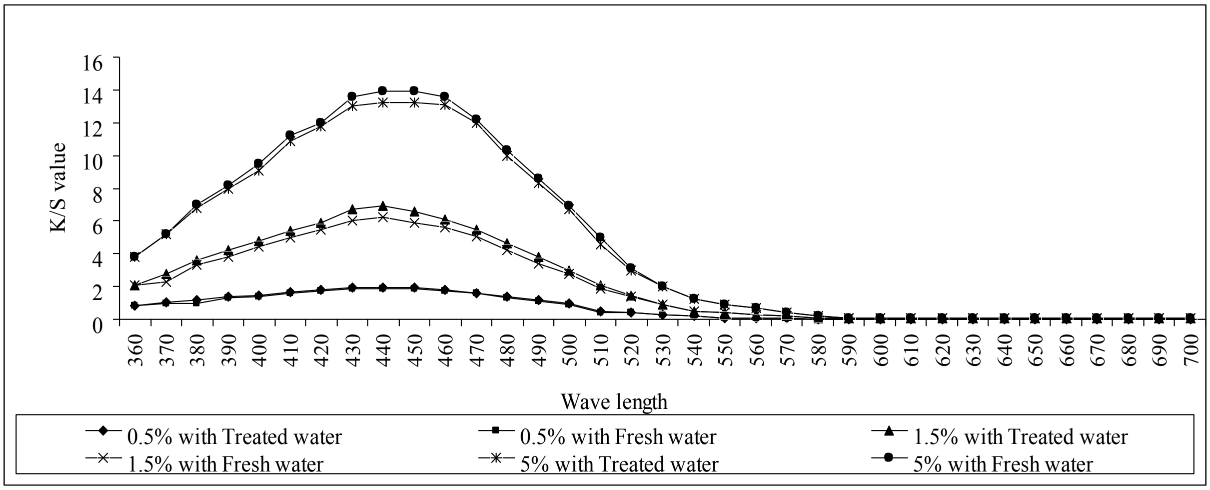


Figure 4.2.7: Dyeabsorption (K/S value versus wavelength) at λ_{max}=440nm of Novacron Yellow FN2R.

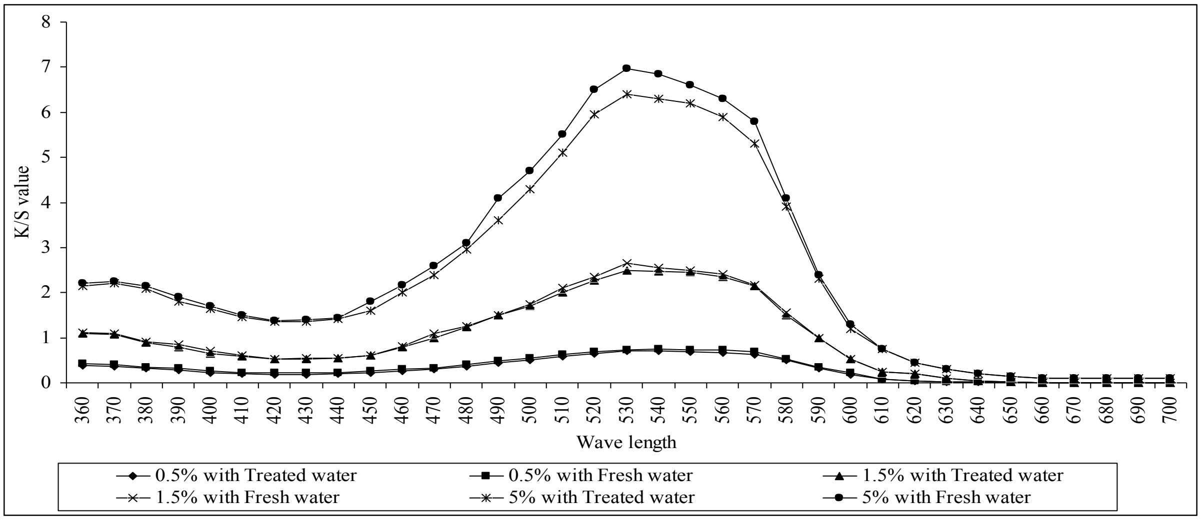


Figure 4.2.8: Dyeabsorption (K/S value versus wavelength) at λ_{max}=540nm of Novacron Red FN2BL.

The Figures-4.2.6, 4.2.7 & 4.2.8 for each color showed six different curves for three different shade percentages.More the dyestuff in the fabric the deeper the shade, resulting higher K/S value in the curve (Broadbent, 2001). The curves formed by the 5% shade have shown elevated K/S value whereas the curves for 0.5% shade forms almost flatten curves due to lower K/S value. However, the fabrics dyed in fresh and treated wastewater showed nearly similar curves for a particular shade percentage of each color. This indicated that the fabric absorbed same amount of dyestuff from both types of dyebath (fresh and treated water). As a consequence of absorbing the same amount of dyes, the depth of shades was also found almost similar in the freshwater dyed samples and irradiated wastewater dyed samples.

4.2.2.3 Comparison of Color Fastness

Three types of color fastnesses such as color fastness to rubbing, washing and perspiration of the dyed fabrics were measured as described in experimental section and assessed by grey scale. Color fastness to washing and perspiration were assessed by color change options and the washing of the dyed fabrics was carried out with respect to medium cellulosic wash (Saville, 1999). Rubbing fastness of dyed fabric samples was evaluated in dry and wet condition. The color fastness ratings of fresh water and treated water dyed fabrics are tabulated in the Table-4.2.1-4.2.3.

Table 4.2.1: Color fastness to rubbing (dry and wet) of dyed cotton fabric

Dye	**Shade (%)**	**Fresh water dyed**		**Treated water dyed**	
		Dry	**Wet**	**Dry**	**Wet**
Novacron Yellow FN2R	0.5	4/5	4/5	4/5	4/5
	1.5	4/5	4/5	4/5	4/5
	5.0	4	3/4	4	3/4
Novacron Red FN 2BL	0.5	4/5	4/5	4/5	4/5
	1.5	4/5	4/5	4/5	4/5
	5.0	4	4	4	3/4
Novacron Blue FNR	0.5	4/5	4/5	4/5	4/5
	1.5	4/5	4	4/5	4
	5.0	4	3/4	4	3/4

Table 4.2.2: Color fastness to washing (color change) of dyed cotton fabric

Dye	Shade (%)	Fresh water dyed	Treated water dyed
Novacron Yellow FN2R	0.5	4	4
	1.5	4/5	4/5
	5.0	4/5	4/5
Novacron Red FN 2BL	0.5	4/5	4/5
	1.5	4/5	4/5
	5.0	4/5	4
Novacron Blue FNR	0.5	4	4/5
	1.5	4	4
	5.0	4	4

Table 4.2.3: Color fastness to perspiration (color change) of dyed cotton fabric

Shade	Shade (%)	Fresh water dyed	Treated water dyed
Novacron Yellow FN2R	0.5	4	4
	1.5	4/5	4/5
	5.0	4/5	4/5
Novacron Red FN 2BL	0.5	4/5	4/5
	1.5	4/5	4/5
	5.0	4/5	4/5
Novacron Blue FNR	0.5	4	4/5
	1.5	4	4
	5.0	4	4

All the fabric samples were dyed in similar dyeing conditions except water (fresh and treated) that was used as dyeing medium resulting similar depth of shade. As a consequence of similar depth of shade, it can be predict that the dyed fabrics will also show similar fastness properties. The results of all fastness values for both irradiated and fresh water dyed fabric samples have supported the prediction. The color fastness results in the tables showed that fresh and treated water dyed fabrics has almost similar fastness rating of ‘good’ to ‘excellent’ (within numerical grade 4 to 5) (Saville, 1999) with very negligible variation.

4.2.2.4 Presence of Carcinogenic Azo Dyes and Formaldehyde in Dyed Fabric

Textile effluent contains dyes and chemicals that are not only toxic but also carcinogenic, mutagenic or teratogenic to various organisms (Novotny et al., 2006). The carcinogenicity of azo dyes, which constitute a significant proportion of textile dyes, is well known (Umbuzeiro et al., 2005). Many dyes are made from known carcinogens like benzidine and have been linked to bladder cancer in humans; to splenic sacromas, hepatocarcinomas and nuclear anomalies in experimental animals and to cause chromosomal aberration in mammalian cells (Percy et al., 1989). The European Parliament Directive 2002/61/EC of July 2002, the European Union (EU) has decided that, those azo dyes, which can break down under reductive conditions to release any such group of aromatic amines like benzidine, are prohibited from being used in those consumer goods which are considered to have regular skin contact.

Again in the dyeing process, formaldehyde-based fixative is often used to improve color fastness of cotton fabric. Moreover, formaldehyde based durable press finishing agents are also used to develop the anticreasing property of cellulosic fiber (Heywood, 2003). The fixation of fixing agent with cellulose is performed by cross linking reaction but some environmental condition especially in sweat, these reaction products are hydrolyzed resulting the release of formaldehyde. It can be absorbed by the skin through sweat, and then immersed in the human body, serious harm to human health (Tomasino, 1992). So the identification of formaldehyde and carcinogenic azo dyes in dyed fabric is crucial in order to protect the human health.

Table 4.2.4: Presence of banned amines in dyed fabric

Test Item	Test Method	Banned Amines in Dyed Fabric (mg/kg)		Remarks
		Result	Limit	
Dyed fabric	EN 14362-1:2012	< 10 (individual)	30 (individual)	Pass

Table 4.2.5: Screening of water soluble formaldehyde in dyed textile material

Test Item	Result
Dyed fabric	Negative

The results of the test on fabrics dyed with irradiated wastewater showed that, it didn’t contain formaldehyde or any carcinogenic azo dye which is presented in Table-4.2.4 & 4.2.5. Though the discharge of formaldehyde or carcinogenic azo dyes from the dyebath, may accumulate in the mixing tank of textile effluent. But the absence of those perilous chemicals in the dyed fabric signifies the destruction of organic pollutants by gamma irradiation (Getoff, 1999) or presence of lower level of formaldehyde or carcinogenic azo group in dyeing wastewater.

PART THREE

Reuse of Irradiated Textile Wastewater for Irrigation Purposes

4.3.1 Analysis of Growth and Yield Characteristics of Malabar Spinach

4.3.1.1 Plant Height

The morphological characteristics of plant can be described easily by using the height and diameter of plant. Plant height is a useful measure of quality and correlated with survival and growth after planting. The heights of Malabar Spinach plant irrigated in fresh and irradiated water at different day's interval are shown in Table-4.3.1.

