Absorption study of fuchsin stain using watermelon rind

By
Sivakami.S
(17PZO017)

Thesis submitted to

Avinashilingam Institute for Home Science and Higher Education for Women
Coimbatore – 641 043

In Partial Fulfilment of the Requirements for the Degree of
Master of Science in Zoology

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Signature of the
Head of the Department

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Signature of the
Supervisor

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I. INTRODUCTION

Environmental pollution due to development in modern industrial practice is one of the most significant problems of this century. Of this, the contamination of water resources by hazardous pollutants has attracted much serious attention in the last few decades. Despite various awareness programs and campaigns, water pollution is on the rise owing to continually increasing amounts of industrial wastage and waste from domestic sewage (Abdelwahab, 2007).

Colour is considered as the first pollutant to be identified in wastewater and it is mostly caused by the effluents discharged from dyeing industries such as paper, rubber, cosmetics, textile and plastics. Approximately 10,000 different dyes and pigments are used for industries and over 7 × 105 tons of these dyes are annually produced worldwide (Mane *et al.,* 2007). Majority of the dyes are visually detected even at the concentration of less than 1 mg/l. In addition, some dyes or their metabolites are either toxic or mutagenic or carcinogenic (Pavan *et al.,* 2007). The discharge of these dyes in the environment is worrying for both toxicological and esthetical reasons (Pignon *et al*., 2003).

Most of the industries use dyes and pigments to colour their products. The larger consumers of dyes are textile, tannery paper and pulp, pharmaceuticals, cosmetics and food processing industries which are the most serious pollutants of our environment. The textile industries are one of the oldest and largest industries in India. These mills require volumes of water of high purity and generate equally large volume of waste water, which is highly colored and pollex. Colour removal from these effluents has been getting more attention in last few years not only because of its toxicity but also due to its visibility (Jain *et al*., 2003).

Fuchsine or rosaniline hydrochloride is a magenta dye with chemical formula C_{20} H_{19} N_3 HCI. There are other similar chemical formulations of products sold as fuchsine, and several dozen other synonyms of this mole (Goyal *et al*., 2007).

Watermelon (Citrullus lanatus Thunb) is cultivated throughout the globe in 96 countries. There are around 1200 varieties of watermelon found in different parts of the world. Total global production of watermelon was 108.9 million tons whereas India's production was 0.4 million tons in 2013 (FAO, 2016). The leading growers were China, Turkey, Iran, Brazil and United. Watermelon is cultivated in hot and dry climate with mean temperature of 22-30ºC and little available water. The shape of fruit varies from globular to oblong. It is harvested in summer season and liked by consumer due to its delicate flavor and attractive color (Tressler and Joslyn, 1971).

Watermelon is the third most popular fruit (Zhao *et al*., 2013) in the world containing good quantity of nutrients. Pigments extracted from watermelon acts as a fictional ingredient and can be incorporated into breakfast cereals, frozen dairy desserts, yoghurts, spreads, candy, carbonated beverages, confectionary, sauces and soups etc (Olempska, 2006).

Textile industries are one of the most important sources to produce the various dyeing wastewaters. The concentration of used dyes in textile industries ranges from 10 to 1000 ppm and it depends on the quality and process of operation (Garcia *et al.,* 2006).

Textile dyes generally are made of synthetic, organic, and aromatic compounds that may be contain some heavy metals in their structure. Complex structure and heavy metals in the dyes may be a mutagen, teratogen or carcinogen and causes toxicity to human health (Venkatamohan, 1998). Dyes can threaten human health by inducing skin dermatitis and also affects the respiratory system (Neta *et al.,* 2011).

Textile industry is basically divided into dry and wet processing. The dye processing industries includes ginning, spinning, weaving, knitting, preparation and process of non-woven materials. The wet processing industries line up as processing dyeing and finishing unit; the textile wet processing industries consume large volume of water and chemicals. The chemical reagents used are diverse in composition ranging from polymers, organic and inorganic compounds (All and Muhammad, 2008).

The textile industry uses huge quantities of water in all processing operations. Almost all dyes, specially chemicals and finishing chemicals are applied to textiles in water baths. Most of the fabric preparation steps, including de-sizing, scouring, bleaching and mercerizing use water. Furthermore, each of these steps involves through washing of the fabric to remove all chemicals used (Tasso *et al*., 2012).

The water used in the processing is usually returned to the environment without proper treatment. The textile industry releases huge amounts of colored effluent daily. Wastewater released by these industries pollutes the fresh water of streams, ponds and rivers as well as underground water bodies (Hambarde, *et al*., 2012). Dyes are used widely in many industries, such as textile production, dyestuff manufacturing, leather tanning, food preparation, paper production and printing in order to give color to their products. The textile industry occupies a unique place in the industrial map of India and is centered mainly on large cities like Ahmedabad, Mumbai, Coimbatore and Bangalore, In India 82% of textile are cotton and remaining 18% are synthetic industries. There are more than 68 mills manufacturing cotton and manmade fibres all over the country (sheath and patel, 2004).

Wastewater from the food coloring, paper, carpet, rubber, plastics, cosmetics and textile industries are polluted by dyes (Namasivayam *et al*., 1996; Crini, 2006; Azhar *et al*., 2005). The presence of very low concentrations of dyes in these effluents is highly visible and undesirable (crini, 2006; Nigan *et al.*, 2000). Colours affect the nature of the water and inhibit the penetration of sunlight into the water bodies, which has and deleterious effects on photosynthesis and thus aquatic life (Arami *et al*., 2005; Gomez *et al*., 2007). Some dyes are also carcinogenic and mutagenic (Namasivayam and kavitha, 2002).

Water is one of the most valuable resources on the planet earth. It is the lifeline of almost all living things on earth. Although this fact is widely recognized, pollution of water resources is a common occurrence. Textile industry is one of the biggest and most established commercial industry which exhibit all around, expending 80-200m^3 of water for every ton of product and discharges 1,650m^3 of waste water every day (Grereffi, 2002; Ranganathan *et al.*, 2007; Gruwez *et al.*, 1999) and it is the largest consumer of water mainly as process water (90-94%), and cooling water(6-10%) that becomes finally loaded with different pollutants, dyes, surfactants, acids or bases, salts, heavy metals, and suspended solids (Zaharia and suteu, 2012).

Textile fabric manufacturing uses mixtures of dyes with various additives including solvents, antifoaming, whitening agents and pH conditioners. The waste water thrown out from industries is either used for irrigation purpose or it runs off into natural source of water (Ahlawat and Kumar, 2009).

Water pollution by industrial effluents has become a great concern in the recent years. The contaminants present in the effluents are found to be toxic and hazardous not only to human beings but also to the surroundings (Patil and Hande, 2004).

Heavy metals are most hazardous pollutants because of their non-degradable nature and property to affect all kinds of ecological system (Buccolieri *et al*., 2005). Electroplating industry is one of the major contributors of heavy metal pollution in surface water (Siddigui *et al.*, 1999).waste water from eleproplting industries are characterized with the presence of strong toxic components such as simple and complex cyanides of heavy metals, salts of hexavalent chromium, organic additions, minerals acids and ases (Stefanova, 2000).

Watebr pollution is one of the major environmental problems that cause severe threat to living organisms. Increased population, industrialization and urbanization are responsible for environmental pollution. Industrialization of numerous sectors such as food, pharmaceuticals, leather, textile, cosmetics paper, printing, etc. utilize dye compounds to colour their end products (Amita, *et al*., 2004).

This wastewater consist of high content of other products besides dye compounds such as dispersants, acids, bases, salts, detergents and oxidant (Preuuzzo *et al.*, 2008). Therefore, discharge from textile industries were usually high in colour content, biological oxygen demand (BOD), chemical oxygen demand (COD) and suspended solids (Kumar *et al*., 2004).

The textile industry uses huge quantities of water in all processing operations. Almost all dyes, specially chemicals and finishing chemicals are applied to textile in water baths. Most of the fabric preparation steps, including de-sizing, scouring, bleaching and mercerizing use water. Furthermore, each of these steps involves through washing of the fabric to remove all chemicals used (Taso *et al*., 2012).The water used in the processing is usually returned to the environment without proper treatment. The textile industry release huge amounts of colored effluent daily. Wastewater released by these industries pollutants the fresh water of streams, ponds, and rivers, as well as underground water bodies (Hambarde, *et al*., 2012).

Every year tons of dyes are produced worldwide and significant amounts of the total production are lost in wastewater during synthesis and processing. This release of high colored effluents into natural water has become a serious environmental problem. Specifically, highly colored effluents into natural water bodies obstruct light penetration disturbing biological processes within the aquatic environment (Shrivastava *et al*., 2012*)*. In addition, many dyes are toxic to various organisms, causing direct damage to aquatic species in particular. Some dyes can cause allergic dermatitis, skin irritation, cancer and mutation in humans also *(*Hambarde Patil *et al*., 2011). Dealing with these types of pollution is therefore very important, especially in developing countries.

Synthetic dyes and heavy metals are widely used textiles, leather, paper, plastics, electroplating, cement, metal processing, wood preservatives, paints, pigments and steel fabricating industries (ponnusami *et al.*, 2008).

Now days, dyed wastewaters are mainly treated by physical and chemical procedures which have several shortcomings (Soldatkina *et al*., 2015). Improving biological treatment efficiency is the key solution to this problem due to their possibly complete mineralization of dyes at low cost.

Adsorption is one of the effective methods for the removal of dyes from waste effluent. It is inexpensive, universal nature and ease of operation. This can remove soluble and insoluble organic pollutants because its removal capacity may be up to 99.9%. The process of adsorption is advantageous over other methods because it is sludge-free, offers clean operation and the dyes are completely removed, even from diluted solutions. Activated carbon is the most widely used adsorbent because it has excellent adsorption efficiency for organic compounds. However, commercially available activated carbons are expensive. This has recently prompted many studies on production of low cost alternatives adsorbents. A number of agricultural waste types and byproducts of cellulosic source have been studied for their capacity to removed dyes from aqueous solutions (Dandge *et al.*, 2016).

