GROUNDNUT SHELL POWDER AS AN ADSORBENT FOR THE REMOVAL OF TEXTILE DYE FROM AQUEOUS SOLUTION

SOWNDARYA V.

16PZO012

A THESIS SUBMITTED TO AVINASHILINGAM INSTITUTE FOR HOME SCIENCE AND HIGHER EDUCARTION FOR WOMEN, COIMBATORE

IN PARTIAL FULFILMENT OF THE REQUIRMENTS FOR THE DEGREE OF

MASTER OF SCIENCE IN ZOOLOGY

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1.INTRODUCTION

Colour is an important aspect of human world. We like to wear clothes of all kinds of colour and hues, eat food decorated with colours and even our medicines are colourful (Zolinger,1987).

Dyes are coloured compounds which are widely used in textile, printing, rubber, cosmetic, plastic and leather industries to colour their products. Among all dye using industries, textile industries are placed in the first position in the usage of dyes for colouration of fiber . Dyeing in textiles is a process in which color is transferred to a finished textile or textile material like fibers and yarns to add permanent and long-lasting colour. Dyes can come as powders, crystals, pastes or liquid dispersions and they dissolve completely in an aqueous solution like water. When the textile and the dye come into contact, the textile is completely saturated by the dye and colored (Gürses *et al*.,2016).

Humans have been dyeing textile for a very, very long time and in fact, scholars find early mention of dyeing textiles as far back as 2600 BC. There are many ways to dye textile materials. In most dyeing processes, water is used with the dye and other additives to affix colour to textiles. When the textile is rinsed, the colour stays. A dye may also be pressed into a fabric through a thick paste, or the textile material may be immersed into a dye vat or tub. Sometimes dyeing textiles requires high temperatures and some synthetics like polyester dye more easily at temperatures above 100 degrees.No kind of dye effectively colors all natural and synthetic textiles. Different dyes and dyeing processes work best on different materials (Krizova 2015).

In India ,textile industry accounts for the largest consumption of dyestuffs figuring around 80% (Mathur *and kumar*2003), taking in every type of dye and pigment produced, amounting close to 80000 tonnes. Also, India is the second largest exporter of dyestuffs, after China. It occupies an unique position in the Indian economy in terms of its contribution to industrial production,employment and exports. It is one of the largest segments of Indian economy accounting for 14% of industrial production and one –third of total exports with only 1-15% of import bills. It is closely linked with agriculture and rural economy and is the single largest employer in the industrial sector, employing about 35 million people and if the employment in the allied sectors like agriculture, ginning, pressing cotton trade etc.is added then the total employment is estimated at 93million people (Zollinger 1987)..

Dyes derived from natural sources are without any chemical treatment and include plants, insects, animals and minerals. Dyes derived from plant sources are indigo and saffron. Insects include cochineal beetles and lac scale insects. Animal sources are some species of molluscs or shellfish and minerals are ferrous sulfate and ochre(Kumari *et al*,.2016)

The introduction of mauve in 1857 triggered the decline in the dominance of natural dyes in world markets. Mauve had a short commercial lifetime lasting about seven years, but its success catalyzed activities that quickly led to the discovery of better dyes. Today only one natural dye, logwood, is used commercially, to a small degree, to dye silk, leather, and nylon (Choudhary*et al.*,2006).

.The world's first commercially successful synthetic dye, named mauveine, was discovered by accident in 1856 by William Henry Perkin. These synthetic compounds can be defined as colored matters that color fibers permanently, such that they will not lose this color when exposed to sweat, light, water and many chemical substances including oxidizing agents and also to microbial attack By the end of the 19th century, over ten thousand synthetic dyes had been developed and used for manufacturing purposes The expansion of worldwide textile industry has led to an equivalent expansion in the use of such synthetic dyestuffs, resulting in a rise in environmental pollution due to the contamination of wastewater with these dyestuffs (Choudhary,2006).

Environmental pollution is one of the major and most urgent problems of the modem world. Industries are the greatest polluters, with the textile industry generating high liquid effluent pollutants due to large quantities of water used in fabric processing. In this industry, wastewaters differing in composition are produced and the coloured water released during the dyeing of fabrics may be the most problematic since even a trace of dye can remain highly visible. Other industries such as paper and pulp mills, dyestuff, distilleries, and tanneries also produce highly coloured wastewaters but it is in the textile industry that the largest quantities of aqueous wastes and dye effluents are discharged from the dyeing process, with both strong persistent colour and a high biological oxygen demand (BOD), both of which are aesthetically and environmentally unacceptable (Wang *et al*. 2007).

A survey carried out by The Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD) showed that of a total of approximately 4,000 dyes that had been tested, more than 90% showed LD50 values above 2 x 103 mg/kg, the most toxic being in the group of basic and direct diazo dyes and azo dye which does not cause acute toxicity, is of concern due to the possible generation of carcinogenic aromatic amines (Golka *et a*l., 2004).

During the coloration process, a large percentage of the dye does not bind to the fabric and is lost to the wastewater stream. Approximately 10-15% dyes are released into the environment during dyeing process making the effluent highly colored and aesthetically unpleasant (Chequer2013).

A great environmental concern with dyes is the absorption and reflection of sunlight entering the water. Light absorption diminishes photosynthetic activity of algae and seriously influence the food chain as the algae are the base of the food chain, thus affecting every organism above it. The lack of algae is one of the main reasons that the aquatic life suffers in areas where dyes are discharged, but another is because of the toxicity of the dyes themselves.The highly toxic and mutagenic dyes not only decrease light penetration and photosynthetic activity, also causes oxygen deficiency limiting downstream beneficial uses such as recreation, drinking and irrigation (Ramakrishna *et.al* 2010*).*

The chemicals of textile dyes affect the normal life of animals. Toxic compounds from dye effluent get into aquatic organisms, pass through food chain and ultimately reach man and cause various physiological disorders like hypertension, sporadic fever, renal damage, cramps etc The apparel products, purchased and used by consumers often contain chemicals, harmful for the human health. Harmful chemicals can be acquired through the skin, bronchially or through digestion. Textile materials can cause allergic reactions. Textile materials can even be carcinogenic and mutagenic(Akarslan and Demiralay 2015).

Public perception of water quality is greatly influenced by the colour. So, the removal of colour from wastewater is often viewed as more important than the removal of the soluble colourless organic substances(Oliver et.al.,2000).

The public demand for color-free waste discharge to receiving waters and tougher color standards have made decolorization of a variety of industrial wastes a top priority. Unfortunately, with the complicated color-causing compounds, the decolorization of these wastes is a difficult and challenging task. (Oliver et.al.,2000).

The removal of anionic dyes is considered as the most challenging task as they are water soluble and produce very bright colour in water with acidic properties (Gürses *et al*.,2016).

Decolourisation of waste water has now become a major problem for the treatment plants in various industries. Many industries use synthetic dyes to colour their products such as textiles, rubber, paper, plastics, leather, cosmetic, food etc. Nearly 10-15% of synthetic textile dyes, used yearly are lost to waste streams and about 20% of these losses enter the environment through effluent from waste water treatment plant.(Sharma,et.al.,2012)

The adsorption process is one of the effective methods for removal of dyes from the waste effluent. The process of adsorption has an edge over the other methods due to its sludge free clean operation and complete removal of dyes even from the diluted solution. Activated carbon is the most widely used adsorbent because it has excellent adsorption efficiency for the organic compound. Nevertheless, commercially available activated carbon is very expensive(Wang et al, 2005).

Although activated carbon is the commonly preferred adsorbent, its widespread use is restricted due to high cost. In view of the high cost and tedious procedure for the preparation and regeneration of activated carbon studies have been focused on various natural solid supports, which are able to remove pollutants from contaminated water at low cost (david *et al*.,1990)

Experimental studies proved that the effective removal of dyes is obtained using several cheaply available non-conventional adsorbents also. Therefore, studies related to searching for efficient and low cost adsorbents derived from existing resources are gaining importance for the removal of dyes (Kandisa et.al., 2016)

In India alone more than 400 million tonnes of agricultural residue is generated annually, which includes rice husk, bagasse, stalk, coir pith etc. Exploring application of the agricultural residues for use as adsorbents can provide suitable alternatives for the removal of spent dyes from industrial effluents(Upadhye and Yamgar 2016).

The adsorption capacity depends on several variables, such as the concentration of the pollutants, the pH of the medium, the contact time, and the accessibility of the pollutants to the inner surface of the adsorbent, which in turn depends on their size, among others (Salman*et al.*,2014).

Hence the present study was undertaken to find out the adsorption capacity of groundnut shell to remove acid violet dye from aqueous solutions and to optimize the conditions for dye removal such as pH ,dye concentration, temperature and adsorbent dose.

2.REVIEW OF LITERATURE

The literature reviewed for the present study on 'Groundnut shell powder as an adsorbent for the removal of textile dye from aqueous solution' was presented as follows.