Table 4.3.1: Height of Malabar Spinach plant at different days after sowing (DAS)

Samples	**Average Plant Height (cm)**					
	20 DAS	**27 DAS**	**34 DAS**	**41 DAS**	**48 DAS**	**55 DAS**
Plant irrigated with fresh water	5	9.8	21	24	29.1	37.5
Plant irrigated with raw wastewater	5.2	8.16	12.6	18.6	22.4	29.3
Plant irrigated with Treated water	5	13.5	23.3	35.5	48.3	62.4

From Table- 4.3.1, no significant difference was found in the plant height of Malabar Spinach at 20 days after sowing. But considerable height of plant was observed from 34 days to 55 days (during harvesting). The height of a plant depends on the vigor and growth habit (Rop et. al., 2012). Malabar Spinach is a vigorous growing plant and nitrogen had a significant effect on the length of stem. Nitrogen is essential for plant cell division especially vegetative growth in plant (Salisbury & Ross, 1986). The timing and application of nitrogen level are crucial in production of leafy vegetables. The effluents from the textile industries were enriched with organic wastes and contain higher amounts of N, P, and K (Begum at. el., 2011) which affects the growth of vegetables. Again the considerable increase of height of

Malabar Spinach plant irrigated with gamma irradiated wastewater specify the higher amount of nitrogen content in irradiated wastewater and act as a bioferitilizer. It is assumed that, amount of nitrogen is increased in irradiated wastewater due to the breakage of azo group (-N=N-) of dye molecules (Bagyo et al., 2001) after gamma radiation.

4.3.1.2 Root Length

The root is the organ of a plant that typically lies below the surface of the soil. Root length and diameter distribution are important characteristics to be considered when describing and comparing root systems (Bouma at. el., 2000).The radicle is the first root that comes from a plant and the root system of a plant is important parameter for the growth and yield characteristics of a plant.

Table 4.3.2: The average root length of Malabar Spinach plant after harvesting

	Irrigation of Malabar Spinach		
Samples	**Fresh Water**	**Raw Wastewater**	**Irradiated water**
Average Root Length (cm)	11.8	8.1	15.9

Figure 4.3.1: Malabar Spinach plant irrigated with fresh water, raw and gamma irradiated wastewater.

The average length of the roots of Malabar Spinach plant was found 11.8 cm for fresh water on the other hand in case of gamma irradiated water the length was 15.9 cm as shown in Table-4.3.2. The length of roots is very important for the plant that are anchoring of the plant body to the ground and supporting it.The considerable increase in length of roots of the plant irrigated with treated wastewater was due to the absorption of nutrients from water and soil since textile wastewater was enriched with organic wastes and contains higher amounts of N, P, and K (Begum at. el., 2011). In response to the concentration of nutrients, roots also synthesize cytokinin, which acts as a signal for the growth ofthe shoots of plant. Again roots often function in storage of food and nutrients which is essential for the growth and yield of the plant.

4.3.3 Number of Leaves per Plant

The average number of leaves of Malabar Spinach plant irrigated with fresh and treated water is tabulated in Table- 4.3.3. The significant increase of leaves was observed incase of plant irrigated with treated water from 34 days after sown. The number of leaves of plant was about 60 percent higher than fresh water sample during harvesting. The higher number of leaves of irradiated water plant was due to the better height and stem length of the plant. Nitrogen had a significant effect on the height and stem length of the plant and irradiated wastewater contains improved amount of nitrogen and acts as a biofertilizer resulting increased number of leaves and height of the plant.

Table 4.3.3: Average number of leaves of plant at different days after sowing (DAS)

Samples	Number of Average Leaves					
	20 DAS	27 DAS	34 DAS	41 DAS	48 DAS	55 DAS
Plant irrigated with fresh water	5	7	12	19	24	28
Plant irrigated with raw wastewater	6	7	10	14	16	19
Plant irrigated with treated water kGy	5	11	21	28	34	45

4.3.1.3 Mineral Content

The mineral content in the Malabar spinach plants were also investigated by 'Tandem accelerator'. The analysis was performed in case of Zinc, Manganese, Calcium, and Potassium of plant after irrigation with irradiated wastewater. The values found after investigation are tabulated in Table-4.3.4.

Table 4.3.4: Mineral content (in ppm) in Malabar Spinach plant after irrigation

Samples	Mn	Zn	K	Ca
Plant irrigated with fresh water	101	38	11417	20082
Plant irrigated with wastewater	108	52	5529	11843
Plant irrigated with treated water	172	66	12185	25347

From Table-4.3.4 it was observed that, significant increase of minerals content was found in the analysis of the samples from the plant irrigated with treated effluent than the samples from the plant irrigated with fresh water. Concentration of Zinc, Manganese, Calcium and Potassium were found 74, 70, 7 and 26 percent increased respectively. The uptake of the nutrients varied from the plant to plant depends on plant's root geometry and morphology (Falk et. al., 2007). The increase of the mineral content of the plant irrigated with treated wastewater might be due to the increased root length of the plant. As discussed earlier, the major function of roots is the absorption of inorganic nutrients from soil and water. Improved root length can provide higher amount of nutrients to the plant resulting better mineral content of the vegetable irrigated with treated effluent.

CHAPTER: FIVE

CONCLUSIONS AND RECOMMENDETIONS

5.1 Conclusions

The decoloration and degradation of textile wastewater by gamma irradiation and the performance of irradiated water in fabric processing and irrigation have been investigated. The detailed study has demonstrated that, gamma radiation can effectively degrade the coloring substances and organic pollutants of textile wastewater. Again the irradiated wastewater can be applied in textile wet processing satisfactorily and have shown similar performance in the pretreatment and dyeing of cotton knit fabric with respect to the fresh water. Moreover, the treated wastewater can also be used in irrigation acceptably. The yield and food value of plant irrigated with irradiated wastewater was found better than irrigated with fresh water. The findings of this thesis work can be summarized as below;

- The treatment of textile wastewater by gamma radiation can effectively decomposes the coloring substances resulting in higher color removal percentage and lowering the pH values.
- Higher radiation dose can also greatly promote the degradation of organic materials and decrease the COD, BOD_5 and TSS of irradiated water. But insignificant change of TDS, EC and heavy metals in wastewater specify the ineffectiveness of radiation to eliminate those pollutants from wastewater.
- Gamma irradiated wastewater can perform perfectly as an alternative to the fresh water in the pretreatment of cotton fabric. The irradiated wastewater can also be used

satisfactorily as a medium for the coloration of textile materials in case of light, medium and deep shades.

- Irradiated wastewater can also be used in irrigation and acts as a biofertilizer for the plant. Remarkable results have been noticed for the plant growth, leaves count and root length. The improvement of mineral content in the plant was also analyzed and significant increase of minerals content was found in the samples irrigated with treated effluent than the samples irrigated with fresh water.

5.2 Recommendations

Textile industrial sector is one of the most important and largest industrial sectors of Bangladesh with regard to production, source of foreign exchange and labor force employment. But textile industrieshave been condemned as being one of the world's worst offenders in terms of pollution because these industries discharge millions of gallons of effluent each year, full of perilous chemicals, heavy metals and others. Treating industrial textile wastewater is complicated due to the high levels of biological oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS) and nonbiodegradable nature of the organic dyes present in the wastewater. The color of the textile wastewater is not removed efficiently by ordinary treatment technology. Ionization radiation technology is a promising technique to decolorize and decompose the textile wastewater with no further generation of secondary waste. The treatment of textile wastewater by gamma radiation and the recycling and reuse of irradiated wastewater is an effective way for sustainable development of textiles. This research work has been designed for recycling and reuse of treated textile wastewater to develop the sustainability of textile industries of Bangladesh. For the continuation of present research work the following recommendations can be taken into consideration.

- In this study, wastewater samples were collected only from one factory. Further research could be done collecting the wastewater samples from the different textile dyeing and washing factories.
- The existing gamma radiation source is not suitable for the irradiation of large volume of wastewater. For the continuous treatment of large volume wastewater new radiation source should established.

- The recycling of irradiated wastewater was performed in laboratory dyeing machine. Further investigation should be carried out in bulk production of fabric dyeing and printing.
- The reuse of treated wastewaterin irrigation was carried out on only one vegetable (Malabar spinach plant). Other vegetables and fruits could be irrigated with irradiated wastewater to observe the effect yield, growth and nutrient qualities.
- Detail investigation is required for the plant irrigated with treated wastewater to determine the presence of any toxic compound which is harmful for human health.

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APPENDIX

Appendix A: Physicochemical parameters of raw and irradiated wastewater at different radiation doses.

Table A.1: Reduction of pH of wastewater after gamma irradiation at different radiation doses

Radiation dose	pH of Raw wastewater	pH of Irradiated wastewater
3 kGy	8.3	7.4 7.4 7.3
5 kGy		7.2 7.1 7.1
8 kGy		7.0 7.1 7.2
12 kGy		7.0 7.1 7.1

Table A.2: Color reduction of dyeing wastewater at different radiation doses

Radiation dose	Decoloration %	Absorbance at λ_{max}
3 kGy	58.26 62.88 59.82	420 nm
5 kGy	73.45 68.88 70.34	
8 kGy	76.36 79.90 78.42	
12 kGy	85.54 82.65 83.56	

Table A.3: Reduction of Chemical Oxygen Demand (COD) values of textile wastewater after gamma irradiation

Wastewater Sample	COD mgL^{-1}
Raw wastewater (RW)	278 267 282
Radiation dose 3kGy	223 226 219
Radiation dose 5kGy	214 212 217
Radiation dose 8kGy	205 211 213
Radiation dose 12kGy	208 204 209

Table A.4: Reduction of Biological Oxygen Demand (BOD_5) values of textile wastewater after gamma irradiation

Wastewater Sample	BOD_5 mgL^{-1}
Raw wastewater	197 188 182
Radiation dose 3kGy	154 159 151
Radiation dose 5kGy	146 150 141
Radiation dose 8kGy	139 145 141
Radiation dose 12kGy	134 128 136

Table A.5: Total suspended solids of raw wastewater and irradiated wastewater at different radiation doses.

Wastewater Sample	TSS mgL^{-1}
Raw wastewater	310 318 306
Radiation dose 3kGy	276 271 265
Radiation dose 5kGy	262 264 261
Radiation dose 8kGy	246 238 248
Radiation dose 12kGy	226 215 218

Table A.6: Total dissolved solids of raw wastewater and irradiated wastewater at different radiation doses.

Wastewater Sample	TDS mgL^{-1}
Raw wastewater	1026 1022 1027
Radiation dose 3kGy	976 971 968
Radiation dose 5kGy	972 964 947
Radiation dose 8kGy	963 953 950
Radiation dose 12kGy	960 955 940

Table A.7: Electrical conductivity of raw wastewater and irradiated wastewater at different radiation doses

Wastewater Sample	Conductivity (µs/cm)
Raw wastewater	2010 1990 1987
Radiation dose 3kGy	1970 1952 1968
Radiation dose 5kGy	1960 1964 1947
Radiation dose 8kGy	1923 1945 1920
Radiation dose 12kGy	1925 1930 1940

Appendix B: Recycling of gamma irradiated wastewater in cotton fabric processing.