Objectives

- To find out the adsorption capacity of watermelon rind to remove fuchsine stain from aqueous solution.
- To optimize parameters for dye decolourization such as dye concentration, adsorbent dose, pH, temperature and contact time using watermelon rind.
- To analyse the FT-IR spectrum of the watermen rind before and after bio adsorption.
- To characterize the dye adsorbent interaction and surface structure by Scanning Electron Microscope analysis.
- To analyse the phytotoxicity study of adsorbent treated dye solution.

II. REVIEW OF LITERATURE

The review of literature pertaining to the topic "**Absorption study of fuchsin stain using watermelon rind**" present investigation is organized and presented under the following headings.

2.1. Pollution

2.2. Impact of textile dyeing effluent

2.3. Bioadsorption - A green approach for dye removal

2.4. Removal of stain using adsorbents

2.5. Candidate dyes and adsorbent used in the study

2.5.1. Fuchsine stain

2.5.2. Watermelon rind

2.6. Phytotoxicity studies

2.1. Pollution

Upadhye *et al.* (1998) studied the effluent from textile mill deteriorates the quality of air and exhibits their effect on human body through skin by ingestion or inhalation. Number of chemicals and dyes used in the industry pose a great danger to the environment which includes air, water as well as human beings and living bodies in the nature.

Asolikar and Abhyankar (2000) examined that Bleaching releases chemicals like peroxide and hypo chlorides which contributes 10% of total pollution load in effluents. Golka *et al.* (2004) claimed that the total world colorant production is estimated to be 80,000 tons/year, and generally 20% of the used dyestuff enters the environment through wastes. Most of these dyes are toxic, potentially carcinogenic; hence their removal from industrial effluent is a major environmental problem. The problems of environmental pollution caused by the industrial waste have become more serious year by year. Han *et al.* 2006) reported that the development of practical waste treatment systems or recycling systems is gathering global interest.

Amutha *et al.* (2002) summarized that the aquatic organisms pass through food chain and ultimately reach human and cause various physiological disorders like hypertension, sporadic fever, renal damage, muscle cramps etc.

Kulshrestha *et al.* (2004) reported that the number of dyeing and printing industries release their wastes without any treatment. These waste polluted the ground water and soil. The polluted water consumed by the humans may cause health hazards like eczema, contact dermatitis, asthma and chronic bronchitis. Khan *et al.* 2002 observed that the colorations of the water by the dyes, even in small concentration may have an inhibitory effect on the photosynthesis and thus affecting the aquatic ecosystem.

Kumar and Abraham (2007) observed that the pollution of surface and ground water bodies due to indiscriminate discharge of industrial effluents from the thousands of small scale textile bleaching and dyeing units located in industrial clusters in different states of India like Tamilnadu, Gujarat and Maharashtra is a topic of public and government concern today.

Chojnacka (2010) explained that in recent decades environmental pollution has become one of the major problems in the industrial society. Among the pollutants, dyes have serious effects on both humans and the environment. Their release has continuously increased as effluents due to the growing industrial activities.

Phugare *et al.* (2010) noted that the use of different dyes, especially the textile dyes makes the world beautiful and colorful, they pose serious pollution problems, as the waste water from the textile industry is not only colored but it has high fluctuating pH, large amount of suspended solids along with high chemical oxygen demand (COD).

Saratale *et al.* (2010) reported that discharge of the colored waste water into water source damages the environment as they disturb human health and they may be toxic to the flora and fauna and significantly reduce photosynthetic activity of autotrophic organism. Hamed *et al.* 2006 reported that one of the major problems concerning textile industry is dye effluent.

Khatee and Zarei (2011) noted these dyes are being designed to be highly resistant to soap, water , light and oxidizing agents, so that they can import colour on various raw materials. Hence, the treatment of effluent containing dyes has been a challenging problem among environmental technologies and it has always been necessary to find efficient methods for dye removal.

Khatae *et al.* (2013) described that Synthetic dyes are the main groups of the pollutants which are widely used in various industries such as paper, food, textile, leather, cosmetics and carpet.

2.2. Impact of textile dyeing effluent

Pervez and Pandey (1994) reported that in India, there are about 700 cotton textile mills producing over 9000 million meters of cloth each year. The effluent is discharged by the textile mills in massive volumes (235 liters per kg of cloth produced). The presence of chemicals like hydrosulphate, sulphite, sulphide and sulphur dyes causes rapid depletion of dissolved oxygen, affecting the aquatic life adversely. The surface soils are rendered infertile by the discharge of these effluents. Certain metal ions having catalytic properties Cr (II), Hg (II), Mn (II), Ca (II) has been reported to be in this effluent

Kumaraguru (1995) reported that the combined effect of industrial effluents and sewage killed 26.5 million fish in Florida in 1969. Kumaran and Dharani, 2011 Investigated the dye decolourisation at different temperature, dye concentration, pH, carbon and nitrogen sources.

Ranganathan and Joseph (1997) surveyed that textile bleaching and dyeing unit consume larger quantity of water and generate almost equivalent quantity of waste water. During bleaching and dying process, the effluent discharged from these units contains chemicals such as caustic soda, hydrochloric acid, sodium sulphate, soap oil, hypochlorite and peroxides, dyes, sodium, chloride, flexing agents, detergents, mineral and acids. The effluents as a result, have high total dissolved solids (TDS) and intense color caused by the spent dyes.

Ranganathan and Joseph (1997) described that the effluent will impact colour to the water making it aesthetically unacceptable. In addition some of the dye stuffs causing colour contain heavy metals and photosynthetic activities may affect aquatic life. Sharma (1997) Waste water from textile industry destroys the quality of water body in which they are disposed and affects the marine life. It also has deleterious effect on sewage handling system and the agriculture land.

Iyer (2000) summarized that the effluent derived from textile and dyestuff activities can provide serious environment impact in the neighboring receptor water bodies because of the presence of toxic dyes and chlorolignin residues.

Jothimani *et al.* (2003) explained that the textile and dyeing industries contribute water and soil pollution in larger extent. The released effluent and sludge contaminate the river water, underground water as well as the soil nearby and thus making it unsuitable for crop production.

Faryal and Hameed (2005) reported that the presence of metal based colored dyes and foaming chemical in textile waste water not only retards the biological activity by reducing the light penetration but also caused metal toxicity to both aquatic and terrestrial life.

Lal and Nishkam (2005) surveyed that the effluent generated at various stages of textile dyeing differs in its composition, strength as well as volume. The high pollution load of dye effluent arises from spent dye bath composed of unexhausted, hydrolyzed and surface deposited dyes as well as chemicals and auxiliaries.

Omelechenko *et al.* (2005) explained that Textile wet processing is one of the largest and oldest industries worldwide responsible for the substantial resource consumption and pollution especially in terms of water.

Saritha *et al.* (2010) discovered that Textile and dyeing industry is one of the important industries in India, which releases organic pollutants. Inorganic pollutants and coloring agents. The discharge of raw effluents into the river renders the water useless and also pollutes the soil eco-system.

Ponraj (2011) studied that the textile industry utilizes about 10000 different dyes and pigments. The worldwide annual production of dyes is over 7.105 tons which usually have a synthetic origin and complex aromatic molecular structures that makes them more stable and difficult to biodegrade.

Anjana and thange (2011) reported that dye concentration at 50 mg/L amended with glucose and urea showed high percentage of decolorization by *Pleurotus sajorcaju and Phanerocheate chrysosporium*, treated the synthetic dyes such as direct congored, direct dark blue 6B and direct black HM with *Eichhornia, salvinia* and pistia species.

Mathiyazhagani *et al.* (2011) observed that the decolourization of direct brilliant violet and direct greenish blue dyes using *Phanerocheate chrysoporium, Trichoderma viridie and Aspergillus niger*. The dyes were effectively decolorized to 9% at a concentration of 0.025% when compared with other fungal isolates.

2.3. Bioadsorption – A green approach stain removal

Moraweet *et al.* (1995) and Geeneus *et al.* (2001) studied that over the last few years; a sizeable research investigation has been undertaken by various researchers for wastewater treatment using adsorption process. It is utilized a stage of integrated chemical-physical process for the treatment of wastewater simultaneously with a biological process (Sasaki *et al*. 2014). Adsorption is a surface phenomenon in which a multi-components fluid (gad or liquid) mixture is attached to the surface of a solid adsorbent to form attachments via physical or chemical bond.

A1-Godah (2000) noted that the adsorption process of dye molecules usually consists of four consecutive steps. Noroozi (2013) stated that the first step involves the diffusion or convection of dye molecules will diffuse through the bulk solution. In the next stage, the dye molecules will diffuse through a diffusion boundary layer (film diffusion). This is followed by the diffusion of dye molecules from the surface into the interior of the adsorbent materials. Lastly, the dye molecules will attach to the surface of the materials through molecular interactions. The dye concentration and agitation force may affect step 2. Step 3 is the rate determining stage which will affect the adsorption of dye molecules on the substrate. While step 4 is dependent on the nature of the dye molecules, such as anionic and cationic structures. It is important to highlight that the step 3 could involve two different phenomena. The first is porous diffusion (the adsorbate first diffuses in the liquid filling the pores and then is adsorbed), another is surface diffusion. (The adsorbate is first adsorbed then diffuses from one site to another).

Singh *et al*. (2001) observed that although some existing technologies may have certain efficiency in the removal of dyes, their initial and operational costs are so great, that they constitute an inhibition to dyeing and finishing industries. On the other hand low cost technologies do not allow a wishful colour removal or have certain disadvantages. Hence, research has been directed to the materials and procedures for dyes removal that will combine effectiveness with cheapness.