2.1.CHARACTERSTICS OF TEXTILE DYE

Color is an important aspect of human world. We like to wear clothes of all kinds of colors and hues, eat food decorated with colors, even our medicines are colorful. No wonder then, that a lot of research has gone into the production of color. Today there are more than ten thousand dyes available commercially and seven lakh tons of dyes are produced annually (Zolinger,1987).

Goetz(2008) examines different classes of dyes, the processes they require, their use on different textiles, and their potential effects on the environment. Additionally, experiments with natural dyes were conducted and documented. Natural berries, roots, and other dyestuffs were collected and used to dye both natural and synthetic textiles. Through research and experimentation, the different types of dyes and techniques were compared and contrasted. Each type of dye has benefits and disadvantages. Every system of dyeing produces waste along with the finished product. Current government standards regarding textile waste are discussed as well as ways to reduce costs while adhering to these standards.

Dyes are organic compounds which contain in their molecules color imparting chromophoric groups and acid or basic auxochromic groups responsible for dyeing ability. Due to the auxochromes, dye molecules can be permanently bonded with fibers or other materials. Besides their traditional use in textile, leather, paper, as well as the paint and varnish industries, dyes have become indispensable in other fields such as microelectronics, medical diagnostics and information recording techniques and they continue to be intensively developed (Hoffmann and Puszynski, 2011)

Color is the main attraction of any fabric. No matter how excellent its constitution, if unsuitably colored it is bound to be a failure as a commercial fabric. Manufacture and use of synthetic dyes for fabric dyeing has therefore become a massive industry today. In fact the art of applying color to fabric has been known to mankind since 3500 BC. WH Perkins in 1856 discovered the use of synthetic dyes. Synthetic dyes have provided a wide range of colorfast, bright hues. However their toxic nature has become a cause of grave concern to environmentalists. (Kant 2012).

Dyes can be of many different structural varieties like acidic, basic, disperse, azo, anthraquinone based and metal complex dyes among others. The textile industry is the largest consumer of dye stuffs. During the coloration process a large percentage of the synthetic dye does not bind and is lost to the waste stream (Weber & Adams, 1995). Approximately 10-15% dyes are released into the environment during dyeing process making the effluent highly colored and aesthetically unpleasant(Ratna and padhi 2012).

Color removal from wastewater has been a matter of concern, both in the aesthetic sense and health point of view. Color removal from textile effluents on a continuous industrial scale has been given much attention in the last few years, not only because of its potential toxicity, but also mainly due to its visibility problem. There have been various promising techniques for the removal of dyes from wastewater. However, the effectiveness of adsorption for dye removal from wastewater has made it an ideal alternative to other expensive treatment methods. In this review, an extensive list of sorbent literature has been compiled. The review evaluates different agricultural waste materials as low-cost adsorbents for the removal of dyes from wastewater. The review also outlines some of the fundamental principles of dye adsorption on to adsorbents. Bharathi and Ramesh(2013)

Dyes and pigments are the most important colorants used to add a color or to change the color of something. They are widely used in the textile, pharmaceutical, food, cosmetics, plastics, paint, ink, photographic and paper industries. Dyes are colored substances which are soluble or go into solution during the application process and impart color by selective absorption of light. Pigments are colored, colorless, or fluorescent particulate organic or inorganic finely divided solids which are usually insoluble in, and essentially chemically unaffected by, the vehicle or medium in which they are incorporated. On the other hand, the color, which is highly dependent on the chemical and physical properties of a matter, is a result of the interaction between light and substance(Gurses 2016).

2.2.ENVIRONMENTAL IMPACT OF TEXTILE DYE

The textile effluents has been proved to impart adverse effects on humans, animals and plantation. The present study reveals that the impact of textile effluents on a protenious edible fresh water fish Mastacembelus Armatus by examining the changes in the ionic regulations of some selected tissues like liver , kidney and muscle before and after exposure to the Acid Blue 92 (CI.No. 13390). Mastacembelus Armatus were exposed to sub lethal concentration of textile dye - Acid Blue 92 (CI.No. 13390) for a period of 35 days. After the exposure period it was observed that a decrease in concentration of Sodium and Chloride ions and an increase in concentration of potassium, Calcium and magnesium ions. The magnesium ion concentration increased, but only slightly, when compared to the fluctuations of the other ions. The cationic concentrations of the test individuals indicate that the impact of textile effluents has an adverse effect the ionic regulations(Karthikeyan *et al*., 2006)

Haematological and serum biochemical studies on Swiss albino rats were carried out by Sharma *et a*l.,2007 for a period of 15 days to investigate the effects of untreated (Influent) and treated (Effluent) textile dye wastewaters collected from an Effluent Treatment Plant in Sanganer, Jaipur, India. In comparison to control animals (potable water), values of RBC, WBC, Hb, PCV and MCHC decreased significantly in wastewater exposed animals (12-46%). Also RBC size decreased (13-27%) and the shape modifi ed (poikilocytosis). In contrast, WBC size increased (8-23%)

. The serum biochemical parameters viz. AST, ALT, urea, creatinine and bilirubin increased signifi cantly (5-97%), whereas an opposite trend was noted for cholesterol, glucose, total protein, albumin and globulin contents (8-53%). The alteration in values was more pronounced in the influent-treated animals. When wastewater-exposed animals were kept under control conditions (supplied with potable water) for a period of 45days, the effluent group recovered faster, attaining values of various investigated parameters similar to the controls. The present study has thus established the toxicity of both untreated and treated textile dye wastewater to the haemopoietic system of male albino rats(Sharma *et al*.,2007).

The investigations were conducted on fresh water fish Oreochromis mossambicus (Peters.) to check out the effect of different concentrations of nine different textile dyes on antioxidant status such as Glutathione – S – transferase, Glutathione reductase, Catalase and Reduced glutathione, marker enzymes such as Aspartate transaminase (AST), Alanine transaminase (ALT) and Lactate dehydrogenase (LDH), electrolytes such as Calcium, Phosphorus, Magnesium, Sodium, Potassium and Zinc, essential nutrients such as Vitamin C, Folic acid and Lysine, protein pattern, conformation of biomolecules and histology of gill, intestine, liver and muscle for different duration of days. The different concentrations of textile dyes were 0.5, 1.0 and 1.5 ppm and exposure period were 7, 14 and 21 days.The results indicate that chronic exposure of fish to 1.5 ppm of textile dyes for 21 days significantly altered the antioxidant status. A decrease in concentration of calcium, phosphorus, magnesium, sodium, potassium and zinc in 7, 14 and 21 days group were adsorbed which shows an adverse effect of textile dyes on ionic and osmotic regulation. A significant depletion of essential nutrients such as vitamin C, Folic acid and Lysine was observed suggestive of disturbed growth and metabolism Structural variations in the biomolecules especially protein was demonstrated by FT-IR. Histological analysis of gills and intestine revealed significant morphological alterations such as degeneration of secondary lamellae, lamellar fusion due to hyperplasia and hypertrophy of epithelial cells. The main histopathological changes observed in liver are hyperemia, necrosis and in muscle hyperemia and degeneration.(Sharmila 2010)

Tartrazine is an artificial azo dye commonly used in human food and pharmaceutical products. The present study by Gao et.al.,(2011) was conducted to evaluate the toxic effect of tartrazine on the learning and memory functions in mice and rats. The decline in the activities of catalase, glutathione peroxidase (GSH-Px), and superoxide dismutase (SOD) as well as a rise in the level of malonaldehyde (MDA) were observed in the brain of tartrazine-treated rats, and these changes were associated with the brain from oxidative damage. The dose levels of tartrazine in the present study produced a few adverse effects in learning and memory functions in animals. The mechanisms might be attributed to promoting lipid peroxidation products and reactive oxygen species, inhibiting endogenous antioxidant defense enzymes and the brain tissue damage.

Water pollution due to effluents from textile dyeing industry is a cause of serious concern. The techniques for detection of dyes are cost intensive and futile because the dyes undergo chemical changes under environmental conditions and the transformation products may be more toxic and carcinogenic than the parent molecule. Hence instead of detecting each chemical individually it is advisable to study the toxiceffect of the effluents on various living organisms. Remediation using physical, chemical and biological methods has also been critically reviewed by Rantna and Padhi., 2012.