Table B.1: Weight loss% of chemically singed fabric samples processed in irradiated and fresh water

Fabric Sample No.	Weight loss% Treated in Fresh Water	Weight loss% Treated in Irradiated Water
1.	0.77	0.72
2.	0.76	0.73
3.	0.71	0.75
4.	0.79	0.81
5.	0.88	0.87
6.	0.78	0.80
7.	0.83	0.76

Table B.2: Weight loss% of different scoured fabric samples processed in irradiated and fresh water

Fabric Sample No.	Weight loss% Treated in Fresh Water	Weight loss% Treated in Irradiated Water
1.	6.1	6.2
2.	5.9	6.2
3.	7.3	7.1
4.	6.5	6.8
5.	5.6	5.8
6.	7.8	7.4
7.	6.8	6.5

Table B.3: Whiteness index of different white bleached fabric samples processed in irradiated and fresh water

Fabric Sample No.	Whiteness Index Treated in Fresh Water	Whiteness Index Treated in Irradiated Water
1.	77.12	74.80
2.	76.40	74.31
3.	77.31	75.44
4.	77.77	75.58
5.	77.60	76.91
6.	76.34	73.47
7.	78.66	76.88

Table B.4: Color difference (ΔE values) of dyed cotton knit fabrics, dyeing in irradiated wastewater and fresh water at different shade percentages

Dye	**Shade%**	**ΔE_{CMC}**
Novacron Red FN 2BL	5.0%	0.33
	1.5%	0.10
	0.5%	0.38
Novacron Blue FN 2BL	5.0%	0.10
	1.5%	0.17
	0.5%	0.36
Novacron Yellow FN 2BL	5.0%	0.42
	1.5%	0.75
	0.5%	0.26

Appendix C: Reflectance curve of white bleached fabric samples treated in fresh and irradiated water.

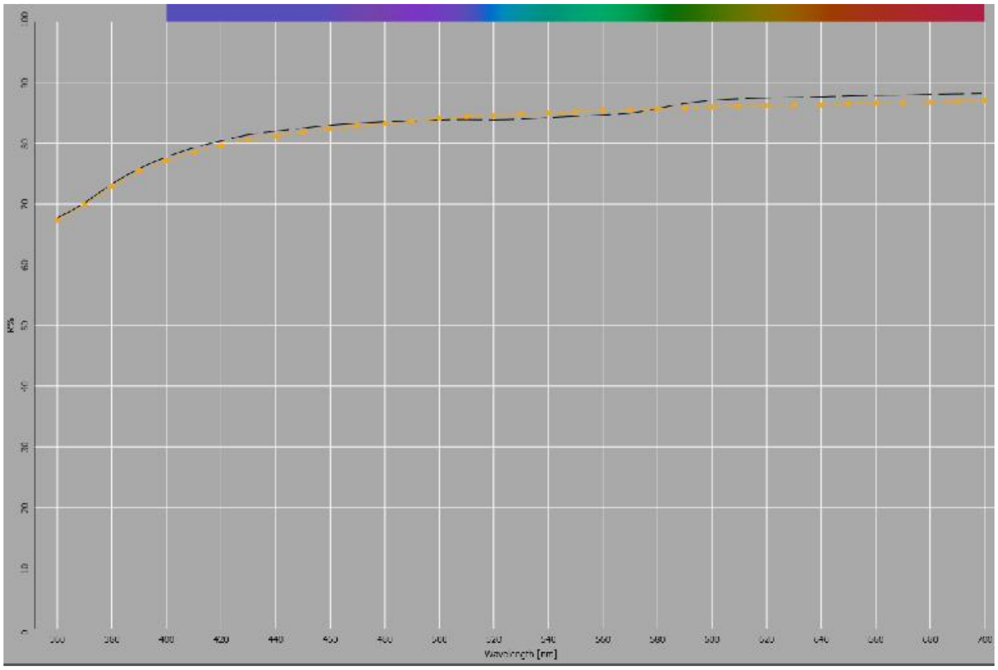


Figure C.1: Reflectance curve of white bleached fabric sample 1 treated in fresh and irradiated water.

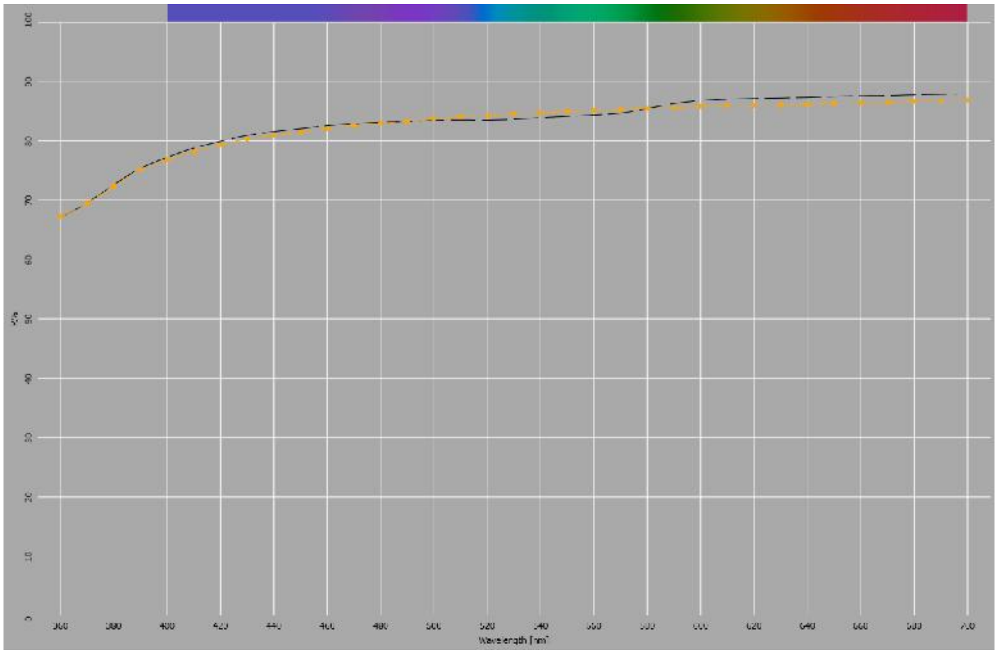


Figure C.2: Reflectance curve of white bleached fabric sample 2 treated in fresh and irradiated water.

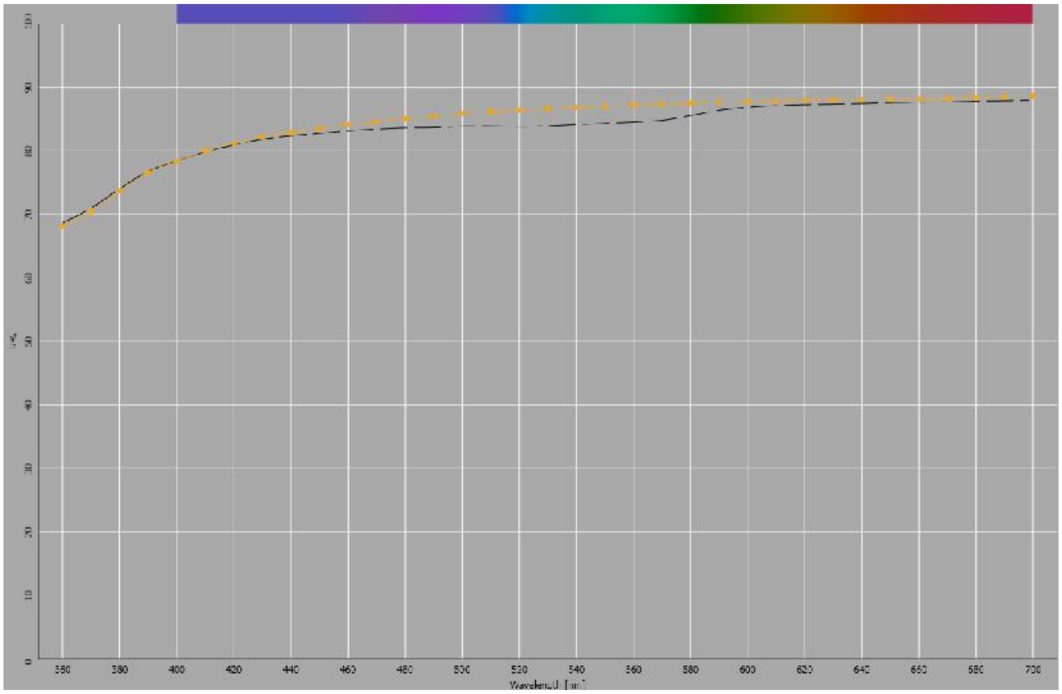


Figure C.3: Reflectance curve of white bleached fabric sample 3 treated in fresh and irradiated water.

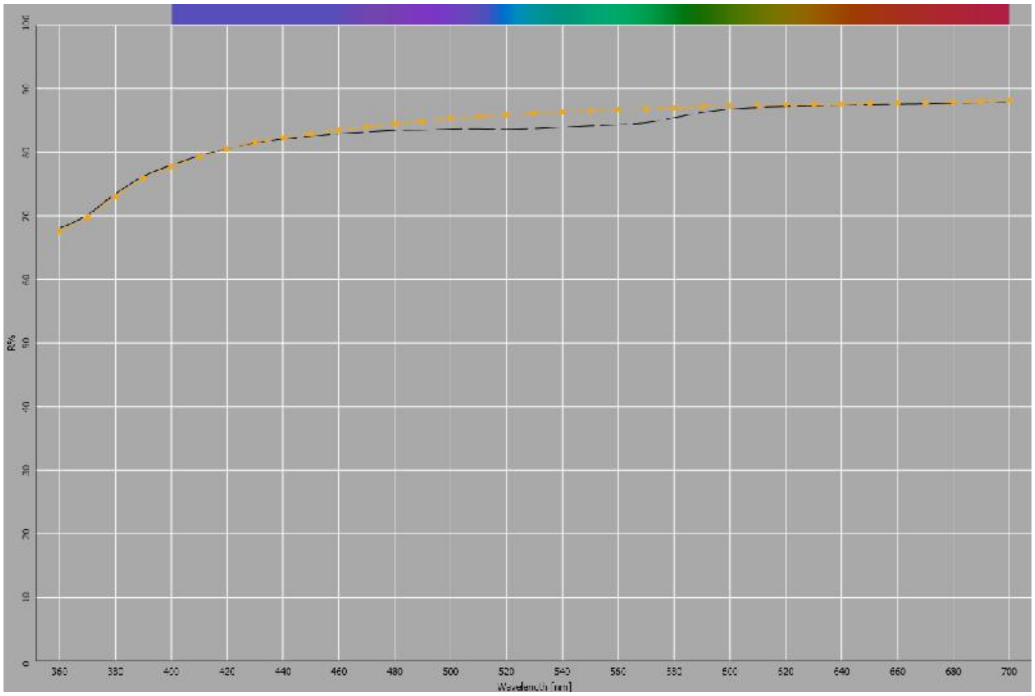


Figure C.4: Reflectance curve of white bleached fabric sample 4 treated in fresh and irradiated water.