Allen (2005) observed that adsorption can be divided into two type i.e. chemisorptions and physisorption. Chemisorptions defined by the formation of strong chemical association between molecules or ions of adsorbent, which is generally due to the exchange of electrons where the process generally is irreversible. Whereas physisorption involves the weak vanderwaals, intraparticle bonds between adsorbate and adsorbent and thus physisorption generally is reversible in most cases.

Baral *et al.* (2006) and Stankovic *et a*l. (2009) investigated that The Sawdust, a low cost locally available material and a solid waste can be used as bio-sorbent for the removal of contaminant. Sawdust is an abundant by-product composed of fine particles of wood. It is readily available in the countryside at zero or negligible price. Sawdust has proven to be a promising effective material for the removal of dyes from wastewaters of many types of pollutants, such as dyes, oil, salts, and heavy metals.

Suteu *et al.* (2008) summarized that some conventional technologies (precipitation, coagulation, flocculation, UV/ozone treatment, electrochemical reduction, and biological treatment) may be efficient in the removal of dyes, but their operational costs are very high. Among these methods, adsorption is one of the most economic methods in decolourisation of textile effluents because of simple design and operation, availability, non-toxicity, superior removal of pollutants. The great advantage of this method is the possibility to use inexpensive and readily available materials with adsorptive and ion exchange properties.

Suteu *et al.* (2008) observed that Natural materials that are available in large quantities or certain waste from agricultural operations may have the potential to be used as low cost adsorbents. Waste materials from industry or agriculture such as sawdust and active or inactive biomass resulted from industrial fermentative technology (food and pharmaceutical industry) are also used as adsorbate. Replacing synthesized compounds, wastewater treatment by sorption onto unconventional natural or biological materials (green or environmental friendly) have recently become the subject of considerable interest.

Chowdhury (2011) noted that Surface of NMRH, may be due to the formation of surface hydrogen bonds between the hydroxyl groups on the NMRH surface and the nitrogen atoms of CV as given as Fig.1. The surface hydrogen bonds were formed between the hydroxyl group of adsorbent surface and O/N-containing groups of the adsorbate.

Sudevi *et al.* (2013) explained that watermelon peel, mosambi outer peel, adsorbents were effective in removal of crystal violet, methylene blue and malachite green dyes at 100mg/L but dye removal efficiency reduced at 500mg/L. similarly watermelon rind adsorbents were efficient in the removal of methylene blue

Lakshmipathy *et al*. (2015) reported that many fruit peels and seeds are investigated and reported as low cost adsorbents for the removal of heavy metal ions, synthetic dyes and organic contaminants from waste water. Most of the studies were carried out in batch process and very few adsorbents were studied in continuous column studies. It was observed that the chemical activation or modification of adsorbents increases the removal efficiency and the loading capacities. However, the loading capacity of adsorbents without any pretreatments was found to be low and the treatment technique employed were costlier limiting its application. Hence low cost, easily and abundantly available adsorbents are still in need for the effective removal of organic and inorganic contaminants from waste water.

Alexander *et al*. (2015) investigated that in this work Chitosan modified watermelon rind composite was successfully prepared and applied as an adsorbents for the color removal of textile effluent. Compared to other adsorbents CWR composite was low cost can treat the textile effluent effectively and efficiently. The Colour of the textile effluent was removed completely. The effects of various parameters such as pH, temperature and adsorbent dosage on adsorption were studied. The treated CWR composite was recyclable. So, this composite can be an alternative to high cost activated carbon and can be applied as an adsorbent for large scale treatment process in textile effluents for colour removal.

Dandge *et al.* (2016) reported that the removal of color from wastewater using a low cost adsorbent was performed by using thick rid of water melon. The results of the study reveals that adsorption process using thick rind water melon is a very effective process for the decolourisation of fuchsine basic from waste water and it was observed that within 60 min TRWM removed 50% of fuchsine basic relative to the initial concentration. The results also indicated that the adsorption process was also enhanced by varying the parameters. The parameters used to investigate the adsorption process were adsorbents dose, contact time of adsorbent with dye solution, initial dye concentration on adsorbent, pH and temperature. The test results for these parameters reveled that TRWM strongly influences the adsorption process.

In order to further understand the adsorption process and select desorption approach, adsorption mechanism of organic pollutants removal onto agricultural waste was discussed. As usual the adsorption on adsorbent is controlled by physical force with some exception of chemisorptions. Physical adsorption is carried through Vander Waals force, hydrophobicity, hydrogen bonds, polarity and steric interaction, dipole induced dipole interaction, π-π interaction, or their combine. While, chemical adsorption involves the sharing of electrons between the pollutant and the surface of adsorbent form a chemical bond. In addition, film diffusion and particle diffusion models have been often used for investigating their diffusion mechanism. In the physical adsorption, pollutants accumulated on adsorbent surface by the above mentioned interactions.

There are many factors which affects the adsorption of dye molecules such as solution pH, initial dye concentration adsorbent dosage, contact time and temperature. In-depth study and optimization of these parameters will greatly helping the development of industrial scale treatment process for the dye removal.

Acevedo *et al.* (2005) Studied the effect of solution pH on the adsorption of two commercial dyes, basic Astra on Yellow 7GLL and Reactive Rifafix Red 3BN on activated carbon made up of reinforcing fibers from tire waste and low- rank bituminous coal. The results obtained shows that the adsorption of reactive dye was more favored in solution pH 2, whereas the basic dye was adsorbed more easily in a solution of pH 12.

Aksu and Isoglu (2006) reported the effect of solution pH on the adsorption of Gemazol turquoise blue-G a reactive dye using sugar beet pulp and they noticed that the adsorption was maximum at pH 2 where the adsorption capacity was 83.7 mg/g and then decreased with a further increase in pH and reached Zero at pH 6.

Onal *et al*. (2006) the pH of solution is a very important parameter in the dye adsorption process. The magnitude of electrostatic charges which are impacted by a ionized dye molecules is controlled by the solution pH As a result the rate of adsorption will vary with a pH of the medium used. Salleh *et al*. 2011 in general, at a low solution pH, the percentage of dye removal will decrease for cationic dye adsorption; will for ionic dyes the percentage of removal will increase. Ozcan *et al.* (2007) In contrast, high solution pH is preferable for a cationic dye adsorption but shows a lower efficiency for anionic dye adsorption.

Salleh *et al*. (2011) at high solution pH, the positive charge at the solution interface will decrease while the adsorbent surface appears negatively charged. As a result, the cationic dye adsorption will show an increase and the anionic dye adsorption will decrease. At a low pH solution, the positive charge on the solution interface will increase and the adsorbent surface will appear positively charged, which results in the decrease of cationic dye adsorption and an increase in anionic dye adsorption.

Liu *et al*. (2012) the adsorption ability of the surface and the type of surface active centers are indicated by the significant factor which is known as point of zero charge (pH_{pzc}). In order to determine the pH_{pzc}, dye solution with different pH should be prepared and considered as $pH_{initial}$ and then the fixed amount adsorbent was added to the dye solution. Qadeer (2007) The dye solution was shaken until the equilibrium is achieved were the pH at equilibrium is regarded as pH_{final}, then plot the pH_{final} values against $pH_{initial}$ where pH_{pzc} is the point then $pH_{initial} = pH_{final}$.

The value of pH is used to describe $pH_{(pzc)}$ only for the systems in which H+/OH-are the potential determining ions. due to the presence of function groups such as OH^-, COO^- groups, cationic dye adsorption is favored $pH > pH_{pzc}$, whereas, anionic dye adsorption is favored at $pH < pH_{pzc}$ where the surface becomes positively charged. Dawood and Sen, (2012) Studied the effect of solution pH on the adsorption of cango red by pine cone and they noticed that the adsorption was maximum at pH 3.5.

Senthilkumar (2006) investigated that the temperature is an important factor that serves as an indicator, to whether the adsorption is an exothermic or endothermic process. If the adsorption is an endothermic process. The adsorption capacity will increases with increasing temperature. This may be possibly due to the dye molecules at higher temperature. Ofomaja (2007) in contrast, if the adsorption is an exothermic process, the adsorption capacity will decrease with increasing temperature. In this case, higher temperature may decrease the adsorptive forces between the dye molecules and the active sites on the adsorption surface.

Hameed and Ahmad (2009) observed that the adsorption of methylene blue like garlic peel and they found that the adsorption capacity increase 82.64 to 142.86 mg/g when the temperature increased from 30^{o}C to 50^{o} C indicating that the adsorption is endothermic in nature.

Ofomaja (2008) surveyed that generally the dye removal increases with increasing adsorbent dosage, where the amount of sorption sites at the surface of adsorbent will increase the percentage of dye removal from the solution. Salleh *et al.* 2011 By analyzing the effect of adsorbent dosage, it gives an idea for the ability of a dye adsorption to be adsorbed with the minimum amount of adsorbent, so as to identify the ability of dye from an economic point of view.

Sonawane and Shrivastava, (2009) analyzed the effect of adsorbent dose on the removal of malachite green by maize cob. They concluded that at 20mg/ L of dye, pH of 8 and a contact time of 25 minutes increased the percentage of dye removal from 90% to 99% when the adsorbent dose increased from 0.5 to 12g/L.

Saleh *et al*. (2011) Adsorbent dosage is an important parameter in order to determine the adsorbent's capacity for a given amount of the adsorbate at the operating conditions. In order to study the effect of adsorbent dosage on the adsorption process, it can be carried out by prepare adsorbent-adsorbate solution with different amount of adsorbents added to fixed initial dye concentration then shaken together until equilibrium time.

Garg *et al.* (2004) reported that the adsorption of methylene blue by sulphuric acid treated sawdust (SDC). It is observed that when methylene blue concentration was increased from 50mg/L to 250mg/L the percentage of dye removal decreased from 99.9% to 82.2% at an adsorbent dose of 0.4g/100Ml temperature of 26±1^{o} C and pH 7.