Use of synthetic dyes has an adverse effect on all forms of life. Presence of sulphur, naphthol, vat dyes, nitrates, acetic acid, soaps, enzymes chromium compounds and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, and cobalt and certain auxiliary chemicals all collectively make the textile effluent highly toxic. Other harmful chemicals present in the water may be formaldehyde based dye fixing agents, chlorinated stain removers, hydro carbon based softeners, non bio degradable dyeing chemicals. These organic materials react with many disinfectants especially chlorine and form by products (DBP'S) that are often carcinogenic and therefore undesirable. Many of these show allergic reactions. The colloidal matter present along with colors and oily scum increases the turbidity, gives the water a bad appearance and foul smell and prevents the penetration of sunlight necessary for the process of photosynthesis. This in turn interferes with the Oxygen transfer mechanism at air water interface which in turn interferes with marine life and self purification process of water. This effluent if allowed to flow in the fields' clogs the pores of the soil resulting in loss of soil productivity. If allowed to flow in drains and rivers it effects the quality of drinking water in hand pumps making it unfit for human consumption. It is important to remove these pollutants from the waste waters before their final disposal(Kant 2012)

A study was conducted to investigate the impact of textile dye on the early seedling stage of 3 crop s: barley, maize, and wheat. Seeds were imbibed in diff erent concentrations of textile dye for 12 h and were then grown in a controlled growth room for 8 days with a related dye solution. Some growth and polyphasic chlorophyll fluorescence parameters were measured and analysed to appraise the effect of textile dye on the 3 crops. Although different crop species showed differences in response to different concentrations, textile dye generally affected almost all radicle growth parameters more adversely than coleoptile growth parameters. (Nuran *et al*.,2012)

The effect of indigo dye effluent on the freshwater microalga Scenedesmus quadricauda ABU12 was investigated under controlled laboratory conditions. The microalga was exposed to different concentrations of the effluent obtained by diluting the dye effluent from 100 to 175 times in bold basal medium (BBM). The growth rate of the microalga decreased as indigo dye effluent concentration increased ($p<0.05$).The EC50 was found to be 166 dilution factor of the effluent. Chlorophyll a, cell density and dry weight production as biomarkers were negatively affected by high indigo dye effluent concentration, their levels were higher at low effluent concentrations ($p<0.05$)Changes in coenobia size significantly correlated with the dye effluent concentration. A shift from large to small coenobia with increasing indigo dye effluent concentration was obtained. We conclude that even at low concentrations; effluents from textile industrial processes that use indigo dye are capable of significantly reducing the growth and biomass production, in addition to altering the morphological characteristics of the freshwater microalga S. quadricauda. The systematic reduction in the number of cells per coenobium observed in this study further confirms that environmental stress affects coenobium structure in the genus Scenedesmus, which means it can be considered an important biomarker for toxicity testing (Mathias *et al*.,2013).

Adegoke and Bello,2015 demonstirated that low-cost adsorbents have outstanding removal capabilities for dyes and the optimal equilibrium time of various dyes with different charcoal adsorbents from agricultural residues is between 4 and 5 h. Maximum adsorptions of acidic dyes were obtained from the solutions with pH 8–10. The challenges and future prospects are discussed to provide a better framework for a safer and cleaner environment.

The effluent from textile is an important source of dye pollution. Many dyes and their breakdown products may be toxic for living organism. Methylene blue is a basic aniline dye with the molecular formula $C_{16}H_{18}N_3SCl$. At room temperature, it appears as a solid, odourless, dark green powder that yields a blue solution when dissolved in water. The dyeing industry effluents contain high BOD and COD value. Therefore, decolourisation of dyes is an important aspect of wastewater treatment before discharge. (Aswathy *et al*.,2016).

2.3TREATMENT OF TEXTILE DYE

The public demand for color-free waste discharge to receiving waters and tougher color standards have made decolorization of a variety of industrial wastes a top priority. Unfortunately, with the complicated color-causing compounds, the decolorization of these wastes is a difficult and challenging task. This article first describes the background information of dye molecules and dye waste characteristics. The methods for color measurements and standards are then discussed. Different techniques including almost all the known physical, chemical and biological techniques are described for decolorization. Each process alone may not be able to meet the requirements. A combination of these processes, for example, chemical-biological, biological-chemical, chemical-physical, chemical-chemical, etc. is often used. The formation of intermediates during the decolorization process is emphasized. These byproducts may be more toxic than the parent compounds. Thus, the extent of the mineralization in waste decolorization should be evaluated (Oliver *et al*.,2000).

The acid anthraquinone dye Tectilon Blue (TB4R) is a major coloured component from the aqueous effluent of a carpet printing plant in Northern Ireland. The aerobic biodegradation of TB4R has been investigated experimentally in batch systems, using three strains of bacteria, namely, Bacillus gordonae (NCIMB 12553), Bacillus benzeovorans (NCIMB 12555) and Pseudomonas putida (NCIMB 9776). All three strains successfully decolourised the dye, and results were correlated using Michaelis±Menten kinetic theory. A recalculation of the reaction rate constants, to account for biosorption, gave an accurate simulation of the colour removal over a 24-h period. Up to 19% of the decolorisation was found to be caused by biosorption of the dye onto the biomass, with the majority of the decolorisation caused by utilisation of the dye by the bacteria. The reaction rate was found to be intermediate between zero and first order at dye concentrations of 200±1000 mg/l (Walke and Weatherley 2000).

The adsorption of Congo Red by coir pith carbon was carried out by varying the parameters such as agitation time, dye concentration, adsorbent dose, pH and temperature. Equilibrium adsorption data followed both Langmuir and Freundlich isotherms. Adsorption followed second-order rate kinetics. The adsorption capacity was found to be 6.7 mg dye per g of the adsorbent. Acidic pH was favourable for the adsorption of Congo Red. Desorption studies suggest that chemisorption might be the major mode of adsorption (Namasivayam and Kavithal 2002).

Mane and Bhusari(2004) used banana and orange peel for removal of colour from waste effluent of textile industry. The colour removal capacity of banana peel was 87% and of orange peel was 68 % at normal pH and temperature conditions. The equilibrium time was 55min for orange peel and 45min for banana peel. The experimental adsorption data fitted with Langmuir and Freundlich adsorption isotherms.

The removal efficiency of activated carbon prepared from coir pith towards three highly used reactive dyes in textile industry was investigated. Batch experiments showed that the adsorption of dyes increased with an increase in contact time and carbon dose. Maximum decolourisation of all the dyes was observed at acidic pH. Adsorption of dyes was found to follow the Freundlich model. Kinetic studies indicated that the adsorption followed first order and the values of the Lagergren rate constants of the dyes were in the range of 1.77 · 102 –2.69 · 102 min1 . The column experiments using granular form of the carbon (obtained by agglomeration with polyvinyl acetate) showed that adsorption efficiency increased with an increase in bed depth and decrease of flow rate. The bed depth service time (BDST) analysis carried out for the dyes indicated a linear relationship between bed depth and service time. The exhausted carbon could be completely regenerated and put to repeated use by elution with 1.0 M NaOH. The coir pith activated carbon was not only effective in removal of colour but also significantly reduced COD levels of the textile wastewater (Santhy and Selvapathi,2006).

Treatment of textile wastewater was carried out by Sahunin *et al*.,(2006) at room temperature in a batch reactor by using the Photo-Fenton oxidation process. The effects of initial pH of the solution (pH = 1-7), ferrous ion concentration (0-100 mg×l-1) and UV power (0-120 W) on chemical oxygen demand (COD) and color removal were examined. The results showed that this process was enhanced at the acidic pH range. The optimum removal was found to be at pH = 3, 80 mg Fe2+×l-1, 5-10 minutes operating time, 60 W UV power and 200 mg H2 O2 ×l-1. At this condition, approximately 52% and 90% of COD and color were removed respectively. During the treatment process, a small amount of sludge (5.8×10-5 kg×kg COD-1) was generated. The presence of heterogeneous photocatalyst such as TiO2 in the system accelerated the removal percentage of COD and color.

Applicability of Fenton reagent in the treatment of textile dyeing wastewater was investigated by Perkowsi and Kos(2002). The optimum conditions and efficiency of the method were determined by taking three types of wastewater produced while dyeing cotton, polyacrylonitrile and polyester. The effect of the type and dose of coagulant was investigated. Two types of iron (II) salt were used: sulphate ($FeSO_4 \times 7 H_2O$) and chloride ($FeCl_2 \times 4 H_2O$); to adjust the pH of the wastewater, a 1% solution of calcium oxide (CaO) was used. The process of pollutant decomposition which took place in the wastewater under the influence of hydrogen peroxide alone at different concentrations was investigated. When the Fenton reagent was used both for sulphate and iron (II) chloride, the optimum doses of the two salts and hydrogen peroxide were determined. It was found that the tested dyeing wastewater revealed high susceptibility to treatment using a combined action of ferrous salts and hydrogen peroxide. The main parameters of wastewater, i.e. the colour threshold number, chemical oxygen demand and anionic surfactants, were reduced by dozens of percent. Investigations of the wastewater after treatment showed a remarkable increase in susceptibility to biodegradation.

The serum biochemical parameters viz. AST, ALT, urea, creatinine and bilirubin increased signifi cantly (5-97%), whereas an opposite trend was noted for cholesterol, glucose, total protein, albumin and globulin contents (8-53%). The alteration in values was more pronounced in the influent-treated animals. When wastewater-exposed animals were kept under control conditions (supplied with potable water) for a period of 45days, the effluent group recovered faster, attaining values of various investigated parameters similar to the controls. The present study has thus established the toxicity of both untreated and treated textile dye wastewater to the haemopoietic system of male albino rats(Ramesh *et al*.,2007).