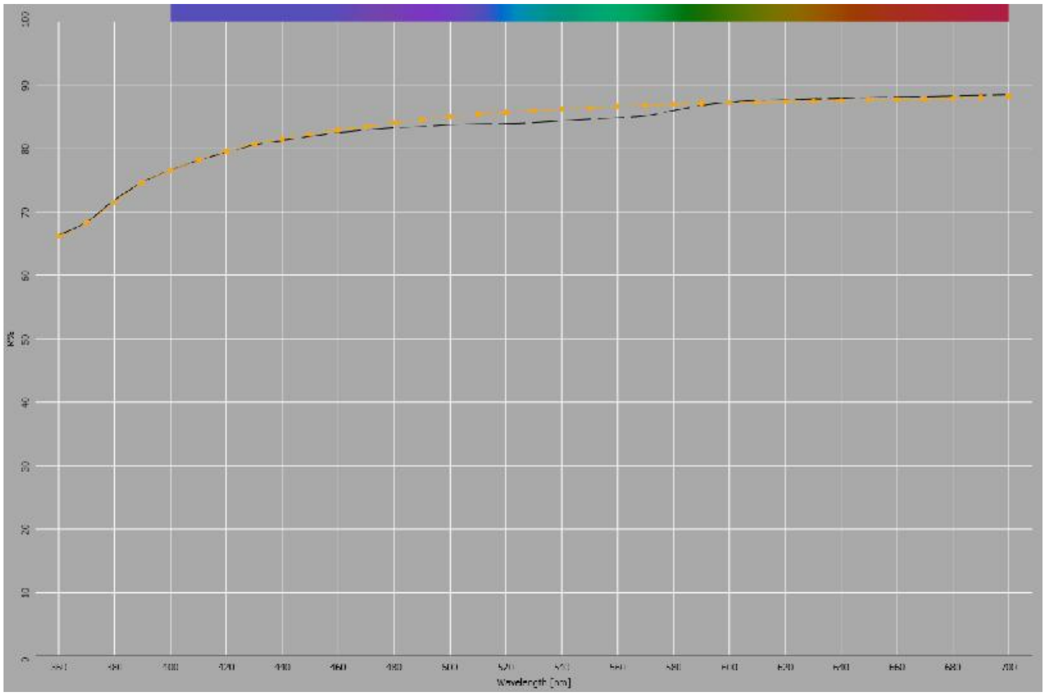


Figure C.5: Reflectance curve of white bleached fabric sample 5 treated in fresh and irradiated water.

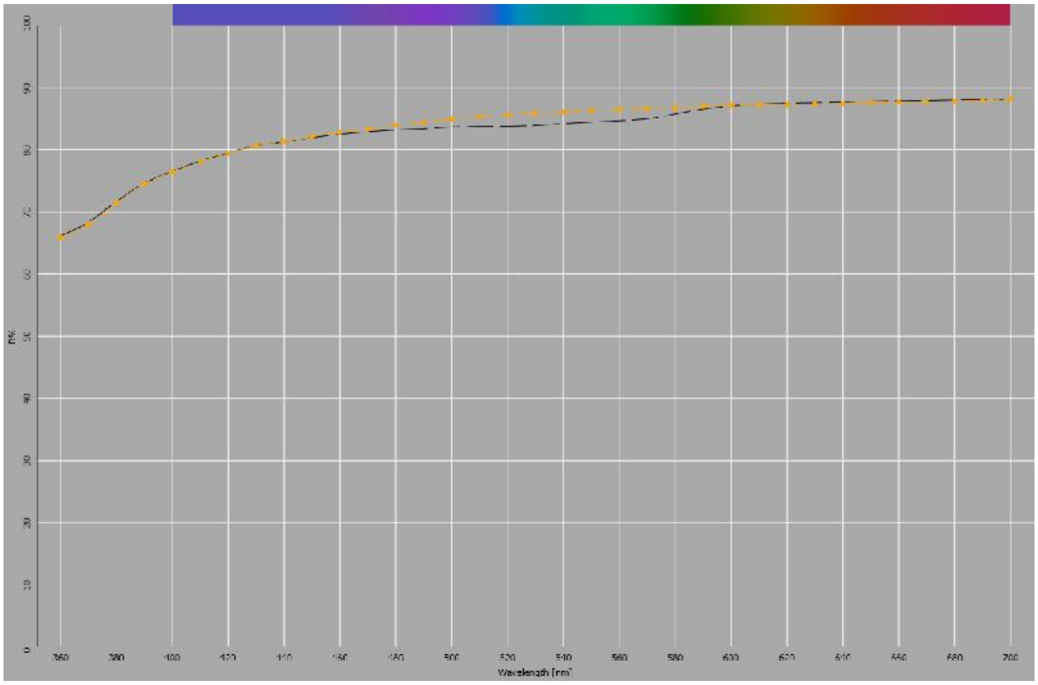


Figure C.6: Reflectance curve of white bleached fabric sample 6 treated in fresh and irradiated water.

Appendix D: Color difference of dyed fabric treated with fresh and irradiated water at different shade percentages.

Dhaka University Of Engineering & Technology (DUET)
Department Of Textile Engineering
Gazipur-1700, Bangladesh

Standard Name: 40 of 54

5% RED 29/04

Standard: 12429 650 %R LAV SCI UV Inc

Batch Name: 1 of 1

BATCH1

Date: 29-Apr-14 Time: 10:25:15

Batch: 12420 650 %R LAV SCI UV Inc

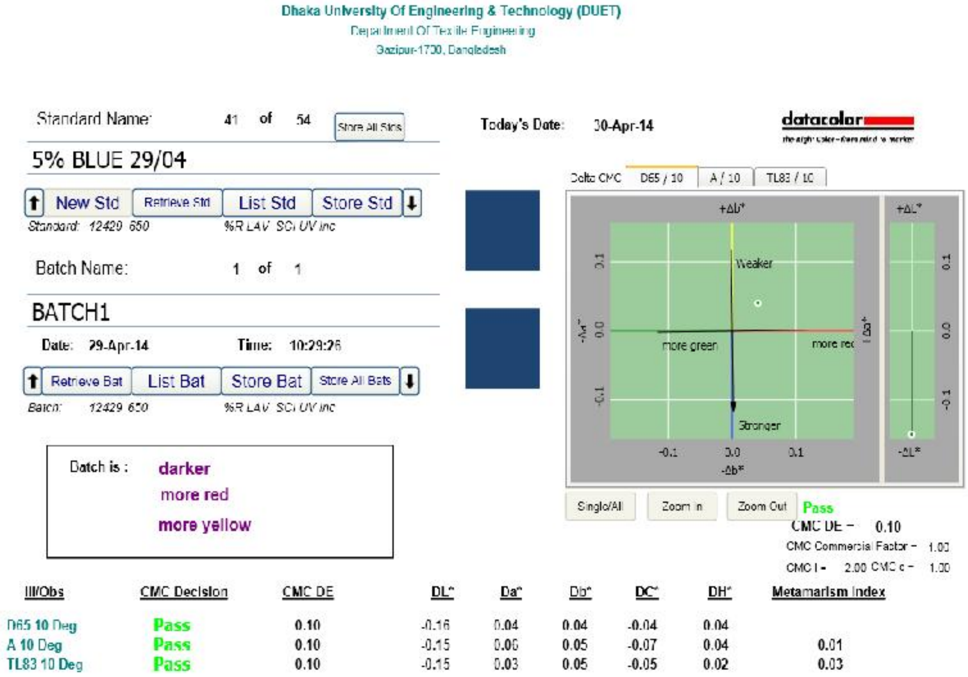
Batch Is : darker
more red
more yellow

Today's Date: 30-Apr-14

Pass
CMC DE = 0.33
CMC Commercial Factor = 1.00
CMC l = 2.00 CMC c = 1.00

Ill/Obs	CMC Decision	CMC DE	DL*	Da*	Db*	DC*	DH*	Metamerism Index
D65 10 Deg	Pass	0.33	0.60	0.27	0.21	0.23	0.25	
A 10 Deg	Pass	0.32	-0.54	0.21	0.32	0.24	0.30	0.28
TL83 10 Deg	Pass	0.31	-0.54	0.16	0.29	0.14	0.30	0.26

Figure D.1: Color matching of fabrics dyeing in fresh and irradiated water with Novacron Red FN 2BL at 5.0% shade.



Dhaka University Of Engineering & Technology (DUET)
Department Of Textile Engineering
Gazipur-1700, Bangladesh

Standard Name: 41 of 54

5% BLUE 29/04

Standard: 12420 650 %R LAV SCI UV Inc

Batch Name: 1 of 1

BATCH1

Date: 29-Apr-14 Time: 10:29:26

Batch: 12429 650 %R LAV SCI UV Inc

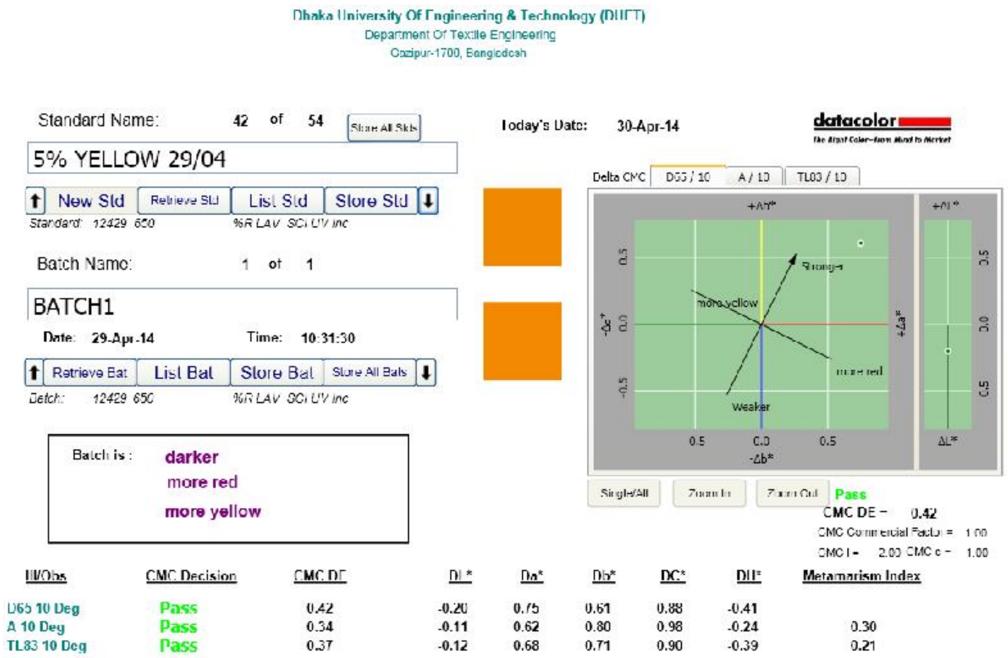
Batch is : darker
more red
more yellow

Today's Date: 30-Apr-14

Pass
CMC DE = 0.10
CMC Commercial Factor = 1.00
CMC l = 2.00 CMC c = 1.00

Ill/Obs	CMC Decision	CMC DE	DL*	Da*	Db*	DC*	DH*	Metamerism Index
D65 10 Deg	Pass	0.10	-0.16	0.04	0.04	-0.04	0.04	
A 10 Deg	Pass	0.10	-0.15	0.06	0.05	-0.07	0.04	0.01
TL83 10 Deg	Pass	0.10	-0.15	0.03	0.05	-0.05	0.02	0.03

Figure D.2: Color matching of fabrics dyeing in fresh and irradiated water with Novacron Blue FNR at 5.0% shade.