Eren (2006) explained that the dye removal efficiency is highly dependent on the initial dye concentration. The effect of initial dye concentration relies on the immediate relation between the dye concentration and the available binding sites on the adsorbent surface. The removal efficiency will decrease with an increase in the initial dye concentration due to saturation of adsorption sites on the adsorbent surface Salleh *et al.* (2011). There will be unoccupied binding sites on the adsorbent surface at low dye concentration, and when the initial dye concentration increases, there will be insufficient sites for the adsorption dye molecules, thus decreasing the dye removal efficiency Bulut (2006). On the other hand, the increase in initial dye concentration will cause an increase in the loading capacity of the adsorbent and this may be due to the high driving force for mass transfer at a high initial dye concentration.

Yagub *et al*. (2012) studied the effect of initial dye concentration on the adsorption of methylene blue by pine leaves and they found that as the initial dye concentration increased from 10 to 90 mg/L, the percentage of dye removal decreased from 96.5% to 40.9% after 240 min of adsorption process.

2.4. Removal of stain using adsorbent

Sivaraj *et al*. (2001) noted that the use of agricultural materials for the dye removal is advantageous as they are often available in large quantities. Orange peel is used for the removal of acid violet dye from aqueous solution. Namasivayam and Kanchana (1992) Bagasses pith is used for the adsorption of basic blue 69, basic red 22, acid red 114 and acid blue 25 and banana pith for the adsorption of basic violet from wastewater. Robinson *et al*. (2001) Palm- fruit bunch was used for the adsorption of basic yellow, basic red, and basic blue dyes and the adsorption of Cibacron yellow, Cibacron red, Cibacron blue dyes was carried using wheat straw, corncobs and barely husks. Singh and Kaur (2013) Agricultural waste and rice straw adsorbent was employed to remove Malachite green from aqueous solution.

Ncibi *et al*. (2007) summarized that Batch biosorption experiments were carried out for the removal of methylene blue from aqueous solution using *posidonia oceanica* fibers, a marine lignocelluloses biomass. The results had showed that biosorption capacity was optimal in 6-9 pH range. Besides, equilibrium data were very well represented by both Langmuir and Redlich-Peterson isotherm models followed by Freundlich, which confirm the monolayer coverage of methylene blue molecules onto *posidonia oceanic* fibers.

Geetha and Belagali (2010) reported the removal of dye and heavy metals using a cheap adsorbent, to remove Patton and Reeder's indicator, Solochrome black-T, crystal violet, murexide, basic fuchsine and potassium permanganate by batch process. Effect of pH, adsorbent dose, contact time and the concentration of dye has been studied, which showed the high percent removal of dyes and heavy metals at optimized conditions.

Zhang *et al*. (2011) the adsorption of Congo Red (CR) by ball-miled sugarcane bagasse was evaluated in an aqueous batch system. CR adsorption capacity increased significantly with small changes surface area. CR removal decreased with increasing solution pH from 5 to 10 maximum adsorption capacity was noted as 38.2 mg/g bagasse at a dye concentration of 500 mg/L. The equilibrium isotherm fitted the Freubdlich model and the adsorption kinetics obeyed pseudo-second order equation. CR adsorption obeyed the intra-particle diffusion model very well with bagasse surface area in the range of 0.58-0.66m^2/g, whereas it was controlled by multi-adsorption stages with bagasse surface area in the range of 1.31-1.82m^2/g. thermodynamic analysis indicated that the adsorption process is an exothermic and spontaneous process. Fourier transform infrared analysis of bagasse containing adsorbed CR indicated interactions between the carboxyl and hydroxyl groups of bagasses and CR function groups.

Anbia and Zhang *et al.* (2012) investigated that Adsorbent is the most appropriate and proficient method for dye removal in effluents Nouri *et al.* 2009. A significant role was played by phytoremediation in contaminant removal through filtration, adsorption, cation exchange and throughout plant-induced chemical transformations in rhizosphere Kong *et al*. (2009) Plants generally have optimistic outcome on decontamination and play a promising role in CWs.

Ali *et al*. (2012) discovered that adsorption is inexpensive, universal nature and ease of operation. Adsorption can remove soluble and insoluble organic pollutants due to its removal capacity may be up to 99.9% Bhatnager *et al.* (2015) The use of fruit peels based adsorbent for removing various pollutants from wastewater offers many attractive features such as the outstanding adsorption capacity and the fact that these materials are low-cost, non-toxic and biocompatible. Watermelon biomass can be categorized into three main components; the flesh, seed and rind. The flesh constitutes approximately 68% of the total weight, the rind approximately 30% and the seeds approximately 2% Hani *et al.* (2014) in this study, watermelon rind was used as potential low-cost adsorbent Singh *et al*. (1975). The skin of fully ripened watermelon contain approximately 20% cellulose, 23% hemicelluloses, 10% lignin, 13% pectin,7mg/g silica and 12% silica free minerals.

Saba *et al*. 2014 reported that rise husk is a key agricultural waste throughout the world; therefore its appropriate management is very indispensable to lessen its effect on environment. Rice husk, rice bran, rice ash, was used to destroy a number of dyes including methylene blue, crystal violet, brilliant vital red, direct red-31 and direct orange-26 and congo red. So a combination of microbes, plants and constructed wetland would establish itself as an efficient system Alexander *et al.* (2015). Many studies have been conducted to investigate the ability of water melon rind (WR) as an adsorbent and the results shows great rate of removal of various pollutants such as dye.

Low cost adsorbents from agricultural waste like rice husk was developed with various activation methods and tested for the removal of aqueous contaminants. Adsorption of a basic dye, malachite green (MG), from aqueous solution onto nitric acid treated (NRH), and peroxide treated rice husk (PRH) have been investigated. Various experiments were studied using batch absorption technique under different conditions of pH, adsorbent dosage, initial dye concentration, and temperature. Adsorption capacities of MG by the NRH and PRH were essentially due to electrostatic forces. The NRH and PRH adsorbents had a relatively large absorption capacity (18.1 and 26.6 mg/g). The adsorbent PRH had a higher surface charge at alkaline pH and enhanced removal of MG was obtained under alkaline conditions. Typical adsorption kinetics indicated the pseudo second – order kinetics behavior. The adsorption isotherms obeys Langmuir isotherm model. It was observed that the rate of adsorption improves with increasing temperature and the process is endothermic in nature. The negative value of the change in Gibbs free energy indicates that the adsorption of MG on PRH and NRH is feasible and spontaneous.

2.5. Candidate dye and adsorbant used in the study fuchsine stain

Goyal (2007) studied that Fuchsine or rosaniline hydrochloride magenta dye with chemical formula $C_{20}H_{19}N_3HCl$. There are other similar chemical formulations of products sold as fuchsine, and several dozen other synonyms of this molecule. It becomes magenta when dissolved in water; as a solid, it forms dark green crystals. As well as dying textiles, fuchsine is used to stain bacteria and sometimes as a disinfectant. In the literature of biological stains the name of this dye is frequently misspelled, with omission of the terminale which indicates an amine Baker 1958 American and English dictionaries (Webster's, Oxford, Chambers, etc.) Hunger 2003 gives the correct spelling, which is also used in the literature of industrial dyeing Hunger 2003. It is well established that production of fuchsine results in development of bladder cancers by production workers lyon 2008. Production of magenta is listed as a circumstance known to result in cancer.

Briankrans (2015) reported that Watermelon may be one of the most appropriately named fruits. It's a melon that's 98 percent water. It's also got a healthy amount of vitamin A and C, potassium, magnesium, and other important nutrients. The most popular part of the watermelon is the pink fruit, but like its cousin, the cucumber, the whole thing is edible. This includes the green scraps that usually end up in the compost bin. The rind, which is the green skin that keeps all that water-logged delicious fruit safe, is completely edible. Here are just a few reasons why you should consider not throwing it.

2.6. Phytotoxicity studies

Phytotoxicity studies we can know whether biodegradation of dye leads to detoxification of the dye leads to detoxification of the dye or not. In phytotoxicity studies, the seeds of the model plants are treated with particular concentration of the original dye and also with its biodegraded products. The effects of different treatments on germination percentage and length of plumule and radical can be evaluated and the results are compared with the control. Differences in results can be used to know whether the degradation products are less toxic to the growing plants then than the original dye or not. Therefore the impact that caused by textile dyeing effluent on plant growth is summarized below.

Sundaramoorthy *et al.* (2000) investigated the effect of fertilizer factory effluent on seed germination, seedlings growth and dry weight of green gram (*vigna radiate L.),* black gram (*vigna mungo* L.), groundnut (Arachis hypogaea), soyabean (Glycine max), paady (Oryza sativa) and sorghumn (Sorghum bicolor). They observed that the seeds treated with increased concentrations of effluent showed a gradual decline in the germination percentage of seeds, seedilng growth and dry weight.

Pavadai *et al*. (2004) described that the effect of zinc at different concentration on germination seedling growth and biochemical content of black gram were investigated by the growth and biochemical content were increased at lower concentrations and there was gradual decrease at higher concentration of zinc.

Khedhar and Dixit (2005) investigated the effects of Ambanala wastewater on the germination, growth and vigour of spinach. The results revealed that untreated waste water inhibited the biometric parameter of spinach.

Akinci *et al.* (2010) reported that a drastic decrease in leaf area, root and shoot length, fresh and dry weight of tomato seedlings treated with higher concentration of lead.

Mehta and Bhardwaj (2012) conducted a study on the effect of industrial effluents on seed germination and seedling growth of Vigna radiate and cicer arietinum. Germination percentage and seedling growth of both the plants showed considerable reduction in case of untreated effluents. The treated effluent showed inhibitory effect to some extent. Root and shoot length of vigna seedling reduced up to 58.66% and 69.06% respectively, while in cicer the reduction was upto 53.62% and 67.91% in untreated effluent as compared to control. Minimum reduction in root and shoot length was observed in treated effluent in both vigna and cicer.