Palm kernel fibre was investigated for its ability to perform as a suitable sorbent for anionic dye from aqueous solution (Ofomaja and Ho 2007). The effect of sorbent dose and temperature was investigated using a batch sorption technique. The results revealed the potential of palm kernel fibre, an agricultural waste, as a low-cost sorbent for the anionic dye examined. The isotherm data were closely fitted to the Langmuir equation and the dye sorption capacity of palm kernel fibre increased as the sorbent dose decreased. Maximum saturated monolayer sorption capacity of palm kernel fibre for 4-bromoaniline-azo-1,8-dihydronaphthalene-3,6-disodiumsulphate was 38.6 mg/g. Thermodynamic parameters such as change in the free energy, the enthalpy, and the entropy were also evaluated. In addition, relationships between sorbent dose and Langmuir constants were developed .

Experimental investigations were carried out by Meroufel *et al*.(2008) using available Algerian kaolin as alternative adsorbent for removal of toxic anionic dye namely Congo red from aqueous solutions. The effect of contact time, initial dye concentration, pH and temperature were experimentally studied in batch mode to evaluate the adsorption capacity, kinetic and equilibrium. Experimental results revealed that optimal adsorption took place at basic pH and high dye concentration. The dye uptake process obeyed the pseudo second order kinetic expression and was best described by the Langmuir isotherm. Thermodynamic studies showed congo red adsorption on Algerian kaolin was exothermic and spontaneous in nature. The results indicate that this local kaolin could be employed as low-cost alternative for removal of anionic dyes from industrial wastewater.

An adsorption process using cheap adsorbents could be described as a simple, selective and low cost alternative for the treatment of colored waste water compared to conventional physical and chemical processes. In this study the use of a natural waste adsorbent–ash was investigated for the removal of a textile vat dye Ostanthren blue GCD remaining after the dyeing of cotton textile. The ash obtained as a waste material during the burning of brown coal in the heating station of Leskovac (Serbia) was used for the treatment of waste waters from the textile industry, . The effect of ash quantity, initial dye concentration, pH and agitation time on adsorption was studied. The Langmuir model was used to describe the adsorption isotherm. Based on the analytical expression of the Langmuir model, the adsorption constants, such as adsorption capacity and adsorption energy, were found. Pseudo first and second order kinetic models were studied to evaluate the kinetic data(Smelcerovic *et al*.,2010)In this study, Baker's yeast strain (Saccharomyces cerevisiae) was evaluated for its ability to decolorize a synthetic dye aqueous solution and real industry effluent from Giza spinning and weaving company, Giza, Egypt. The removal of color from one of the azo dyes, ramazole blue (Vinyl sulfone), had been carried out by Baker's yeast using repeated-batch process. Factors such as solution pH, dye

Pooja *et al*., 2010 assessed the potential of using waste material of sugar cane industry for the color removal of textile waste water containing dyes This is easily available in our country and is economical than the adsorbents of other processes used for the treatment of wastewater. The parameters of the experiments include initial concentration of dye, adsorbent amount and adsorption time

The use of cheap and ecofriendly adsorbents as an alternative to activated carbon for removal of dyes from wastewater was studied by Velmurugan *et al.*,2011. Treated orange peel was used to adsorb methylene blue at varying dye concentration, adsorbent dosage, pH and contact time. Similar experiments were conducted with banana peel, neem leaves and commercially available powdered activated carbon. The adsorption capacity of orange peels decreased in the order of methyl orange > methylene blue > Rhodamine B > Congo red> methyl violet > amido black 10B Removal efficiency of all the adsorbents is quite effective, but orange peel found to be very effective compared to others adsorbent within for short period. The sorption data were then correlated with the freundlich and the langmuir adsorption isotherm models.Both isotherms exhibited a maximum K value which indicates that the orange peel has greater affinity for methylene blue. The maximum color removal efficiencies of orange peel at dosage of 1.0g for time duration of 45 min found to be 99% from an aqueous solution of 12.32 ppm.

Ramesh and Gandhimathi(2011) testet the possibility of using the spent tea dust and raw coir pith for the removal of methylene blue (MB) from aqueous solution. The effects of the contact time, adsorbent dosage and solution pH were studied in batch experiments at 27 °C. Results showed that a pH of 7 is favourable for the adsorption of dye. The isothermal data could be well described by the Langmuir equations. Kinetic parameters of adsorption such as the Langergen pseudo-first-order, pseudo-second-order rate constant and the intraparticle diffusion rate constant were determined. The adsorption capacities of Spent Tea Dust (STD) and Raw Coir Pith (RCP) were found to be 86.21 mg and 142.86 mg g-1 of the adsorbent respectively. The results indicate that STD and RCP could be employed as low-cost alternatives to commercial activated carbon for the removal of dyes from aqueous solution.

Farahani *et al.*,(2011) used activated carbon made of sugarcane bagasse, to eliminate cationic dyes present in waste water. Increase in the PH of the dye solution caused an equivalent increment in its adsorption efficiency. This study demonstrates that activated carbon made from sugarcane bagasse is an efficient and cheap adsorbent in either stirred tank reactors or in batch reactors. The data obtained could be utilised to design an optimally productive system that uses either stirred tank reactors or batch reactors for removeing cationic dyes from industrial effluents .

The cupuassu shell (Theobroma grandiflorum) which is a food residue was used in its natural form as biosorbent for the removal of C.I. Reactive Red 194 and C.I. Direct Blue 53 dyes from aqueous solutions. This biosorbent was characterized by infrared spectroscopy, scanning electron microscopy, and nitrogen adsorption/desorption curves. The effects of pH, biosorbent dosage and shaking time on biosorption capacities were studied. In acidic pH region (pH 2.0) the biosorption of the dyes were favorable. The contact time required to obtain the equilibrium was 8 and 18 h at 298 K, for Reactive Red 194 and Direct Blue 53, respectively. The Avrami fractionary-order kinetic model provided the best fit to experimental data compared with pseudo-first-order, pseudo-second-order and chemisorption kinetic adsorption models. The equilibrium data were fitted to Langmuir, Freundlich, Sips and RadkeePrausnitz isotherm models. For both dyes the equilibrium data were best fitted to the Sips isotherm model (Cardoso *et al*.,2011).

Systematic batch mode studies of adsorption of methylene blue (MB) on teak tree bark powder (TTBP) were carried out (Patel*et al*.,2011)TTBP was found to have excellent adsorption capacity. Freundlich, Langmuir and Temkin isotherm models were used to test the equilibrium data. The best fitting isotherm models was found to be Langmuir and Freundlich. The linear regression coefficient R 2 was used to elucidate the best fitting isotherm model (R 2 ≈ 0.99).The monolayer (maximum) adsorption capacity (qm) was found to be 333.333 mg g 1 for TTBP. The dimensionless separation factor (RL) values lie between 0.015 to 0.3289 indicated favourable adsorption. Lagergen pseudo –first order, Lagergen pseudo second order, Natrajan and Khalaf first order, Bhattacharya Venkobachar first order and Elovich kinetic models were tested for the kinetic study. Lagergen pseudo second order model best fits the kinetics of adsorption (R 2 = 1, qe(the) ≈ qe(exp)). Intra particle diffusion model showed boundary layer effect and larger intercepts indicates contribution of surface adsorption was high in rate controlling step. Adsorption was found to increase on increasing pH, increasing temperature and decreasing particle size. Thermodynamicanalysis showed negative values of ΔG indicating adsorption was favourable and spontaneous, positive values of ΔH indicating endothermic physical adsorption and positive values of ΔS indicating increased disorder and randomness at the solid solution interface of MB with the adsorbent TTBP.

The adsorption removal of a basic dyes, methylene blue (MB) and crystal violet (CV) on sugar can stalks were investigated using batch adsorption technique. Different variables such as solution pH, dye concentration and temperature were examined to optimize the methods. Removal of both dyes was observed to be most effective at higher pH. Freundlich and Langmuir isotherm models were applied to the equilibrium data. The results showed that Langmuir equation fits better than the Freundlich equation. It was observed that the sugar can stalks adsorbent showed higher adsorption capacity for CV (18.7 mg/g) than MB (9.8 mg/g). The studies show that sugar can stalks, a waste inexpensive material, can be an alternative to other expensive adsorbents used for dye removal in wastewater treatment(El-Sayed *et al*.,2011).