Dhaka University Of Engineering & Technology (DUET)
Department Of Textile Engineering
Gazipur-1700, Bangladesh

Standard Name: 42 of 54

5% YELLOW 29/04

Standard: 12429 650 %R LAV SCI UV inc

Today's Date: 30-Apr-14

Batch Name: 1 of 1

BATCH1

Date: 29-Apr-14 Time: 10:31:30

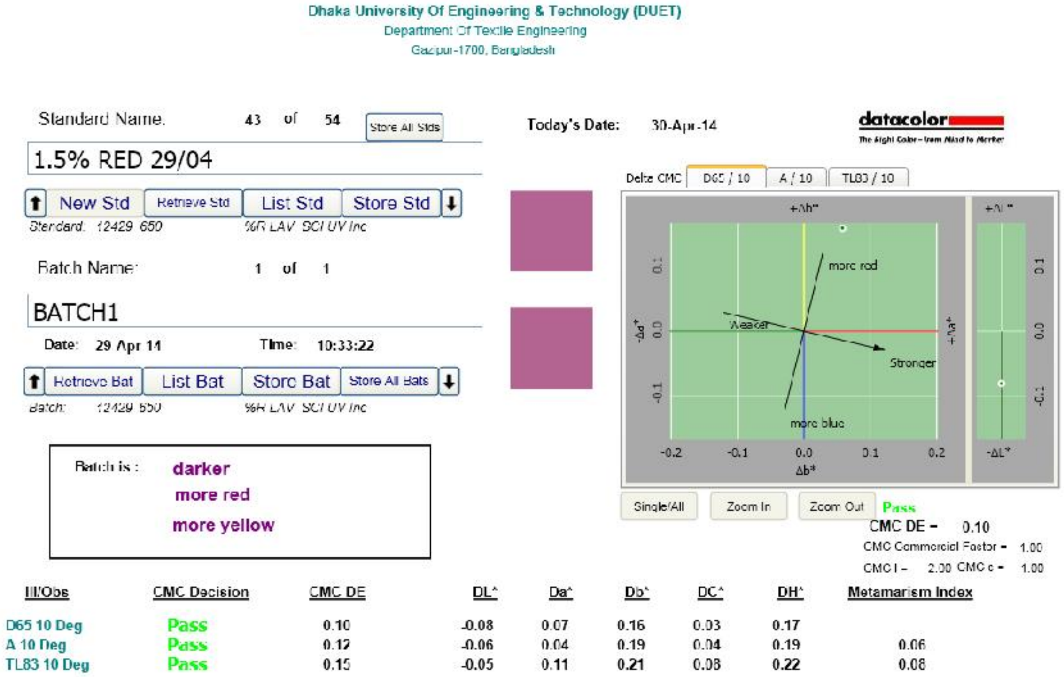
Batch: 12429 650 %R LAV SCI UV inc

Batch is : darker
more red
more yellow

Pass
CMC DE = 0.42
CMC Commercial Factor = 1.00
CMC l = 2.00 CMC c = 1.00

Ill/Obs	CMC Decision	CMC DE	DL*	Da*	Db*	DC*	DH*	Metamarism Index
D65 10 Deg	Pass	0.42	-0.20	0.75	0.61	0.88	-0.41	
A 10 Deg	Pass	0.34	-0.11	0.62	0.80	0.98	-0.24	0.30
TL83 10 Deg	Pass	0.37	-0.12	0.68	0.71	0.90	-0.39	0.21

Figure D.3: Color matching of fabrics dyeing in fresh and irradiated water with Novacron Yellow FN2R at 5.0% shade.



Dhaka University Of Engineering & Technology (DUET)
Department Of Textile Engineering
Gazipur-1700, Bangladesh

Standard Name: 43 of 54

1.5% RED 29/04

Standard: 12429 650 %R LAV SCI UV Inc

Today's Date: 30-Apr-14

Batch Name: 1 of 1

BATCH1

Date: 29 Apr 14 Time: 10:33:22

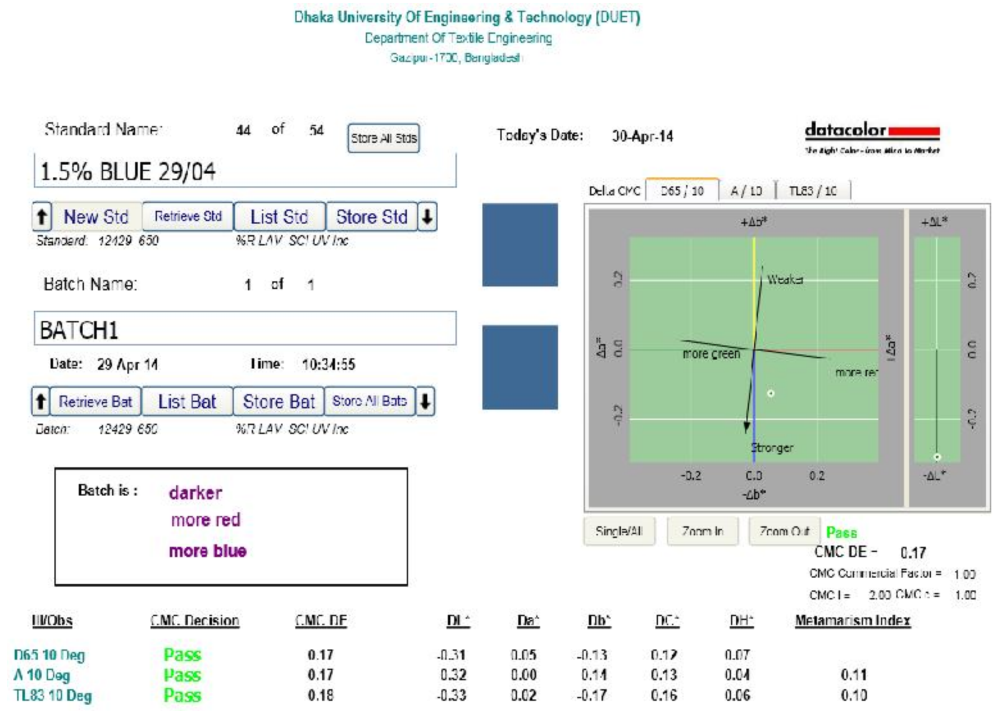
Batch: 12429 650 %R LAV SCI UV Inc

Batch is : darker
more red
more yellow

Pass
CMC DE = 0.10
CMC Commercial Factor = 1.00
CMC l = 2.00 CMC c = 1.00

Ill/Obs	CMC Decision	CMC DE	DL*	Da*	Db*	DC*	DH*	Metamarism Index
D65 10 Deg	Pass	0.10	-0.08	0.07	0.16	0.03	0.17	
A 10 Deg	Pass	0.12	-0.06	0.04	0.19	0.04	0.19	0.06
TL83 10 Deg	Pass	0.15	-0.05	0.11	0.21	0.08	0.22	0.08

Figure D.4: Color matching of fabrics dyeing in fresh and irradiated water with Novacron Red FN2BL at 1.5% shade.



Dhaka University Of Engineering & Technology (DUET)
Department Of Textile Engineering
Gazipur-1700, Bangladesh

Standard Name: 44 of 54

1.5% BLUE 29/04

Standard: 12429 650 %R LAV SCI UV Inc

Batch Name: 1 of 1

BATCH1

Date: 29 Apr 14 Time: 10:34:55

Batch: 12429 650 %R LAV SCI UV Inc

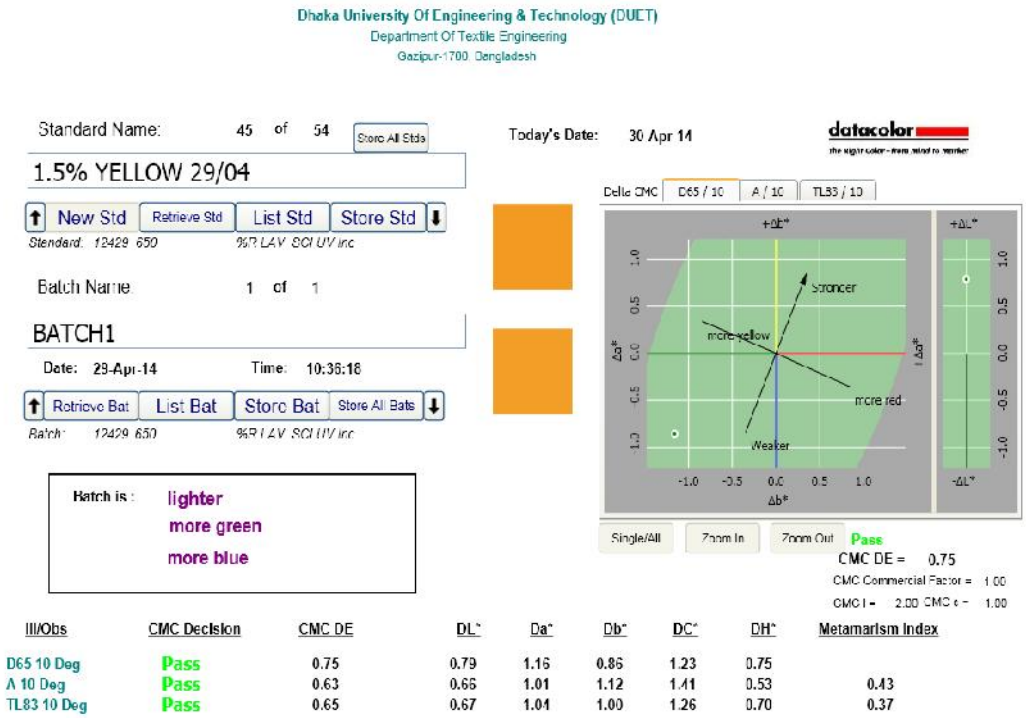
Today's Date: 30-Apr-14

Batch is : darker
more red
more blue

Pass
CMC DE = 0.17
CMC Commercial Factor = 1.00
CMC l = 2.00 CMC c = 1.00

Ill/Obs	CMC Decision	CMC DE	DL*	Da*	Db*	DC*	DH*	Metamarism Index
D65 10 Deg	Pass	0.17	-0.31	0.05	-0.13	0.12	0.07	
A 10 Deg	Pass	0.17	0.32	0.00	0.14	0.13	0.04	0.11
TL83 10 Deg	Pass	0.18	-0.33	0.02	-0.17	0.16	0.06	0.10

Figure D.5: Color matching of fabrics dyeing in fresh and irradiated water with Novacron Blue FNR at 1.5% shade.