Mohmood *et al*. (2013) studied that which treated and untreated textile effluent along with control were applied to the maize (Zeamays L. CV C1415) crop to check their effects on its growth. Plant height, number of leaves, number of nodes and internodes were monitored. Photosynthesis transpiration rate and fresh and dry weights were also measured. The results clearly indicated textile effluent as compared to control but treated effluent showed improved in all the parameters. This study proves that treated water may be used as irrigation water on large scale to overcome water crisis.

Rohit and Ponmurugan (2013) explained that seed germination was drastically affected when increasing concentration of untreated effluent was used. In the control seed germination observed was at 98% whereas in untreated textile effluent at 10% concentration it was 82%. It indicated that lesser contractions textile effluents showed less significance to seed germination. In contrast 50% and 100% concentration be showed 45% and 18% seed germination respectively.

Barathi and Arulselvi (2015) surveyed a phytotoxicity study with dye degraded products. The phytotoxicity studies showed good germination rate and significant growth in degraded metabolites as compared to the dye treated seed. The raw dye treated seeds showed less seed germination rate (53-69%). On the hand dye degraded products showed increased seed germination rate 89-100% and 79-88% respectively.

III. MATERILAS AND METHODS

The methodology adopted in the present investigation is presented under the following headings:

3.1. Collection and preparation of watermelon rind

Fresh biomass of watermelon rind was collected from the local market of Coimbatore, Tamil Nadu and used as adsorbent for dye removal (Plate-1). The effect of various physicochemical experimental conditions that affect the dye adsorption such as solution pH, initial dye concentration, contact time, adsorbent dose and temperature were studied in the present work, under optimized condition watermelon rind was subjected for effective decolourisation of fuchsine stain by the selected sample. Watermelon rind was subjected to FT-IR spectral and SEM analysis before and after treatment with fuchsine stain (Plate 3, 4). The untreated and treated fuchsine stain on the biometric parameters such as germination percentage, shoot length, root length, fresh weight and vigour index of horse gram was studied on 7th day after sowing.

The collected biomass was washed thoroughly with tap water to remove soil and dust, followed by distilled water and dried in an oven at 80°C for complete dryness. Dry watermelon rind was ground into powder and sieved through a mesh to get fine particles (Plate- 2) and stored in an air tight container for further use.

3.2. Batch adsorption study

The batch adsorbent experiments were conducted to optimize various parameters namely dye concentration, pH, contact time, temperature and adsorbent dose to obtain optimum color removal from dye solution. Batch studies were conducted with fixed amounts of adsorbents (100mg- 500mg) which were shaken separately in a rotary orbital shaker at 150 rpm in 100ml of the dye solution (50mg-600mg) at different temperatures (20-60°C) and pH (2-10) for various incubation periods (1-6 days). The pH was adjusted using 0.1N NaOH and 0.1N HCl solutions. At the end of predetermined time intervals, samples were withdrawn from the shaker and the adsorbents were separated from the solution in a centrifuge for a period of 5 minutes. The absorbance of the supernatant was read in a colorimeter at 525nm to estimate the final dye concentration. All experiments were carried out thrice with respect to each condition and the average values were obtained. The percentage decolourisation was calculated using the formula

$$\text{Decolorization percentage} = \frac{\text{Initial absorbance of dye} - \text{final absorbance of dye}}{\text{Initial absorbance of dye}} \text{x}100$$

Plate-1

Watermelon rind

Plate-2

Watermelon rind powder

Plate- 3

Experimental Setup for before decolourisation of Fuchsine Stain

Plate- 4

Experimental Setup for after decolourisation of Fuchsine Stain

3.3. Decolourisation of fuchsine stain using watermelon rind under optimal condition

Under the optimal conditions, the peanut shell was added into fuchsine stain solution and the percentage decolourisation was determined**.**

3.4. Structural characterization of watermelon rind powder

3.4.1. Surface characterization of the adsorbent by SEM

In order to understand the mechanism of dye adsorption, the surface structure of untreated as well as watermelon rind treated with fuchsine stain at a concentration of 100mg/100ml was analyzed by Scanning Electron Microscope (SEM). The untreated and treated watermelon was washed thoroughly with sterilized Triple Distilled Water (TDW), immersed in Glutaraldelyde (2.5% v/v) for 2 hrs at room temperature and washed thoroughly with sterilized Triple Distilled

Water (TDW). The pellet was then subjected to Osmium tetraoxide staining (2% v/v) for 1 hr and washed thoroughly with sterilized TDW. Then, the pellet was dehydrated by transferring it into series of 25, 50, 70, 90 and 100 % (v/v) ethanol for 10 minutes. The dehydrated pellet was then dried overnight in an oven and mounted on a glass slide 120 stab with double – stick carbon tab followed by coating with a thin layer of gold under vacuum to increases the electron conduction and to improve the quality of the micrographs.

3.4.2. FT-IR Spectra of dye loaded and unloaded watermelon rind

Another investigation related to the biosorption phenomenon was FT-IR analysis on the selected adsorbent. FT-IR (Fourier Transform) is perhaps the most powerful tool for identifying the types of chemical bonds (functional group). The wavelength of light absorbed is characteristic of the chemical bond which can be seen in the annotated spectrum. By interpreting the infrared absorption spectrum, the chemical bonds in the adsorbent can be determined before and after bio adsorption. 50ml of the watermelon rind solution was pelleted by centrifugation at 6000rpm for 15 min at 4^{o} C and was lyophilized using an ice dryer. Watermelon rind biomass was washed, dried and powdered after bio adsorption. One milligram of finely crushed biomass was then mixed with 400mg potassium bromide. The mixture was ground into fine powder and translucent sample disks were obtained by using a manual hydraulic press at a pressure of 100 kg cm^{-2} for 10 minutes. The disk was then fixed in a FT-IR spectrometer (FT-IR 8400S SHIMADZU). FT-IR spectra of the adsorbent unexposed and exposed to fuchsine stain at concentration of 0.1 g/100mg was obtained from 400-4000 cm^{-1}

3.5. Phytotoxicity study

The study was conducted to analyze the phytotoxicity of adsorbent treated dye solutions in comparison with the untreated dye solution.

3.5.1. Selection of the experimental plant

Citrullus lanatus (watermelon) rind was chosen for the study because of the following reasons:

1. It is very common food crop in Tamil Nadu with good nutritional value.
2. Germination period is very short.
3. Easy cultivation under laboratory conditions.

3.5.2. Pot culture experiments

In this experiment the effect of fuchsine stain at the concentration of 1g/L was evaluated on seed germination and seedling growth of watermelon rind. The *Macrotyloma uniflorum* seeds were germinated in pots containing equal proportion of red soil and sand. Experimental set up included nine pots arranged in three sets for three different treatments with three replicates for each treatment. Five seeds were sown in each pot and were watered every 24 hours using tap water (T_1) untreated dye solution (T_2), and treated dye solution (T_3). Seed germinated in pots using tap water was used as control. All pots were kept under shade near sunlight for a period of seven days. Germination percentage of seeds in all treatment was recorded. At the end of the experiment the plants were uprooted carefully without damaging the roots. The shoot length, root length and fresh weight of seeding were measured separately for each treatment.

3.5.3. Germination percentage

After 7 days of sowing, germination percentage of the seedlings was calculated using the formula

$$\text{Germination percentage} = \frac{\text{Number of seeds germinated}}{\text{Number of sedds sowed}} \text{X100}$$

The protrusion of radical through seed coats was taken as the criterion for germination.

3.6. Statistical analysis

The data obtained were statistically analyzed by One Way Analysis of Variance.

IV. RESULTS AND DISCUSSION

The problem associated with the release of textile waste water is the presence of synthetic dyes. These dyes are problematic due to the visibility and their recalcitrance. Many dyes and their degradation products are associated with toxicity and mutagencity (Weisburger, 2002). The toxicity of dyes is of serious environmental concern because the effluents coming from dye processing and manufacturing industries are known to be carcinogenic as well as mutagenic to various organisms (Mathur and Bhatngagar, 2007).

4.1. Optimization studies for fuchsine stain decolourisation using watermelon rind

4.1.1. Effect of fuchsine stain concentration on decolourisation

The fuchsine stain at the concentration of 0.01g showed maximum percentage of decolourisation by watermelon rind powder within 4 days of incubation and minimum of 82.3 percent decolourisation was observed at 0.05 g. It was clear that stain concentration was increasing and decolourisation was decreased considerably. The effect of dye concentration and stain decolourisation was depicted in table-I.

Table -I

Effect of dye concentration on decolourization

Dye concentration(mg)	**Decolourization %**
0.01	50
0.02	22.2
0.03	50.2
0.04	75
0.05	**82.3**

The effect of initial stain concentration depends on the immediate relationship between the dye concentration and stain concentration and the available bindings sites of an adsorbent surface (Umorenet *et al.,* 2013). At high concentration, the available sites of adsorption becomes fewer and hence the percentage removal of dyes gets decreased with increase in initial dye concentration (Mohandass and Ganesan, 2016).

The adsorption of dyes on the surface TRWM is rapid in the beginning and slow down later and finally reached towards the equilibrium. A large fraction of the total amount of dye is found to be adsorbed within a few minutes of time. 40-45% of the total amount of dye is observed to be removed from solution within 20-30 minutes. The total time to attain the equilibrium depends on the nature of the adsorbent as well as adsorbate. 100ml of dye solution was kept in contact with 0.9 gm of adsorbent at constant temperature for kinetic study and care has been taken to maintain agitation constant in all the experiments (Giles, 1970).

The attainment of the equilibrium was on the waste of reaction carried out on dilute solutions and the saturation time found to be dependent on the amount of adsorbent. The increase adsorption of the adsorbate on to adsorbent may be due to increase in surface activity and due to micelle formation or the aggregation of the dye molecule in the concentration range studied. Similar results have also been reported by Stephen *et al.,* 1989.