Dye wastes represent one of the most problematic groups of pollutants because they can be easily identified by the human eye and are not easily biodegradable. This literature review paper highlights and provides an overview of dye waste treatments performed over the three years period from 2008–2010. Noteworthy processes for the treatment of dye waste include biological treatment, catalytic oxidation, filtration, sorption process and combination treatments.(Ong *et al*.,2011)

Decolourisation of waste water has now become a major problem for the treatment plants in various industries. Many industries use synthetic dyes to colour their products such as textiles, rubber, paper, plastics, leather, cosmetic, food etc. Nearly 10-15% of synthetic textile dyes, used yearly are lost to waste streams and about 20% of these losses enter the environment through effluent from waste water treatment plant.(Sharma,*et al*.,2012)

Krishna and Prabh 2012.,investicated a total of 84 bacterial strains isolated from Kelambakkam Solar Salt Crystallizer ponds (or salterns) for their ability to produce extracellular tannase and laccase enzymes and eventually to decolorize three widely used textile dyes- Reactive Blue 81, Reactive Red 111 and Reactive Yellow 44. Of these 84 strains, 18 strains exhibited tannase activity and 36 strains showed positive laccase enzyme activity. The 11 bacterial strains that displayed both tannase and laccase enzyme activity were screened for their ability to decolorize the three textile azo dyes (100 mg/L). Out of 11 strains only 2 strains i.e., AMETH72 and AMETH77 showed best decolorization (%) in all the three dyes under static condition at room temperature. The dye degradation products analyzed by FTIR and UVVis techniques displayed complete disruption of azo linkages and biodegradation of dyes to simpler compounds. The treated dyes also improved growth and total chlorophyll content in Wheat and Green gram seedlings, as compared to the untreated dyes. This indicated the nontoxicity of the biologically degraded dye products. Thus the entire study concluded that halotolerant marine bacteria from the salterns can be effectively used to bioremediate the textile dyes.

Bioflocculant-producing bacteria were isolated from activated sludge of a wastewater treatment plant located in Durban, South Africa, and identified using standard biochemical tests as well as the analysis of their 16S rRNA gene sequences. The bioflocculants produced by these organisms were ethanol precipitated, purified using 2% (w/v) cetylpyridinium chloride solution and evaluated for removal of wastewater dyes under different pH, temperature and nutritional conditions. Bioflocculants from these indigenous bacteria were very effective for decolourizing the different dyes tested in this study, with a removal rate of up to 97.04%. The decolourization efficiency was largely influenced by the type of dye, pH, temperature, and flocculant concentration. A pH of 7 was found to be optimum for the removal of both whale and mediblue dyes, while the optimum pH for fawn and mixed dye removal was found to be between 9 and 10. Optimum temperature for whale and mediblue dye removal was 35 °C, and that for fawn and mixed dye varied between 40–45 °C and 35–40 °C, respectively. These bacterial bioflocculants may provide an economical and cleaner alternative to replace or supplement present treatment processes for the removal of dyes from wastewater effluents, since they are biodegradable and easily sustainable(Simphiwe *et al*.,2012).

Numerous techniques were used in the recent past for decolourisation of dyes. Among them adsorption technique has got maximum potential for the removal of dyes. Adsorption being a physical process is in-expensive and less time consuming. From the survey of about 80-85 research papers, it was concluded that low cost adsorbents obtained from agricultural waste products were found to have outstanding removal capabilities. both raw and chemically modified agricultural products were found suitable in the decolourisation of synthetic dyes.(Sharma,*et al*.,2012)

A novel orange peel adsorbent developed by Lgarshi-Mafra and Zuim(2013) from an agricultural waste material was characterised and utilised for the removal of Remazol Brilliant Blue from an artificial textile-dye effluent. The adsorption thermodynamics of this dye-adsorbent pair was studied in a series of equilibrium experiments. The time to reach equilibrium was 15 h for the concentration range of 30 mg L-1 to 250 mg L-1. The adsorption capacity decreased with increasing temperature, from 9.7 mg L-1 at 20 °C to 5.0 mg L-1 at 60 °C. Both the Langmuir and Freundlich isotherm models fitted the adsorption data quite reasonably. The thermodynamic analysis of dye adsorption onto the orange peel adsorbent indicated its endothermic and spontaneous nature. Thus, the application of orange peel adsorbent for the removal of dye from a synthetic textile effluent was successfully demonstrated.

The textile dyeing industry consumes large quantities of water and produces large volumes of wastewater from different processes in dyeing and finishing processes. The low-cost, easily available naturally prepared coagulants like Surjana seed powder (SSP), Maize seed powder (MSP) and Chitosan as ideal alternatives to recent expensive coagulants for Congo Red (CR) dye removal has been investigated. Various process parameters like pH, coagulant dose, flocculation time and temperature and also its optimization were exploited. The maximum percentage CR removal was found to be 98.0, 94.5 and 89.4 for SSP, Chitosan and MSP, respectively, at pH 4.0, coagulant dose of 25 mg/l, flocculation time 60 min and temperature of 340 K. The Sludge Volume Index (SVI) and turbidity were calculated for these parameters including process optimization. SSP found more preferable for CR removal and Chitosan was a better coagulant, which corresponds to SVI than the other coagulants investigated(Patel and Vashi 2012).

Khatod(2013) studied the adsorption of methylene blue dye using low cost adsorbent like neem leaf and orange peel powder. Liquid phase adsorption experiments were conducted. Batch adsorption studies were carried out by observing the effect of experimental parameters, namely amount of adsorbents, dye concentration and contact time. Spectrophotometric technique was used for the measurement of concentration of dye before and after adsorption. The removal data were fitted on Langmuir adsorption equations.

The adsorption of textile dyes such as Direct Red 75 and Direct Red 80 onto calcined bone was studied for their removal from aqueous solutions. The adsorption of Direct Red 75 and

Direct Red 80 occurred by studying the effects of adsorbent amount, dye concentration, contact time, pH media and temperature. The adsorption rate data were analyzed using the intraparticle diffusion model, pseudo first order and the pseudo second order kinetic models to determine adsorption rate constants. The isotherms of adsorption data were analyzed by various adsorption isotherm models such as Langmuir, Freundlich and Tempkin.From the results it was concluded that calcined bone could be effectively employed as an effective new low cost adsorbent for the removal of textile dyes from aqueous solutions.(Mohammadine *et al*.,2013)

A novel orange peel adsorbent developed from an agricultural waste material was characterised and utilised for the removal of Remazol Brilliant Blue from an artificial textile-dye effluent. The adsorption thermodynamics of this dye-adsorbent pair was studied in a series of equilibrium experiments. The time to reach equilibrium was 15 h for the concentration range of 30 mg L-1 to 250 mg L-1. The adsorption capacity decreased with increasing temperature, from 9.7 mg L-1 at 20 °C to 5.0 mg L-1 at 60 °C. Both the Langmuir and Freundlich isotherm models fitted the adsorption data quite reasonably. The thermodynamic analysis of dye adsorption onto the orange peel adsorbent indicated its endothermic and spontaneous nature(Mafra *et al*.,2013).

An attempt was made by Kananan *et al*., 2013 to examine the potential of newly isolated Pseudomonas putida for decolorization of azo dye- Remazol Black B in batch reactor. The influence of different concentration of glucose, pH and temperature on decolorization was studied to find the optimum conditions required for maximum decolorization and degradation. pH 7.0 and 35 0C were considered to be the optimum decolorizing conditions .5g/L glucose present in media showed the maximum decolorization. This new isolate grew well in a high concentration of dye (300mg L -1) and decolorized 97.12% within 48 h and also tolerated upto 1000mg/L of dye. Colorless cells of P. putida and UV Visible spectroscopic analyses suggested that the decolorizing activity was only through biodegradation and not by inactive surface adsorption. The above results showed the potential of this bacterial strain in the biological treatment of textile effluent under optimum conditions.

Coagulation is an important wastewater treatment process used to reduce water turbidity and normally precedes the more complex secondary and tertiary water treatment processes.The effectiveness of a natural coagulant derived from a cactus species for turbidity removal from dye industry effluent was studied were also studied. The amount of cactus added was well correlated with final turbidity of the water and high turbidity removal determined in this study indicates that cactus (opuntia) has the potential for waste water treatment applications(Kannadasan *et al*.,2013).

Two salt-tolerant plants (Medicago sativa L. and Sesbania cannabina Pers) as well as a kind of salt-tolerant azo-dye decolorization bacteria GTY (Gracilibacillus sp.GTY) were selected to treat acid red B or acid scarlet GR contaminated water. Results showed that Medicago sativa L. was more tolerant to the azo dyes and more helpful in promoting the azo-dye wastewater bio-decoloration than Sesbania cannabina Pers, but GTY density was higher in the root exudates of Sesbania cannabina Pers than that of Medicago sativa L. This indicated that the increase of GTY density only partially presented the azo-dye decolorization promoted by plants (Zhoua and Xianga., 2013).