Dhaka University Of Engineering & Technology (DUET)
Department Of Textile Engineering
Gazipur-1700, Bangladesh

Standard Name: 45 of 54

1.5% YELLOW 29/04

Standard: 12429 650 %R LAV SCI UV inc

Batch Name: 1 of 1

BATCH1

Date: 29-Apr-14 Time: 10:36:18

Batch: 12429 650 %R LAV SCI UV inc

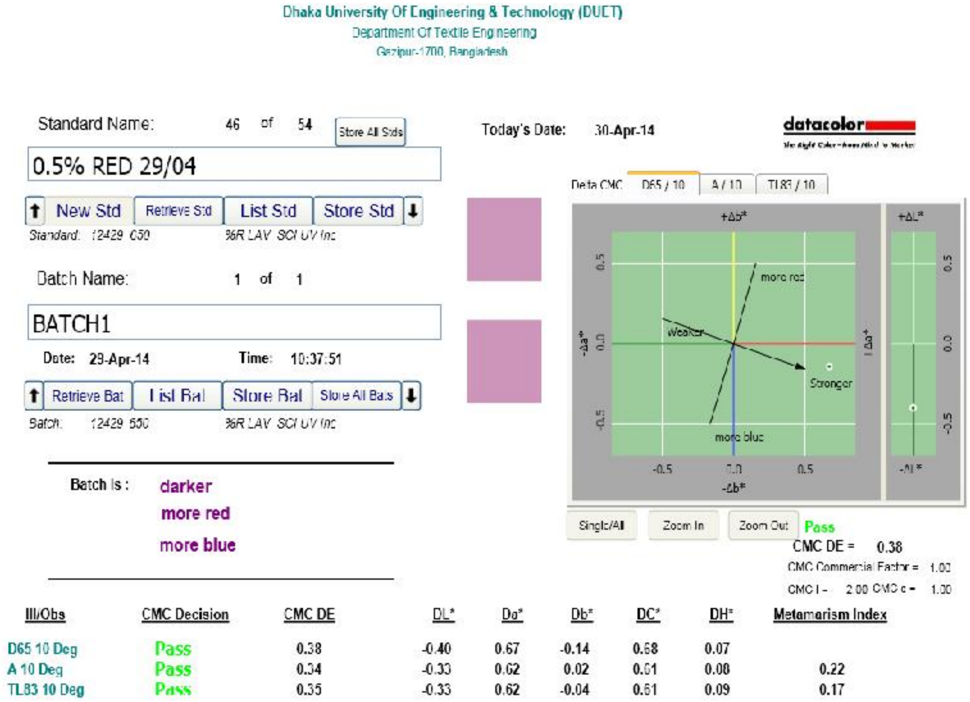
Today's Date: 30 Apr 14

Batch is : lighter
more green
more blue

Pass
CMC DE = 0.75
CMC Commercial Factor = 1.00
CMC l = 2.00 CMC c = 1.00

Ill/Obs	CMC Decision	CMC DE	DL*	Da*	Db*	DC*	DH*	Metamarism Index
D65 10 Deg	Pass	0.75	0.79	1.16	0.86	1.23	0.75	
A 10 Deg	Pass	0.63	0.66	1.01	1.12	1.41	0.53	0.43
TL83 10 Deg	Pass	0.65	0.67	1.01	1.00	1.26	0.70	0.37

Figure D.6: Color matching of fabrics dyeing in fresh and irradiated water with Novacron Yellow FN2R at 1.5% shade.



Dhaka University Of Engineering & Technology (DUET)
Department Of Textile Engineering
Gazipur-1700, Bangladesh

Standard Name: 46 of 54

0.5% RED 29/04

Standard: 12429 650 %R LAV SCI UV Inc

Batch Name: 1 of 1

BATCH1

Date: 29-Apr-14 Time: 10:37:51

Batch: 12429 650 %R LAV SCI UV Inc

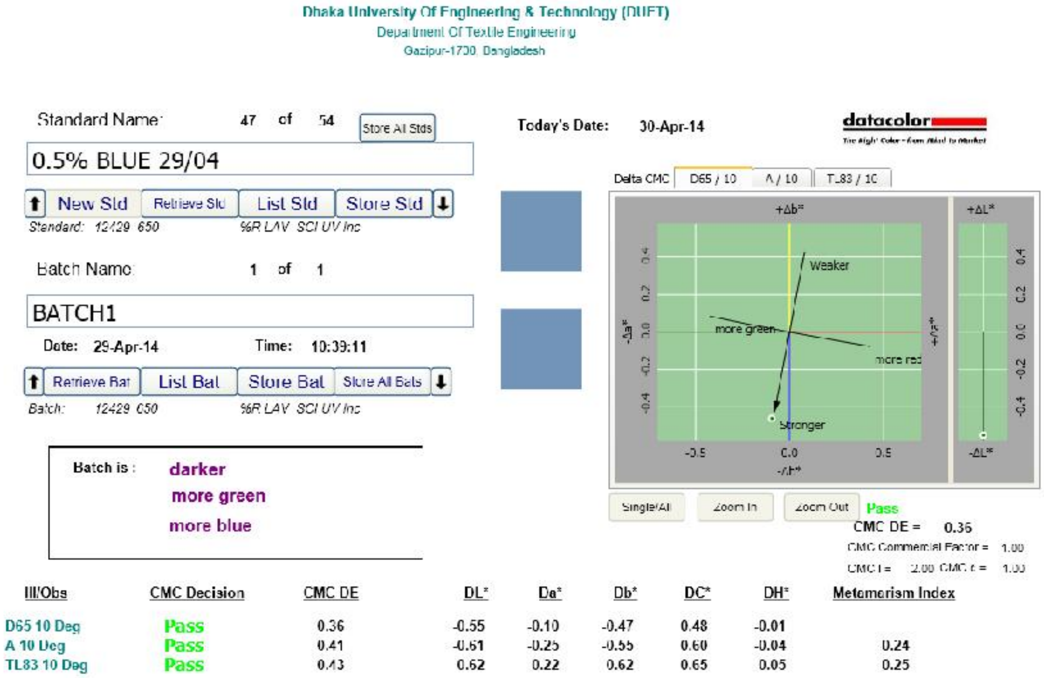
Today's Date: 30-Apr-14

Batch Is : darker
more red
more blue

Pass
CMC DE = 0.38
CMC Commercial Factor = 1.00
CMC l = 2.00 CMC c = 1.00

Ill/Obs	CMC Decision	CMC DE	DL*	Da*	Db*	DC*	DH*	Metamarism Index
D65 10 Deg	Pass	0.38	-0.40	0.67	-0.14	0.68	0.07	
A 10 Deg	Pass	0.34	-0.33	0.62	0.02	0.61	0.08	0.22
TL83 10 Deg	Pass	0.35	-0.33	0.62	-0.04	0.61	0.09	0.17

Figure D.7: Color matching of fabrics dyeing in fresh and irradiated water with Novacron Red FN2BL at 0.5% shade.



Dhaka University Of Engineering & Technology (DUET)
Department Of Textile Engineering
Gazipur-1700, Bangladesh

Standard Name: 47 of 54

0.5% BLUE 29/04

Standard: 12429 650 %R LAV SCI UV Inc

Batch Name: 1 of 1

BATCH1

Date: 29-Apr-14 Time: 10:39:11

Batch: 12429 650 %R LAV SCI UV Inc

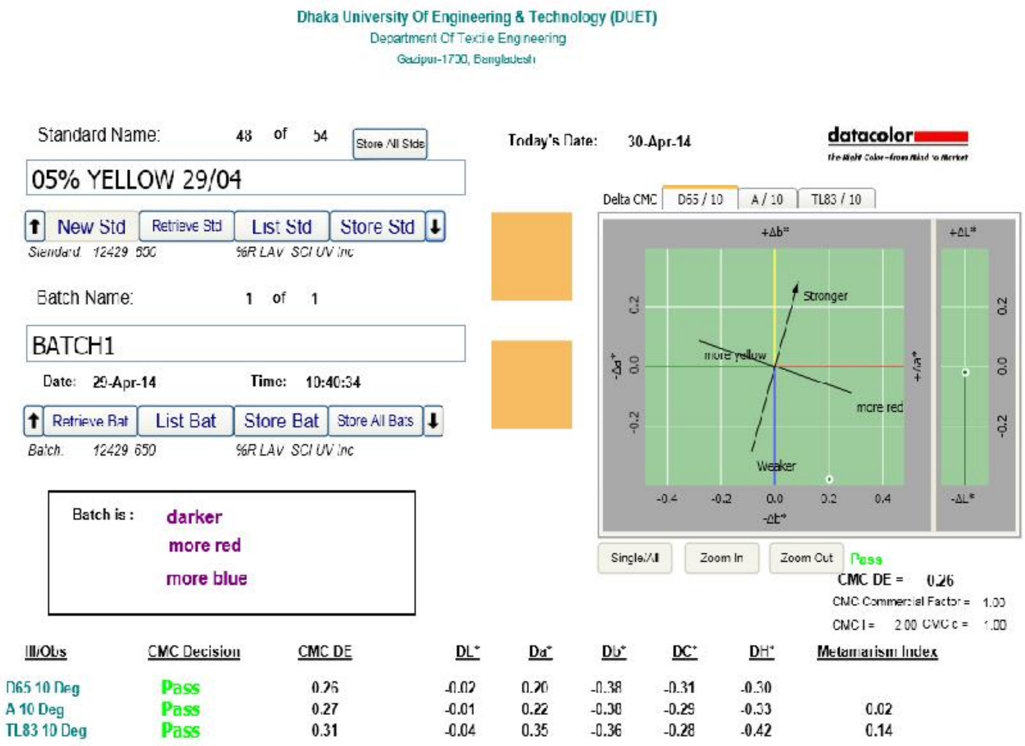
Today's Date: 30-Apr-14

Batch is : darker
more green
more blue

Pass
CMC DE = 0.36
CMC Commercial Factor = 1.00
CMC l = 2.00 CMC c = 1.00

Ill/Obs	CMC Decision	CMC DE	DL*	Da*	Db*	DC*	DH*	Metamarism Index
D65 10 Deg	Pass	0.36	-0.55	-0.10	-0.47	0.48	-0.01	
A 10 Deg	Pass	0.41	-0.61	-0.25	-0.55	0.60	-0.04	0.24
TL83 10 Deg	Pass	0.43	0.62	0.22	0.62	0.65	0.05	0.25

Figure D.8: Color matching of fabrics dyeing in fresh and irradiated water with Novacron Blue FNR at 0.5% shade.


Dhaka University Of Engineering & Technology (DUET)
Department Of Textile Engineering
Gazipur-1700, Bangladesh

Standard Name: 48 of 54

05% YELLOW 29/04

Standard 12429 650 %R LAV SCI UV Inc

Batch Name: 1 of 1

BATCH1

Date: 29-Apr-14 Time: 10:40:34

Batch 12429 650 %R LAV SCI UV Inc

Today's Date: 30-Apr-14

Batch is : darker
more red
more blue

Pass
CMC DE = 0.26
CMC Commercial Factor = 1.00
CMC l = 2.00 CMC c = 1.00

Ill/Obs	CMC Decision	CMC DE	DL*	Da*	Db*	DC*	DH*	Metamarism Index
D65 10 Deg	Pass	0.26	-0.02	0.20	-0.38	-0.31	-0.30	
A 10 Deg	Pass	0.27	-0.01	0.22	-0.30	-0.29	-0.33	0.02
TL83 10 Deg	Pass	0.31	-0.04	0.35	-0.36	-0.28	-0.42	0.14

Figure D.9: Color matching of fabrics dyeing in fresh and irradiated water with Novacron Yellow FN2R at 0.5% shade.