The effect of different dye concentrations on adsorption of CR is shown in figure 3. The amount of CR adsorption increase with increasing initial CR concentration. The amount of CR adsorbent equilibrium increased from 0.65 to 4.81 mg g^{-1} CR when concentration increased from 10.45 to 104.50 mg $L^{-1.}$ This may be attributed to an increasing concentration gradient acting as an increasing driving force to overcome all mass transfer resistances of the dye molecules between the aqueous and solid phase, leading to an increasing equilibrium sorption until saturation is achieved.

Adsorption experiments were conducted to study the effect of the initial concentration of Cu (II) in the solution on the rate of metal adsorption on water melon. The experiments were carried out at a fixed adsorbent dose (0.002g) and at different initial Cu (II) concentrations (6, 10 and 20 ppm) for different time intervals at 30º C as shown in fig-5. It was observed that Cu (II) uptake is rapid for the first 20 min and there after it proceeds at a slower rate and finally attains saturation. This may be explained by a rapid adsorption on the outer surface followed by slower adsorption inside the pores (Salam *et al.,* 1999).

4.1.2. Effect of adsorbent dose on fuchsine decolourisation

In order to find out the optimum adsorbent dose for high percentage decolourisation. Water melon rind powder of varying concentration from 100-500 mg was added into the aqueous solution amended with 100 mg of stain. The effect of adsorption dose on stain decolourisation was presented in table- II.

Table -II

Effect of adsorbent dose on fuchsine decolourisation

Dose concentration(mg)	Decolourization%
0.5	**90**
1	76.9
1.5	66.3
2	77.7
2.5	33.3
3	30.3

The effect of biosorbent dose (0.05-0.6g) on BG dye biosorption on watermelon rind studied. The maximum dye uptake capacity was observed at 0.1g (25.1579mg/g) adsorbent dose and minimum was observed at 0.05g (19.1349mg/g). When the adsorbent dose was further increased from 0.2 to 0.6 there was decrease in the sorption capacity of adsorbent. At the adsorption dose of 0.6g, the dye uptake capacity was only 3.77193mg/g (Kanawade *et al.*, 2011).

The uptake of dye as a function of adsorbent dosage was studied and the results plotted in figure-3 revealed that the percent adsorption of dye on the rice husk carbon increases rapidly and reaches about 96% for safranine and 88% for methylene blue.for 100% removal of safranine and methylene blue (Singh *et al.*, 2001).

The effect of biosorbent dose (0.1-0.6g) on the biosorption of dyes in effluent by sugarcane bagasse was observed. Biosorbent dose plays a very important role in the process of biosorption. The dye biosorption capacity decreased at higher biosorbent doses due to the aggregation of the biomass which results in the decrease in active sites on the surface of biosorbent available for the attachment of dye molecules.

Another important factor is that at high biosorbent dose, the available dye molecules are insufficient to completely cover the available binding sites to the biosorbent, which usually results in low solute uptake (Tangaromsuk *et al.,* 2002).

Adsorbent dose is important parameters influencing adsorption processes since it determine the adsorbent capacity of an adsorbent for a given initial concentration of the adsorbent at the operating conditions (Kushwaha *et al*., 2014).

4.1.3. Effect of incubation period on fuchsine decolourisation

The effect of contact time was observed for a time period ranging from 1 to 4 days and the results were presented in table-III. The results of the present study showed that the percentage decolourisation of fuchsine stain by watermelon rind powder was (95%) at 4th day incubation.

Table- III

Effect of incubation period on fuchsine decolourisation

Days	Decolourization%
1	61
2	68.4
3	86

4	**95**

The effect of contact time on color removal was observed from 20 to 140 minutes and the curve on contact time was found to be smooth and continuous leading to saturation indicating monolayer coverage of dye on adsorbent surface. Sorption rapidly occurs and normally controlled by the diffusion process from the bulk of the surface. In the later stage, the sorption is likely an attachment controlled process due to less available sorption sites. Similar results have been reported in literature for adsorption of malachite green dye over sea shell powder (Chowdhury and Saha, 2010).

The adsorption of CV on CLR was studied as a function of contact time in order to find out the equilibrium time for maximum adsorption. The influence of contact time on color removal by CLR is recorded (Bharathi *et al.*, 2012). This might be due to more biosorption sites available at the beginning. After 30 mins, the removal decreased which can be explained by the exhaustion of the biosorption sites (Chowdhury and Saha, 2010).

The removal of dye by adsorption process using TRWM was found to be rapid at the initial stage of contact time and then related with increase in contact time of adsorbent and adsorbate. It may be attributed to the strong binding forces between Methylene blue molecule and adsorbent TRWM. Our finding is in good agreement with the findings reported by Chamargore *et al.*, 2011).

4.1.4. Effect of pH on fuchsine stains decolourisation

The effect of pH on stain adsorption was studied in the range of 2 to 10. The adsorption capacity for the watermelon rind powder was maximum at pH 6, (90%) and further increases in pH gradually decrease the adsorption percentage and minimum of 18% adsorption was recorded at pH 10. The effect of pH on stain decolourisation was presented in table- IV.

Table-IV

Effect of pH on fuchsine stains decolourisation

pH	Decolourization%
2	50
4	42
6	**90**
7	70
8	70
9	66

10	72

Similar observations were made by Bharathi et *al.*, (2012) stated that the pH is an important factor in controlling the adsorption of dye on to adsorbent. Adsorption experiments were conducted in the pH range 2.0-12.0 keeping all other parameters constant (CV concentration=10mg/l, adsorbent dose=50mg/l; stirring speed= 150rpm; contact time= 180 min; temperature=30^{0}C).

The pH of a solution is an important factor which controls any adsorption process. The dye binding sites on the surface of the adsorbent are often modified by change in the pH of the solution. Similarly the chemistry and the structure of the dye molecules is also department on pH (Kale *et al.*, 2013).

The pH plays a significant role in biosorption process and pH8 had the highest removal with 78.23%. When the pH is low, the H^+ ions from the acid compete with the Zn ions for adsorption sites and hence decreased the removal and the capacity (Lakshmipathy *et al*., 2013). Besides, when the pH is too high, the biosorption decreased. This might be due to the formation of soluble hydroxyl complexes of Zn^{2+} ions and Zn^{2+} ions exists as predominant species (Osman *et al*., 2010).

The pH is amongst one of the important parameters for adsorption process as it controls the protonation of the functional groups on the biomass as well as the metal chemistry (Feng *et al*., 2011). The effect of pH was studied by varying the pH from 3.00 to 10.00. At pH3 the minimum adsorption of 25.00% was observed. With further increase in pH, a gradual increase in adsorption was observed, with 36.00% at pH 5.00, which recorded a maximum of 64.40 at pH7 recorded a slight decrease in adsorption (62.00). Above pH7, the adsorption percentage was gradually decreased and recorded 45.00% at pH10. The above results indicated that the dye adsorption considerably increased when pH was raised from 3.00 to 6.00. At pH 3.00, percent dye removal was very low which increased as pH was raised to 6.00. Slightly acidic pH favors dye adsorption. Similar observation was reported by Ashoka and Inamdar, (2010). They stated that the adsorption efficiency was greatly affected by pH variation and for formaldehyde treated bagasse the dye adsorption considerable increased as pH was varied from 2 to 6. (Sayed *et al.,* 2013).

Solution pH highly affects the efficiency of adsorption process. This is because the charges of adsorbent materials and adsorbate molecules might be changed by solution pH affecting the functional groups on the adsorbate molecules (Osman *et al.,* 2016).

4.1.5. Effects of temperature on fuchsine stain decolourisation

The effect of temperature was studied in the range of 25ºC to 45º C. the percentage stain removal was maximum at 40º C (90%) and further increases in temperature from 40º C to 60º C could not increase the stain removal capacity instead a decrease was observed from 46% to 11% respectively (Table-V). The observations showed the optimum temperature for stain removal was noticed to be 40º C. The effect of temperature on stain decolourisation was depicted in figure -4.

Table- V

Effects of temperature on fuchsine stain decolourisation

Temperature ^{0}C	**Decolourization %**
25	62
30	33
35	33
40	**90**
45	41

The effect of temperature on the adsorption of CV on CLR was investigated under isothermal conditions in the temperature range of 30-50º C. The extent of adsorption of CV was found to increase temperature and indicating the process to be endothermic in nature (Singh *et al.*, 2003).

Temperature is one of the most important factors, which determines the extent of adsorption of given system. Its influence in deciding the actual alternation is both positive and negative (Catalkaya *et al.*, 2008). The level of adsorption at any particular concentration usually decreases with increase in temperature, i.e., the overall process is exothermic (Otter *et al.*, 1980; Gupta *et al.*, 1986).

The effect of temperature was studied in the range from 20^{oC} to 60^{oC}. The dye uptake capacity was increased from 9.47 to 9.77 mg/L for the rise in temperature from 20^{oC} to 35^{oC}. (Abbas *et al.*, 2012). Further increase in temperature from 40^{oC} to 60^{oC} could not increase dye removal, rather a decrease was observed from 9.55 to 8.78 mg/L. Therefore, maximum adsorption of BG dye from aqueous solution was achieved at 35 º C (Deniz *et al*., 2010).

Temperature is significant parameters because it will change the adsorption capacity of adsorbent (Argun et *al.*, 2009). At higher and lower temperature, adsorption efficiency of dye decreases. This decrease in adsorption efficiency was attributed to the fact that at high temperature

Murexide and Brilliant vital red dyes molecules move with larger speed and less time of interaction was available for the adsorbate with urea modified rice husk (Rehma *et al.*, (2013)

4.2. Decolourisation of fuchsine stain using watermelon rind powder under optimal conditions.

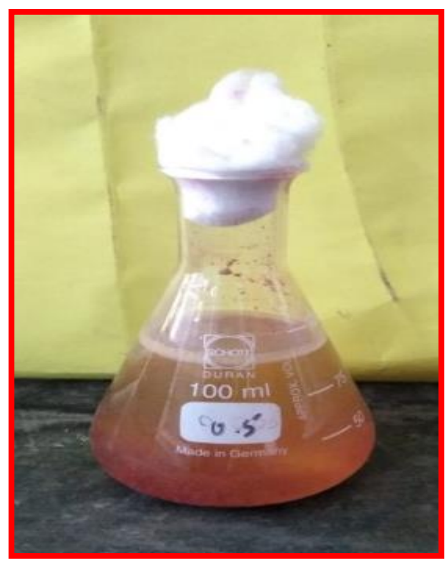
From the batch adsorption studies it can be concluded that the most efficient operational parameters in the current study were found to be, pH of 6, temperature of 40º C, adsorbent dose of 0.5g and contact time of 4th day for the decolourisation of 0.01gm of fuchsine stain solution using water melon rind (Plate 4).