Application of saw dust for the removal of an anionic dye, tartrazine, from aqueous solutions has been investigated by Banerjee and Chattopadhyaya(2013). The experiments were carried out in batch mode. Effect of the parameters such as pH, initial dye concentration and temperature on the removal of the dye was studied. Equilibrium was achieved in 70 min. Maximum adsorption of dye was achieved at pH 3. Removal percent was found to be dependent on the initial concentration of dye solution, and maximum removal was found to be 97% at 1 mg/L of tartrazine. The removal increases from 71% to 97% when the initial concentration of dye solution decreases from 15 mg/L to 1 mg/L. The equilibrium adsorption data were analyzed by Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models. The (Langmuir) adsorption capacity of the adsorbent is found to be 4.71 mg/g at 318 K. Kinetic modeling of the process of removal was carried out and the process of removal was found to follow a pseudo second order model and the value of rate constant for adsorption process was calculated as 2.7 · 103 g mg1 min1 at 318 K. The thermodynamic parameters such as change in free energy (DG), enthalpy (DH) and entropy (DS) were determined and the negative values of DG indicated that the process of removal was spontaneous at all values of temperatures. Further, the values of DH indicated the endothermic nature of the process of removal.

The microalgae biomass production from textile waste effluent is a possible solution for the treatment of effluent .The potential application of Chlorella vulgaris for bioremediation of textile waste effluent (WE) was investigated using 22 Central Composite Design (CCD). This work addresses the adaptation of the microalgae C. vulgaris in textile waste effluent (WE) and the study of the best dilution of the WE for maximum biomass production and for the removal of colour and Chemical Oxygen Demand (COD) by this microalga. The cultivation of C. vulgaris, presented maximum cellular concentrations Cmax and maximum specific growth rates lmax in the wastewater concentration of 5.0% and 17.5%, respectively. The highest colour and COD removals occurred with 17.5% of textile waste effluent. The results of C. vulgaris culture in the textile waste effluent demonstrated the possibility of using this microalga for the colour and COD removal and for biomass production. There was a significant negative relationship between textile waste effluent concentration and Cmax at 0.05 level of signifi- cance. However, sodium bicarbonate concentration did not significantly influence the responses of Cmax and the removal of colour and COD (El-kassas and Mohamed 2014).

Adsorption of Congo red (CR) from aqueous solution using dried roots of Eichhornia crassipes were studied (Wanyonyi and Shiundu 2014). Batch experiments were carried out for sorption kinetics and isotherms. Experimental results obtained showed that adsorption process was highly dependent on contact time, adsorbent dosage, initial dye concentration and particle size. The sorption equilibrium for Congo red dye by E. crassipes (roots) was reached within 90 minutes and adsorption efficiency of up to 96% was achieved. The sorption kinetics followed a pseudo-second-order kinetic model while Freundlich isotherm model was best applicable for obtaining the equilibrium parameters. These results demonstrate that roots of E. crassipes are effective, environmentally friendly and low-cost biomaterial for dye removal from aqueous dye solutions and industrial effluents.

Kabbouta and Taha(2014)studied the ability of biosorption of methylene blue (MB) by Aspergillus fumigatus and optimize the conditions for better absorption. Biosorption reaches 68% at 120 min. Similarly, the biosorbed amount increases up to 65% with pH increase from 4 to 6, and around 90% for pH from 7 to 13. At ambient temperature 20-22o C, the percentage of biosorption of methylene blue was optimal. The kinetic of biosorption is directly related to the surface of biosorbent when the particle size is also an important factor affecting the ability of biosorption. Also the biosorption of methylene blue increases with the dose of biosorbent due to an augmentation of the adsorption surface.

Adsorption of Congo red (CR) from aqueous solution using dried roots of Eichhornia crassipes was studied by Wanyoni and shiundu(2014). Batch experiments were carried out for sorption kinetics and isotherms. Experimental results obtained showed that adsorption process was highly dependent on contact time, adsorbent dosage, initial dye concentration and particle size. The sorption equilibrium was reached within 90 minutes and adsorption efficiency of 96% was achieved. The sorption kinetics followed a pseudo-second-order kinetic model while Freundlich isotherm model was best applicable for obtaining the equilibrium parameters.

In the study, a variety of physical adsorbents (Bio-sorbents) were chosen for the decolorization assessment of five most commonly used dyes viz. Methyl Red, Methyl Orange, Crystal Violet, Erichrome Black and Malachite Green. All these physical adsorbents were dried, powdered and heat- activated before using them as active Bio-sorbents. Among the physical adsorbents chosen, seeds of Nigella sativa displayed the maximum decolorization percentage against Methyl Orange and Methyl Red dyes i.e. 85% and 83% respectively followed by the results on Moringa oleifera (seeds) that too against Methyl Orange and Methyl Red dyes i.e. 80% and 78% respectively. Seeds of Carica papaya ,Tamarindus and Azadirachta indica displayed a mediocre behaviour against all dyes tested. Least results were obtained for coconut shell and orange peels. The most accessible dyes for decolorization were Methyl Orange and Methyl Red and the least accessible dye for decolorization was Malachite Green. Powdered Activated Carbon (PAC) was also taken against each dye for comparison. Seeds of Nigella sativa displayed better results than powdered Activated Carbon (PAC) against each dye tested. (Bari and Bharthwaj,2014)

Effluents containing azo dyes resist many types of treatments due to their molecular complexity. Therefore, alternative treatments, such as biosorption and biodegradation, have been widely studied .The aim of the present study was to evaluate biosorption and biodegradation of the azo dye Procion Red MX-5B in solutions with the filamentous fungi Aspergillus niger and Aspergillus terreus. Decolorization tests were performed, followed by acute toxicity tests using Lactuca sativa seeds and Artemia salina larvae. UV–Vis and FTIR spectroscopy revealed molecular degradation and the formation of secondary metabolites, such as primary and secondary amines. The biodegradation of the dye molecules was evaluated after 24, 240 and 336 h of treatment. The fungal biomass demonstrated considerable affinity for Procion Red MX-5B, achieving approximately 100% decolorization of the solutions by the end of treatment. However, the solutions resulting from this treatment exhibited a signifi- cant increase in toxicity, inhibiting the growth of L. sativa seeds by 43% and leading to a 100% mortality rate among the A. salina larvae. Based on the present findings, biodegradation was effective in the decolorization of the samples, but generated toxic metabolites, while biosorption was effective in both decolorization and reducing the toxicity of the solutions(Almeida and Corso 2014).

Silvana *et al*.,2014 analysed the problem of environmental protection against waste waters generated by textile industry. The methods of pre-treatment of textile waste can be: Primary (screening, sedimentation, homogenization, neutralization, mechanical flocculation, chemical coagulation), Secondary (aerobic and anaerobic treatment, aerated lagoons, activated sludge process, trickling filtration, oxidation ditch and pond) and Tertiary (membrane technologies, adsorption, oxidation technique, electrolytic precipitation and foam fractionation, electrochemical processes, ion exchange method, photo catalytic degradation, thermal evaporation). The selection of the purification method depends on the composition and type of waste waters.

The removal of methylene blue (MB) dye from aqueous solution. Batch adsorption study was carried out with parameters like pH, adsorbent dose, initial dye concentration and time. The response surface methodology (RSM) was applied to design the experiments, model the process and optimize the parameters. The experimental values were in good agreement with the model predicted values. The optimum values of pH, adsorbent dose, initial dye concentration and time are found to be 10, 2.1846 g/L, 50 mg/L and 63 min for complete removal of MB dye respectively. (Subramaniam and Ponnusamy,2015)

Industries engaged in dyeing operation generate coloured effluent due to the presence of spent dyes. Adsorption is among the various treatment processes employed for removal of dyes from effluents. Activated carbon is mostly used as an adsorbent in the treatment process. Attempts have been made by researchers to use non-conventional, low-cost, naturally-occurring biomass as ad sorbents, including fruit peals, seeds, leaves, bark, sawdust, straw, ash, sludge and others that are abundantly available. The literature indicates that the dye adsorption capacities of these non-conventional biomasses largely depend on the methods of processing and the types of dyes(Kharat 2015).

Batch adsorption experiments using Ashoka leaf powder, a low cost, locally available biomaterial as an adsorbent has been used for removal of cationic dyes such as Methylene blue, Malachite Green, Rhodamine B and Brilliant Green from effluent of textile industry(Kaur and Sharma 2015).

Dyes are an important class of pollutants, and can even be identified by the human eye. Among the various treatment technologies, adsorption occupies a prominent place in dye removal. Adsorption techniques are widely used to remove certain classes of pollutants from waters, especially those that are not easily biodegradable. There have been attempts by researchers to explore the adsorption potential of non-conventional, naturally-occurring agricultural residues in dye removal from effluents. In India alone more than 400 million tonnes of agricultural residue is generated annually, which includes rice husk, bagasse, stalk, coir pith etc. Exploring application of the agricultural residues for use as adsorbents can provide suitable alternatives for the removal of spent dyes from industrial effluents. Dyes represent one of the problematic groups. Currently, a combination of biological treatment and adsorption on activated carbon is becoming more common for removal of dyes from wastewater. Although commercial activated carbon is a preferred sorbent for color removal, its widespread use is restricted due to high cost (Upadhye and Yamgar 2016).