Appendix E: Dye absorption i.e. K/S value of fabric dyed with fresh and gamma irradiated wastewater at different shade percentages.

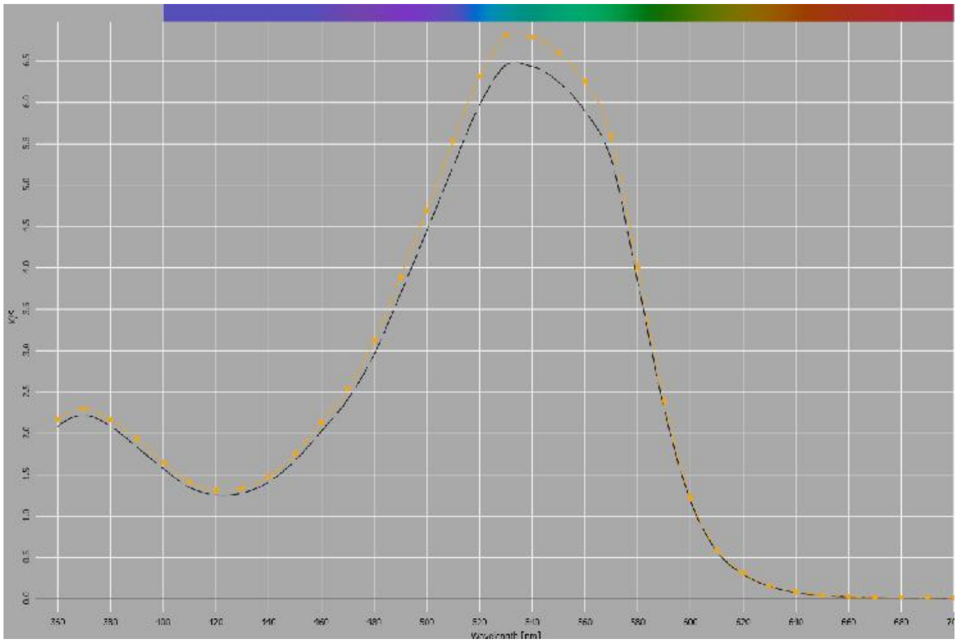


Figure E.1: Dye absorption (K/S value versus wavelength) at λ_{max}=540nm of Novacron Red FN2BL at 5.0% shade.

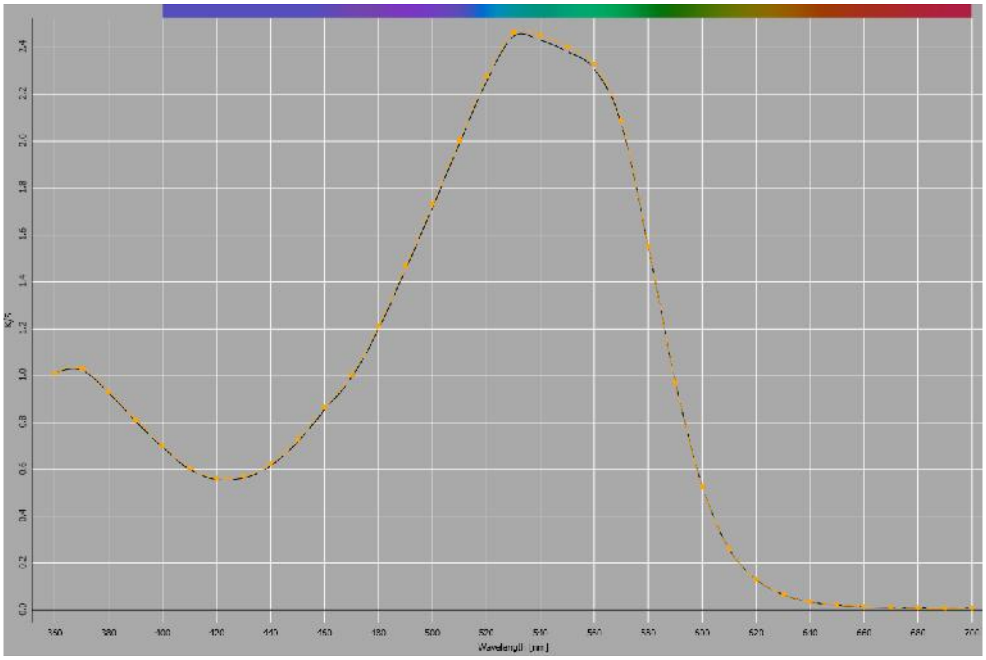


Figure E.2: Dye absorption (K/S value versus wavelength) at λ_{max}=540nm of Novacron Red FN2BL at 1.5% shade.

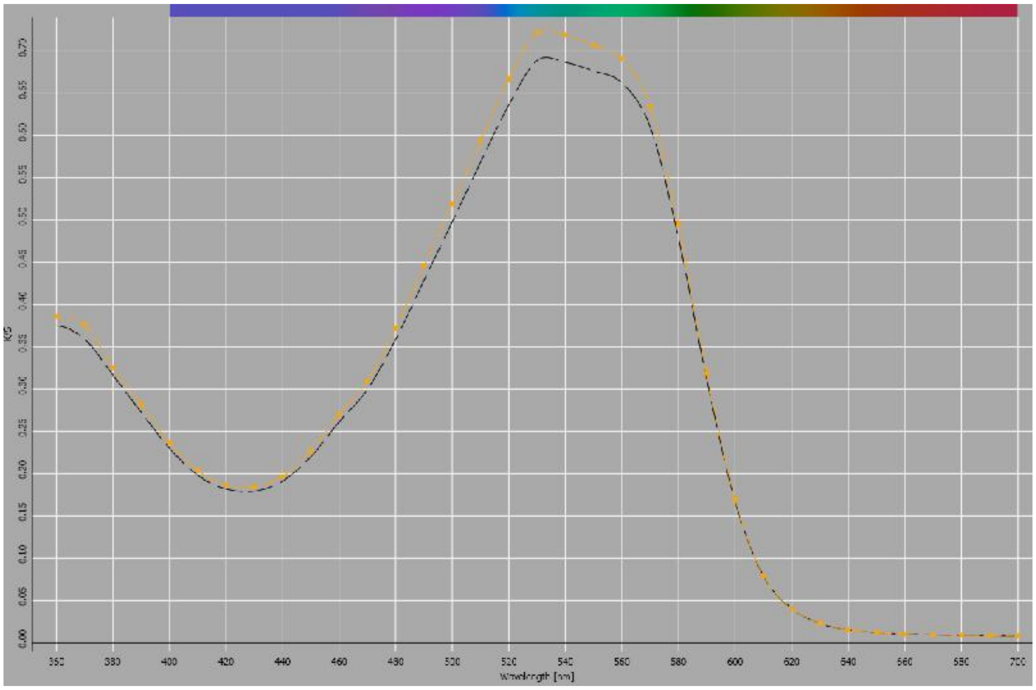


Figure E.3: Dye absorption (K/S value versus wavelength) at λ_{max}=540nm of Novacron Red FN2BL at 0.5% shade.

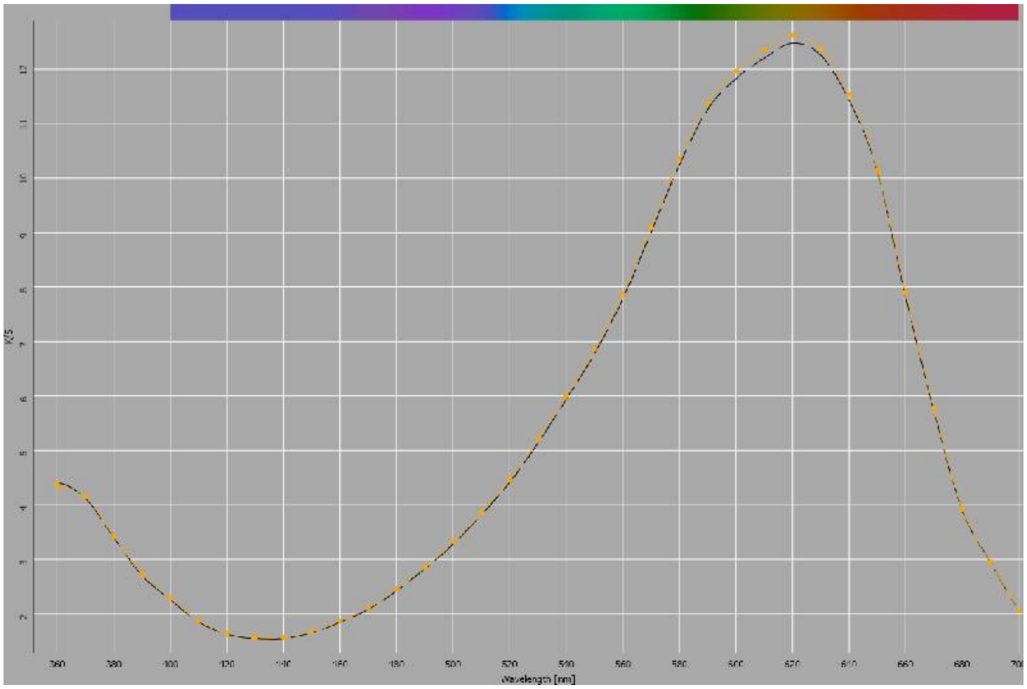


Figure E.4: Dye absorption (K/S value versus wavelength) at λ_{max}=630nm of Novacron Blue FNR at 5.0% shade.

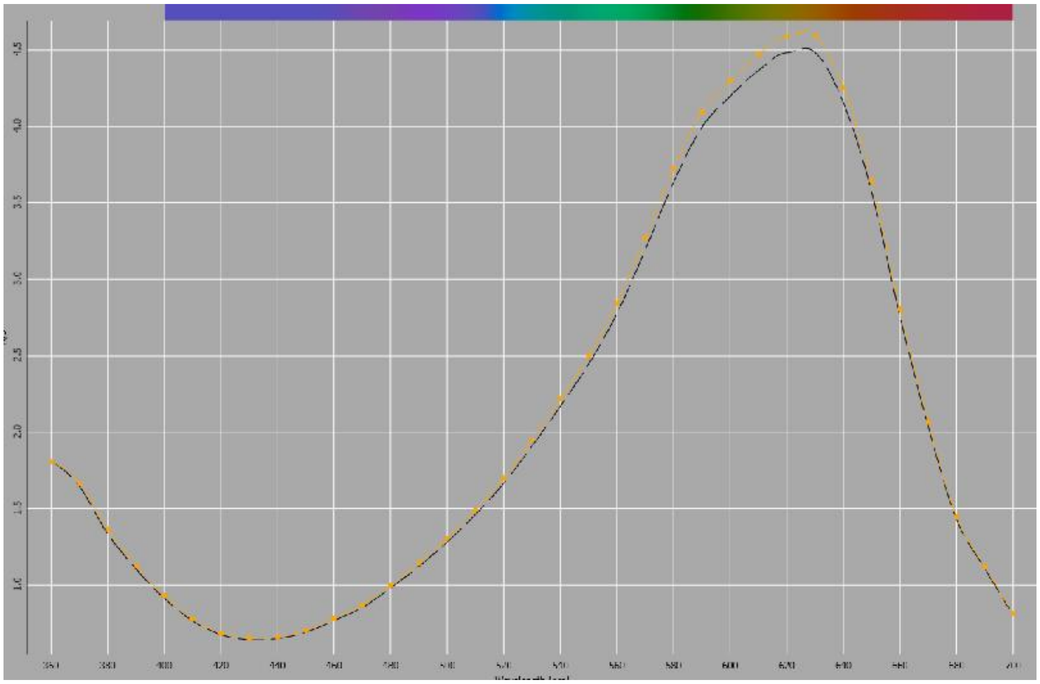


Figure E.5: Dye absorption (K/S value versus wavelength) at λ_{max}=630nm of Novacron Blue FNR at 1.5% shade.