Plate -5

Decolourization of fuchsine stain

(a) Untreated fuchsine stain

(b) Treated fuchsine stain



4.3. Structural Characterizations of watermelon rind powder

4.3.1. Scanning Electron Microscopy Analysis (SEM)

Scanning Electron Microscopy was done to observe the surface characteristics of the adsorbents well before and after adsorption. The Scanning Electron Microscopy of the adsorbents at specific resolution and magnification was depicted (Plate-6). SEM is widely used to study the morphological features and surface characteristics of the adsorbent materials. It also reveals the surface texture and porosity of adsorbent. SEM provides high magnified image of the surface of the material. It images the electrons that are reflected from a sample. The porous structure found in the adsorbent surface collapses to some extent which may be due to the fact that the adsorbent being a natural biological material changes its characteristics (Sharma *et al.*, 2016).

The adsorption capability of watermelon rind in the application of wastewater treatment had been proven in various researches such as the removal of nickel, lead and copper, and trivalent chromium. In this study, different chemical pre-treatments were attempted on watermelon rind using different solvents, namely citric acid, sulfuric acid, calcium hydroxide and sodium hydroxide to investigate the possibility of enhancing the adsorption performance on the removal of Zn2+ ions. The pre-treated watermelon rinds were subjected to characterization studies in order to determine the significance alterations on the surface morphology and chemical properties of the watermelon rind Adsorbents.

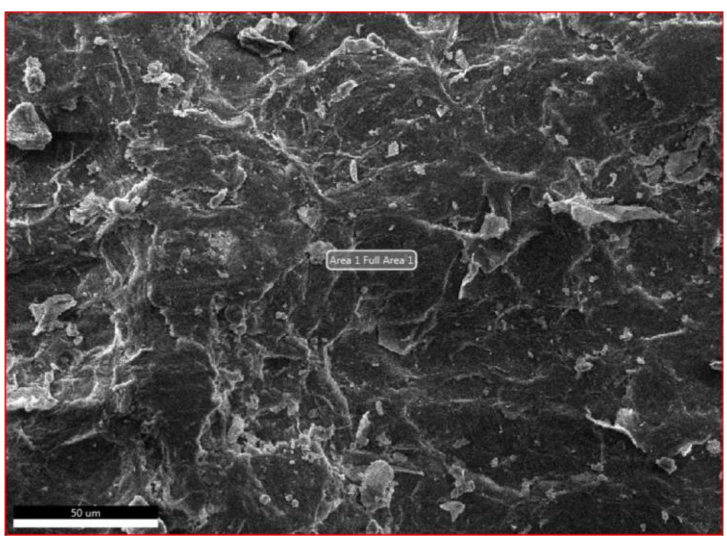
The surface features of the untreated watermelon rinds showed smooth and fine fibers structure with linear morphology. In contrast, the micrographs of chemically treated watermelon rind with both acids and bases revealed the existence of an accumulation of very fine particles, causing an irregular surface structures. To further elaborate on that, the surface of treated watermelon rind was rough, with no fixed shape and size, and was found to be more porous. The particles were of various dimensions, and contained a large number of steps and kinks on the external surface with broken edges. Therefore, it can be further confirmed that chemical treatments improved the surface structure of the biosorbent with improving porosity, thus, larger surface area is resulted as compared to untreated biosorbent. Ibrahim et al 2016.

4.3.2. FT-IR spectra of dye loaded and unloaded watermelon rind

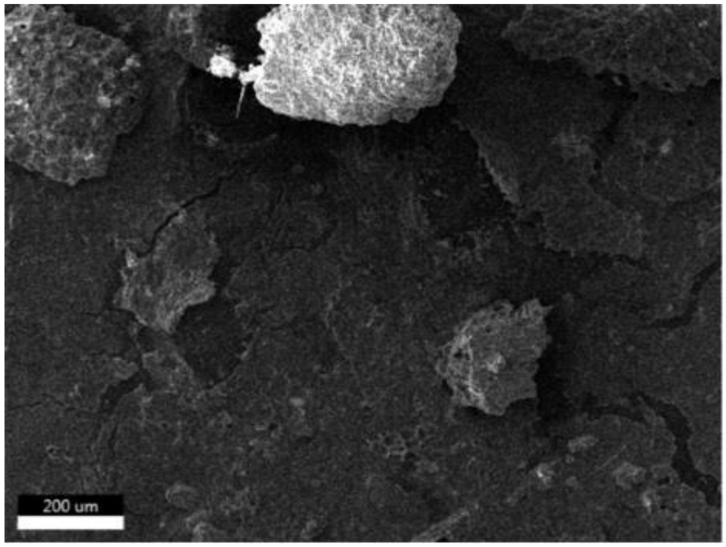
Fourier Transform Infra Red is the preferred method of infra red spectroscopy. In this, IR radiation is passed through a sample and some of the infra red radiation is absorbed representing the molecule adsorption and transmission creating a molecular fingerprint of the sample. The dry powdered samples of watermelon rind were subjected to Fourier Transform Infra Red analysis which resulted in many functional groups based on the wavelength and percentage of transmittance were illustrated in figure 1 and 2.

Plate-6

Scanning Electron Micrographs depicting the effect fuchsine stain on the water melon rind