Decolorization of dyes by free and immobilized Desmodesmus sp. was tested by monitoring the decrease in absorbance of each dye under different culture condition such as incubation time and dye concentrations. The results showed that the maximum decolorization of both dyes with immobilized algae after 6 days at 20 mg.L-1 of dye concentration was 98.6%. The results showed better decolorization ability of immobilized Desmodesmus sp. against the dyes compared with free one. The analysis of the results showed that different factors affected decolorization ability(Abdullah *et al*.,2016).

Fatihaa and Belkacem(2016) used natural clay as an adsorbent for the removal of methylene blue from an aqueous solution. The influence of the initial dye concentration, contact time, pH temperature, and dosage of biosorbent was investigated in batch experiments. The clay was characterized using scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX).

Dyes from the industrial waste water are effectively separated by using activated carbon as adsorbent however its cost restricts the use in large scale applications. Experimental studies proved that the effective removal of dyes is obtained using several cheaply available non-conventional adsorbents also. Therefore, studies related to searching for efficient and low cost adsorbents derived from existing resources are gaining importance for the removal of dyes (Kandisa *et al*., 2016)

The efficiency of electrocoagulation to treat reactive blue 19 dye effluent was investigated, using a recycle batch reactor with aluminium electrodes. A new cell arrangement was suggested where the anode consisted of an array of horizontal aluminium cylinders embedded between an upper and a lower aluminium screen cathode. Different operating parameters, affecting the efficiency of color and COD removal, such as current density, flow rate, initial dye concentration, electrolyte concentration and pH were studied. Increasing the current density and the electrolyte concentration increased the color and COD removal. Inversely, a higher flow rate and a higher initial dye concentration decreased the removal rate. The pH of the waste needed to be neutral or nearly neutral to accomplish a high efficiency. A color removal of 97.4% and COD removal of 93% were achieved under optimum operating conditions. Electrical energy consmption ranged from 1.08 to 33.4 kWh/kg dye removed depending on the operating conditions(Ashtoukhy et.al.,2016)

Adsorption of methylene blue from aqueous solution onto coconut coir dust (CCD) a agricultural in a batch process was investigated by a etim et.al.,. Adsorption was studied as a function of amount of adsorbent, pH and concentration with time. It was found that percentage adsorption varied linearly with the amount of adsorbent and concentration with time but varies non-linearly with pH. Adsorption equilibrium data were represented by isotherm, kinetics and thermodynamics models. Three isotherm models namely Langmuir, Freundlich and Temkin were tested and adsorption was found to fit well into these models with R2 P 0.90. The kinetic data were well described by the pseudo-second order kinetic model. The adsorption process was endothermic with a mean change in enthalpy (DH) (+17.87 KJ mol1) and spontaneous with a mean free energy change (DG) (9.69 KJ mol1). FTIR analyses of the adsorbent suggest that adsorption of the dye was through a chemical interaction of the functional groups on the surface of the adsorbent. (Etim *et al*.,2016)

The sugar cane bagasse (SB), carbonaceous bagasse treated with formaldehyde and sulfuric acid (C-SB) and fly ash bagasse (FA-SB) were tested as adsorbents for the removal of malachite green (MG) dye from aqueous solutions. The removal of dye was carried out by the adsorption process under the optimized conditions of concentration of dye, amount of adsorbent, temperature and contact time. The spectrophotometric technique was adopted for the estimation of concentration of dye before and after the adsorption. The equilibrium data were applied on Langmuir, Freundlich and Dubinin–Radushkevich isotherm models and the values of their corresponding constants were evaluated from the slopes and intercepts of their respective plots. The isotherm data can be best described by the Langmuir equation in the concentration range of 1×10^{-5}–1×10^{-4} M. From the results it was observed that C-SB shows better adsorption capacity as compared to other adsorbents due to increase in the surface area of adsorbent by the chemical treatment. Thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ were also evaluated. The values of $\Delta G°$ show spontaneous behavior of the system. The modified bagasse C-SB shows about 89% removal, due to the formation of new modified surface and enhancement in its surface area. It could be employed as a low-cost alternative method for the removal of dyes and purification of textile effluents. Hajiratahir *et al*,.(2016),

The study describes the synthesis of modified immobilized activated alumina (MIAA) and its application for the removal of textile dye from aqueous media. Immobilization was carried out by using the sol–gel method while modifications were made during the synthesis by adding powder activated alumina. Batch adsorption experiments were carried out at 20 ± 1 C to see the effect of different parameters like contact time, stirring rate, initial concentration of the dye and dose of MIAA. The removal of Cibacron reactive yellow dye with an initial concentration of 400 mg/L was greater than 90% for 90 min contact time. MIAA can be regenerated thermally and chemically and the dye removal efficiency remained above 85% during the first 4 regeneration cycles. Thermal regeneration was achieved in a muffle furnace at 450 C while chemical regeneration was done by immersing MIAA in 0.1 M NaOH solution for 2 h. MIAA also proved effective for the adsorption of dyes from actual textile wastewater giving a removal efficiency of 75%.(Wasti and Awan, 2016)

Water resources are increasingly getting contaminated day by day due to the ignorance lent to the wastewater management.Most of the textile dyes or effluents are a major reason for the pollution of water resources.Although many methods are adopted to treat these textile effluents,but there is a dire need to come up with an eco-friendly,cost effective method for the removal of contaminants from the effluents. Recent researches have shown that plant biomass can be used for this purpose. Different plant parts can be put to use for the removal of textile dyes from wastewater and make the water cleaner for various uses.This is an economical and environment friendly alternative to various other methods that use large amount of chemicals to treat waste water.Different plants like water hyacinth,nirgudi plant,hydrilla verticillata,sunflowers,etc have been researched upon for the adsorption of textile dyes from textile wastewater(Sharma *et al*.,2016).

Availability, pollution and treatment of water are of major concern of present time. Many micro-organisms are used for wastewater treatment. In the present study, feasibility of decolorization of dye contaminated effluents collected from different textile industries was examined using Aspergillus tamarii and Aspergillus flavus in batch and continuous reactor. Aspergillus flavus was found to be more efficient than Aspergillus tamarii to decolorize the effluents. Maximum decolorization of 85.3% was observed at optimized pH with 50% diluted effluent sample (ES1) using Aspergillus flavus (pH 4.5) as compared to 82.2% obtained using Aspergillus tamarii (pH 5). Chemical oxygen demand (COD) reduction has been observed to be 75% after decolorization of ES1 using Aspergillus flavus. Scanning Electron Microscopy (SEM) and Gas chromatography–mass spectrometry (GC-MS) analyses strongly supported biosorption as well as biodegradation of dye during decolorization (Deepika *et al*., 2016).

Waste water is a major environmental impediment for the growth of the textile industry besides the other minor issues like solid waste and resource waste management. Textile industry uses many kinds of synthetic dyes and discharge large amounts of highly colored wastewater as the uptake of these dyes by fabrics is very poor. This highly colored textile wastewater severely affects photosynthetic function in plant. It also has an impact on aquatic life due to low light penetration and oxygen consumption. It may also be lethal to certain forms of marine life due to the occurrence of component metals and chlorine present in the synthetic dyes. So, this textile wastewater must be treated before their discharge. In this article, different treatment methods to treat the textile wastewater have been presented along with cost per unit volume of treated water. Treatment methods discussed in this paper involve oxidation methods (cavitation, photocatalytic oxidation, ozone, H2O2, fentons process), physical methods (adsorption and filtration), biological methods (fungi, algae, bacteria, microbial fuel cell). This review article will also recommend the possible remedial measures to treat different types of effluent generated from each textile operation (Chandrakan *et al*., 2016)

The ability of the bacterial strain Acidithiobacillus thiooxidans to remove sulfur blue 15 (SB15) dye from water samples was examined by Nguyen et.al.,2016. This bacterium could not only oxidize sulfur compounds to sulfuric acid but also promote the attachment of the cells to the surface of sulfidic particles, therefore serving as an efficient biosorbent. The biosorption isotherms were better described by the Langmuir equation than by the Freundlich or Dubinin-Radushkevich equation. Also, the biosorption process followed the pseudosecond-order kinetics. At pH 8.3 and SB15 concentrations up to 2000 mg L1 in the biomass/mineral salt solution, the dye removal and decolorization were 87.5% and 91.4%, respectively, following the biosorption process. Biodegradation was proposed as a subsequent process for the remaining dye (250 e350 mg L1). A central composite design was used to analyze independent variables in the response surface methodology study. Under the optimal conditions (i.e., initial dye concentration of 300 mg L1 , initial biomass concentration of 1.0 g L1 , initial pH of 11.7, and yeast extract dose of 60 mg L1), up to 50% of SB15 was removed after 4 days of biodegradation.