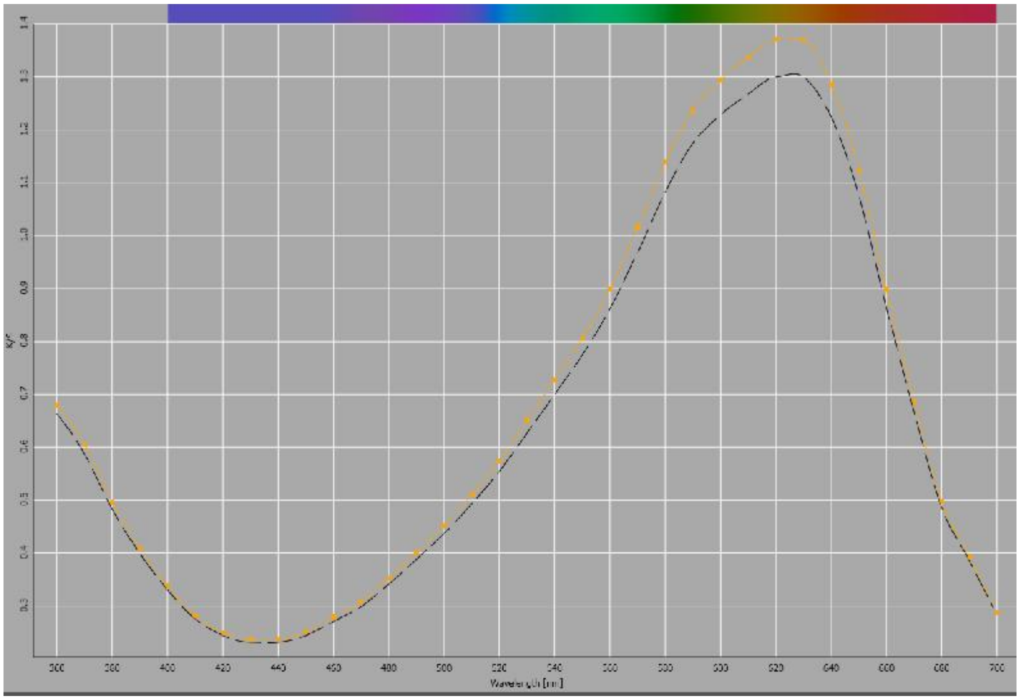


Figure E.6: Dye absorption (K/S value versus wavelength) at λ_{max}=630nm of Novacron Blue FNR at 0.5% shade.

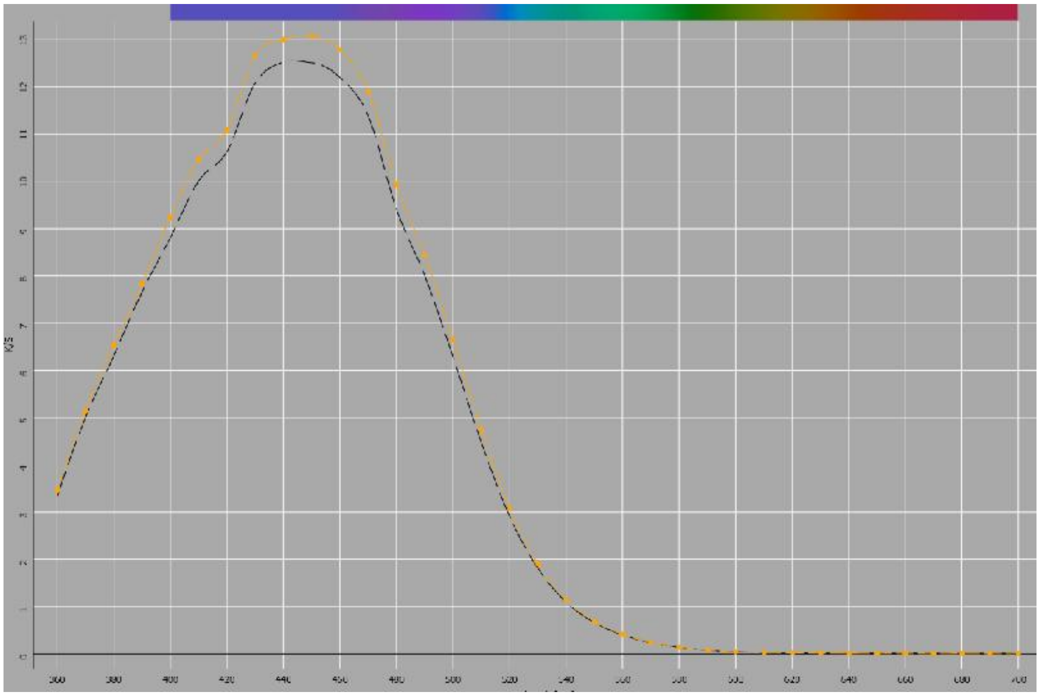


Figure E.7: Dye absorption (K/S value versus wavelength) at λ_{max}=440nm of Novacron Yellow at FN2R 5.0% shade.

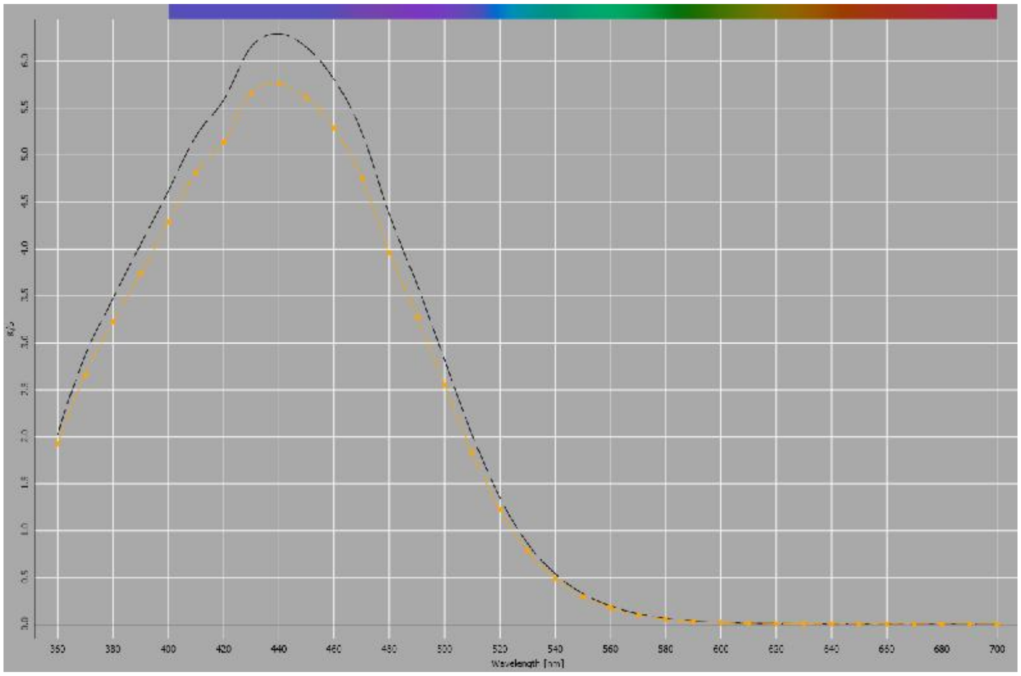


Figure E.8: Dye absorption (K/S value versus wavelength) at λ_{max}=440nm of Novacron Yellow at FN2R 1.5% shade.

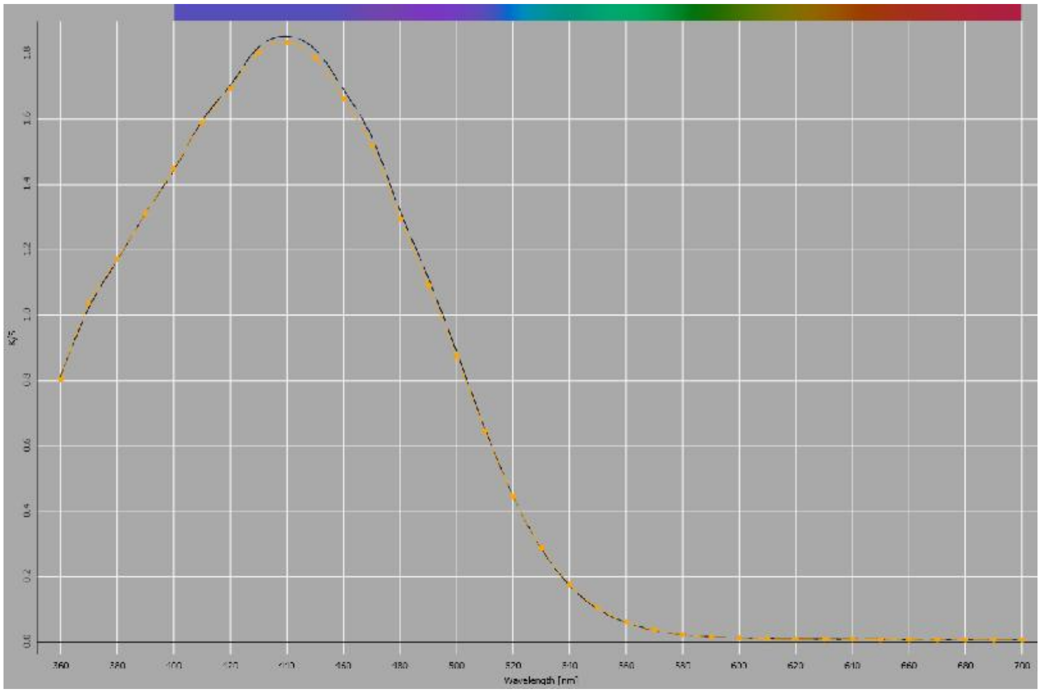


Figure E.9: Dye absorption (K/S value versus wavelength) at λ_{max}=440nm of Novacron Yellow at FN2R 0.5% shade.