a) Water melon rind before adsorption of fuchsine stain



b) Water melon rind after adsorption of fuchsine stain

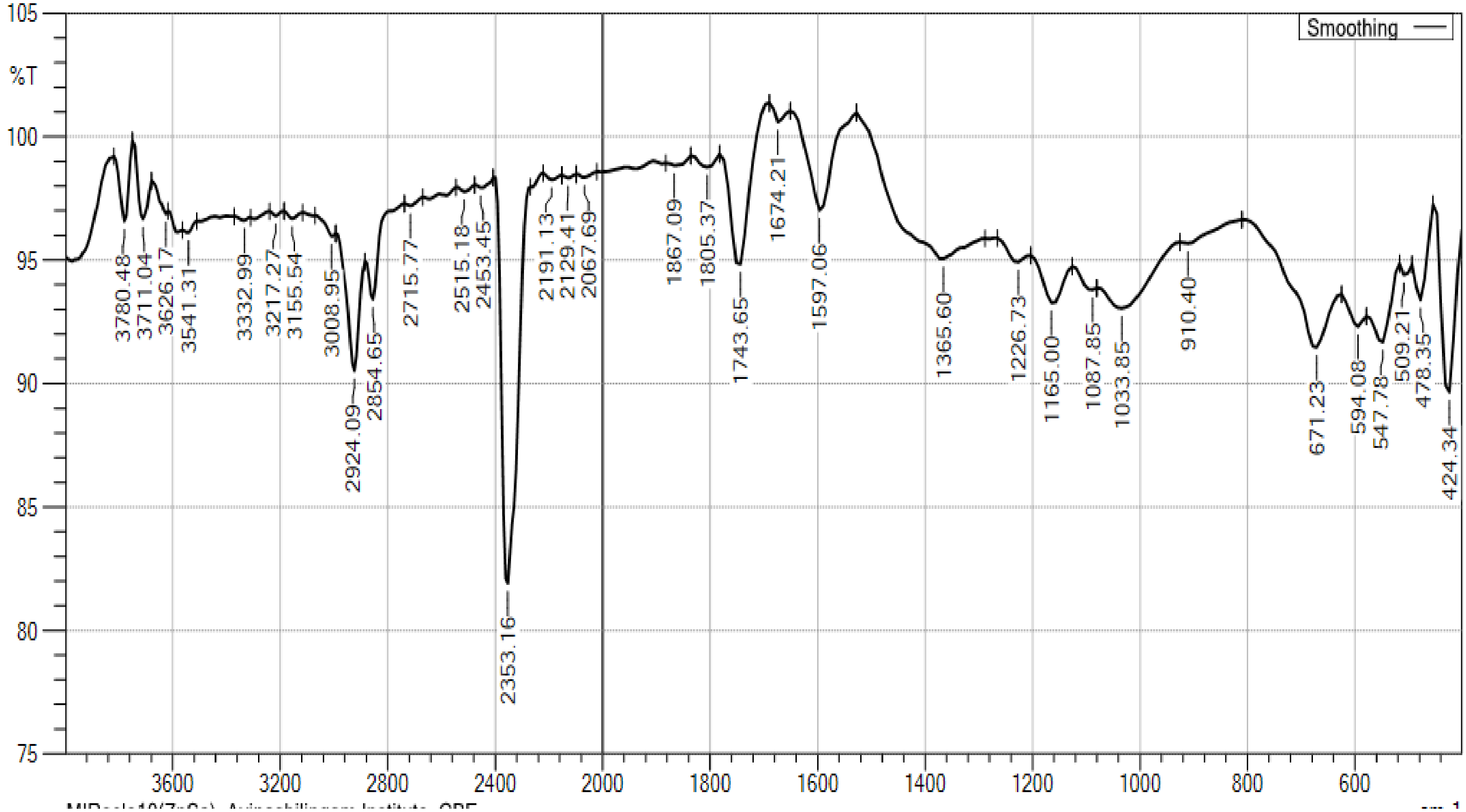


Figure- 1

FTIR spectrum of watermelon rind before adsorption

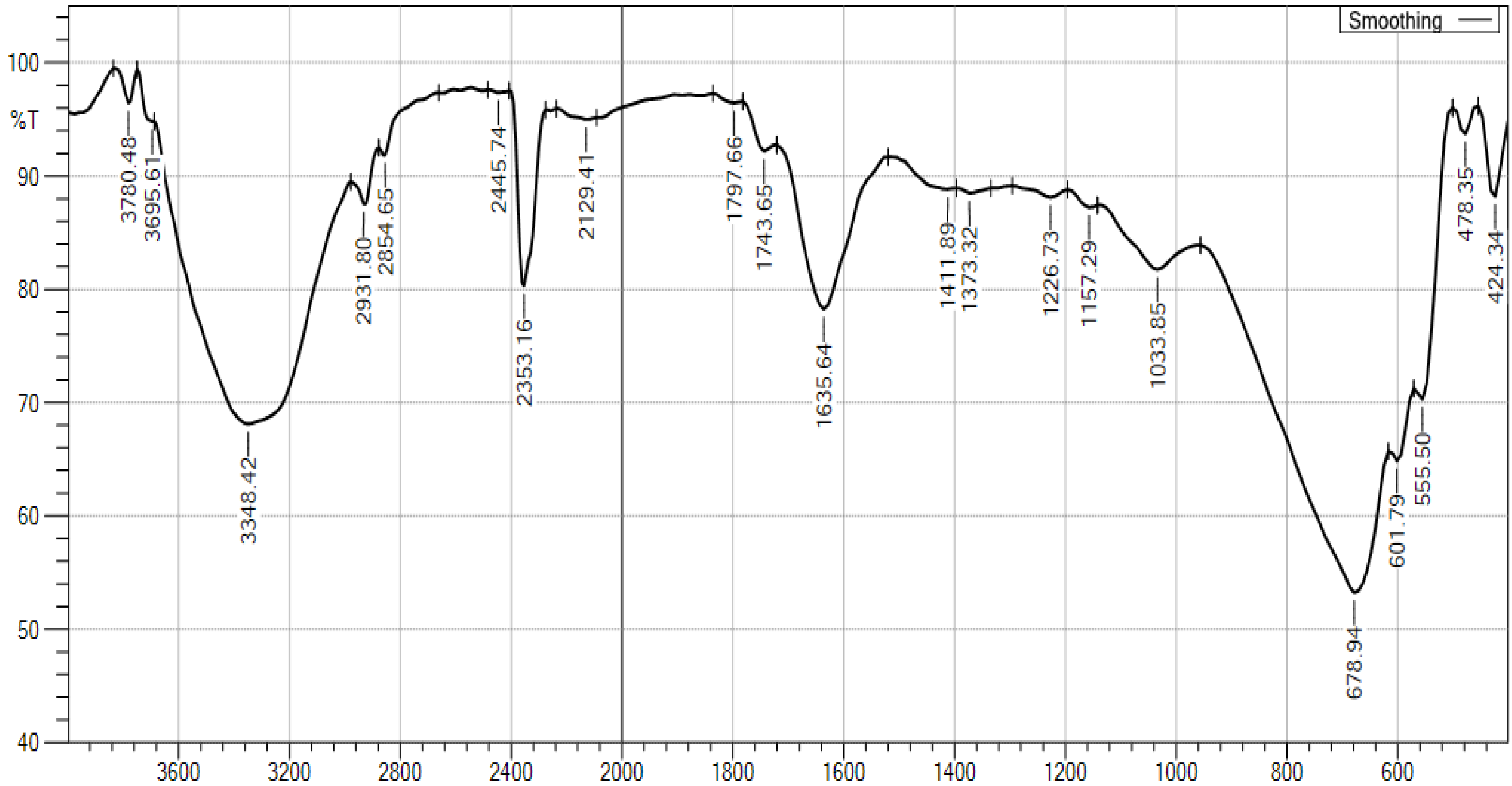


Figure-2

FTIR spectrum of watermelon rind after adsorption

4.5. Phytotoxicity Study

The results of germination percentage , root length, shoot length, fresh weight, dry weight and vigour index of *M. uniflorum* seedlings grown with tap water (T_1), untreated fuchsine stain (T_2), and treated fuchsine stain (T_3), on the 7^{th} day growth of the experimental plant and the results were depicted.

4.5.1. Germination percentage and vigour index

A maximum of 85 percent germination was recorded in *M. uniflorum* seeds grown with tap water (T_1) followed by 52 percent in treated stain solution (T_3). Minimum of 6 percent germination was recorded in seeds grown with untreated stain solution (T_1) (Plate 10, 11).

The reduction in seed germination was also observed by several researches in various agriculture crops grown in dyeing From the above results it was observed that the reduction in shoot and root length of seedlings grown using T_1 might be due to the presence of higher dye concentration which exhibited the uptake of micro and macro element by plant system. Fuschine stain treated with water melon rind has been reported to favour root and shoot length due to the translocation of nutrients to the plants (Jothimani and Elayarajan, 2003).

The vigour index was maximum in T_1 (1752) followed by T_3(764) and minimum was observed in T_2 (25) decrease in the vigour of seeds irrigated with untreated dye observed in the present study might be due to the interaction of different pollutants with the developing radical. Seed vigour may also be correlated with physiological and chemical properties of axes than with those of whole seeds (Anderson and AbdhulBaki, 1971).

4.5.2. Shoot length and root length

Shoot length of old seedlings after treatment with tap water, untreated dye and treated dyes were recorded and root length of 7 days old *M. uniflorum*.

The values recorded for the shoot lengths of *M. uniflorum* Seedlings were 1cm, 10cm and 9cm in T_1, T_2 and T_3 respectively. The values recorded for the seedlings grown in treated stain (T_3) were highly significant when compared with untreated stain (T_2). The root of the *M. uniflorum* was maximum (7.6cm) in T_1 followed by T_3 (3cm) and minimum (0.22cm) in T_2 .T_1 it showed an increase in root length when compared to T2 and T3 plants.

From the above results, it was observed that the reduction in shoot and root length of seedlings grown using T_1 might be due to the presence of higher dye concentration of dye which exhibited the uptake of micro and macro element by plant system. Fuschine stain treated with

T$_1$ **T$_2$** **T$_3$**

Plate – 10

Pot culture of *M. uniflorum*

Plate-11

Root length and shoot length of *M. uniflorum*

T$_1$ - Untreated stain solution **T$_2$ - Treated stain solution** **T$_3$ - Tap water**

Water melon rind has been reported to favour root and shoot length due to the translocation of nutrients to the plants (Jothimani and Elayarajan, 2003).

4.5.3. Fresh weight and dry weight

The fresh weight of water melon rind seedling treated with different treatments was depicted in the table. The highest fresh weight (0.42 g) was observed in $T_{1,}$ followed by treated dyeT_3 (0.20g) and least value (0.20) g) was recorded in T_2. The dry weight of watermelon rind was maximum (0.21 g) in T_1 and minimum (0.030 g) in T_2 and T_3 recorded (0.136 cm). There was an increase in the fresh and dry weight of T_1 plants when compared with treated dye and T_2 plants.

The reduction in the fresh and dry weight of the horse gram, plants selected for the present study may be due to the physiological stress caused by the dye which restricted the plant growth by increasing the soil osmotic pressure (Jothimani and Elayarajan, 2003).

V. SUMMARY AND CONCLUSION

Dyes are designed to be chemically and photolytic ally stable, they are highly persistent in natural environments. During dyeing process, approximately 10-15% of the dyes is released into wastewater stream and can cause serious environmental and health hazards.

A wide range of biological, chemical and physical method has been used to treat textile dye effluents. Although the physical and chemical methods are technically feasible for treatment of color wastewater, they have inherent drawbacks such as high operative cost, formation of hazards by products and intensive energy consumption. As a viable alternative, biological treatment method using aerobic and anaerobic microorganisms has received increasing interest owing to their high effectiveness, lower sludge production and eco friendly nature.

Treatment of wastewater containing dyes by adsorption is an emerging field of research. The process of adsorption has an edge over other methods due to its sludge free clean operation and complete removal of dyes even from the dilute solutions. The commonly used adsorbent for dye removal by adsorption is activated carbon.

Findings of the study

- The study showed that dye concentration, adsorbent dose, temperature, pH, and contact time played a major role in adsorption.
- The percent decolourisation was maximum in 0.05g of stain amended aqueous solution in concentration for water melon rind powder (82.3%).
- The effect of the adsorbent dose on decolourisation of stain indicated maximum stain removal (90%) at 0.05gm of water melon rind powder. Adsorption efficiency decreased with further increase in adsorbent dose.
- An increase temperature showed an initial increase in adsorption percentage and maximum adsorption was recorded at $40^{o\ C}$ for water melon rind powder (90%).
- The adsorption capacity for adsorbent water melon rind powder was maximum at pH 6 (90%) with further increase in pH and the adsorption percentage was gradually decreased.
- The effect of contact time on colour removal was observed from 1 to 4 days and maximum dye removal was observed on 4^{th} day of incubation at 95%.

- FT-IR analysis showed vibration frequency changes in the spectrum after stain adsorption. Peak shifting and intensification were observed which indicates the involvements of functional group in bioadsorption.
- The scanning electron microscopic study proved the accumulation of stain within the adsorbent surface.

M. uniflorum grown with watermelon treated stain solution exhibited significant biometric germination percentage and growth parameters such as shoot length, root length, fresh weight and vigour index when compared with treated stain solution. The plants grown with untreated stain recorded minimum growth when compared with treated and tap water plants on 7^{th} day after sowing.

CONCLUSION

From the study, it can be concluded that, the low cost adsorbent like watermelon rind powder have the potential for the decolourisation of fuchsine stain. The phytotoxicity study also revealed that the treated stain solution is non-toxic and can be utilized for agricultural purpose.

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