Use of various dyes in order to color the products is a common practice in textile industry. The presence of these dyes in water even at low concentration is highly visible and undesirable. The adsorption process is being extensively used for the removal of dyes from dye house effluents by various researchers. The most widely used adsorbent is commercially available activated carbon. Despite the frequent use of adsorption in wastewater treatment systems, commercially available activated carbon remains an expensive material. In recent years, the safe and economical methods are required for the treatment of dye house effluents, whichinvolved researchers to focus towards the preparation of low cost adsorbents from cheapest sources. This study was carried out for the utilization of orange peel as adsorbent for the removal of dyes from wastewater and to establish it as a standard wastewater treatment process for textile dyeing industry. The experiment showed that the removal percentage was 88.04 at a pH of 10,dosage of 2.5g/L, retention time of 120 minutes and RPM of 90(Popuri *et al*.,2016).

Low-cost by-products from agricultural, household and industrial sectors have been recognized as a sustainable solution for wastewater treatment. Low-cost sorbents have been divided into the following five groups: (i) Agricultural and household wastes, (ii) industrial by-products, (iii) sludge, (iv) sea materials, (v) soil and ore materials and (vi) novel low-cost adsorbents. In order to highlight the affinity of sorbents for pollutants (dyes, heavy metals, biorecalcitrant compounds, nitrogen and phosphate compounds), simple methodological tools such as "adsorbents-pollutants" matrices have been proposed and applied and the adsorbent candidates for replacing commercial activated carbons have been identified. (Gisi *et al*.,2016)

The study by kamarajand umamaheswari(2017)describes the preparation of low-cost and eco-friendly groundnut shell activated carbon (GSAC) by combined physical- and chemical activation in a laboratory-scale facility. The fluorescent emission scanning electron microscope analysis exhibited well-defined pore formation and the energy dispersive X-ray analysis showed elemental composition of GSAC which is essential for the strong adsorption of the dye molecule. This study significantly emphasizes that GSAC would be the effective adsorbent to remove Methylene blue dye from aqueous solution.Utilization of groundnut shells serves dual purpose of simultaneous waste eradication, as well as cost-effective pollution treatment

Activated carbon prepared from groundnut shells (GSAC) by sulphuric acid treatment was coated with Fe3O4(GSAC- Fe3O4) and tested for its efficiency as an adsorbent for the removal of methylene blue (MB) dye from aqueous solution. The structural morphology and functional groups present were investigated using scanning electron microscope (SEM) and Fourier transform infrared (FTIR) spectroscopy. Various sorption parameters such as effect of pH, contact time, initial dye concentration and adsorbent dosage were studied. The percentage removal of methylene blue increased with decrease in initial methylene blue concentration and increased with increase in contact time and dose of the adsorbent. Equilibrium data were analysed using Langmuir and Freundlich isotherm models. Kinetic data were studied using pseudo-first order and pseudo-second order kinetic models.(Imam and Abdullahi 2017)

Application of saw dust for the removal of an anionic dye, tartrazine, from aqueous solutions has been investigated by Banerjee and Chattopadhyaya, 2017 . The experiments were carried out in batch mode. Effect of the parameters such as pH, initial dye concentration and temperature on the removal of the dye was studied. Equilibrium was achieved in 70 min. Maximum adsorption of dye was achieved at pH 3. Removal percent was found to be dependent on the initial concentration of dye solution, and maximum removal was found to be 97% at 1 mg/L of tartrazine. The removal increases from 71% to 97% when the initial concentration of dye solution decreases from 15 mg/L to 1 mg/L. The equilibrium adsorption data were analyzed by Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models.The thermodynamic parameters such as change in free energy (DG), enthalpy (DH) and entropy (DS) were determined and the negative values of DG indicated that the process of removal was spontaneous at all values of temperatures. Further, the values of DH indicated the endothermic nature of the process of removal.

A report on the impact of different parameters of current density, anode type, temperature, pH, and electrolyte concentration on the removal of Reactive Red 120 in synthesized wastewater through electrocoagulation using solar energy for the purpose of improving economic efficiency of the process was made by Pirkarami and Olya(2017) Current density of 45 Am2 proved to be optimum level for dye removal. Other optimum alternatives were iron anode, a temperature level of 25 C, a pH of 7, and an electrolyte concentration of 15 mg L1 . The characterization of the post-treatment product using GC–MS studies revealed intermediate compounds. Cost analysis was also performed for the treatment process. Further, the obtained optimum conditions were applied to the treatment of six samples of real textile effluent. Electrocoagulation was satisfactory in only four of the cases. Lastly, efficiency of treating the real samples was evaluated by subjecting the experimental electrodes to the SEM technique.

The preparation of activated carbon from coconut husk with H_2SO_4 activation (CSAC) and its ability to remove textile dyes (maxilon blue GRL, and direct yellow DY 12), from aqueous solutions were reported (Aljeboree *et al.*,2017) Result showed that the adsorption of both GRL and DY 12 dyes was favorable at acidic pH. The adsorption uptake was found to increase with increase in initial dye concentration, and contact time but decreases with the amount of adsorbent, particle size, and temperature of the system. The chemisorption, intra-particle diffuse, pseudo-first-order and pseudo-second-order kinetic models were applied to test the experimental data. The pseudo-second order exhibited the best fit for the kinetic studies, which indicates that adsorption of (GRL, and DY 12) is limited by chemisorption process. The equilibrium data were evaluated using Langmuir, Freundlich, Temkin and Fritz–Schlunder isotherms. The Fritz–Schlunder model best describes the uptake of (GRL and DY 12) dye, which implies that the adsorption of textiles dyes in this study onto coconut husk activated carbon is heterogeneous with multi-layers. Thermodynamic parameters such as Gibbs free energy, enthalpy and entropy were determined. It was found that (GRL and DY 12) dye adsorption was spontaneous and endothermic.

The photochemical decolorization of two dyes, namely Acid Yellow 54 and Basic Blue 9, was studied using the UV/ H2 O2 and UV/Fenton processes. The effects of the amount of H2 O2 and FeSO4 as well as the initial pH solution on decolorization kinetics of both the dyes were investigated(Baffoun *et al*., 2017). The pseudo-first order kinetic model was applied to predict the decolorization of the selected dyes at the different operational conditions and results showed that this model fitted very well with the experimental data. The obtained results also showed the efficiency of UV/Fenton process to quickly degrade aqueous effluents polluted by Acid Yellow 54 and Basic Blue 9 compared to the UV/ H2 O2 process.

3. MATERIALS AND METHODS

Present investication on ‘Groundnut shell as an adsorbent for the removal of textile dye from aqueous solution’ was conducted to asses its decolourization potential for acid violet dye.

3.1.PREPARATION OF GROUNDNUT SHELL POWDER

Groundnut shell (Fig.1)was collected from the local market and washed in tap water to remove soil particles. It was sun dried to remove moisture content, crushed well and ground in to a fine powder in an electric mixture cum grinder. The powder was sifted to get particles of uniform size (Fig.2) and stored for use in the study.

3.2.PREPARATION OF DYE SOLUTION

Acid violet dye was purchased from a local distributer. 100mg of the dye was dissolved in 100ml of distilled water. Each 1ml contained 1mg of the dye. The required concentrations of dye solution (1-10mg)were prepared from the above stock solution.

3.3.DYE ADSORBTION STUDIES

Batch experiments were conducted to get optimum conditions for dye removal namely optimum dye concentration, pH, temperature and adsorbent dose. Fixed amounts of adsorbent(100mg-1.0g)were added to dye solution of varying concentrations (1mg-10mg)and maintained at different temperatures(10-60^0 C)and pH(1-10)for time periods from 24 -90 hours(Fig.3).For adjusting the pH of dye solution diluted NaOH and HCL were used. At the end of each experiment the absorbance of the dye solution was read in a colorimeter at 420nm to estimate final dye concentration. Initial absorbance of each dye solution was also read in the colorimeter and % decolourization was calculated as follows.

$$\%\ \text{decolourization} = \frac{\text{Initial absorbance of dye} - \text{final absorbance of dye}}{\text{Initial absorbance of dye}} \times 100$$

All experiment were conducted thrice for each parameter to get average values for calculation

3.4.CHARACTERIZATION OF GROUNDNUT SHELL

The structural characterization of groundnut shell was done by FTIR analysis and dye decolurization by adsorbent by UV-vis spectral analysis.

3.4.1UV-vis SPECTRAL ANALYSIS

Dye decolourization by the adsorbent was evaluated by subjecting the dye solution before and after adsorbtion to spectral analysis in the UV and visual region

3.4.2FT-IR ANALYSIS (FOURIER TRANSFORMATION INFRARED SPECTROSCOPY)

FT-IR analysis was done in the spectral range of 4000-500cm^{-1} to study the functional groups available on the absorbent surface for adsorbtion.

Fig.1. GROUNDNUT SHELL

Fig.2.GROUNDNUT SHELL

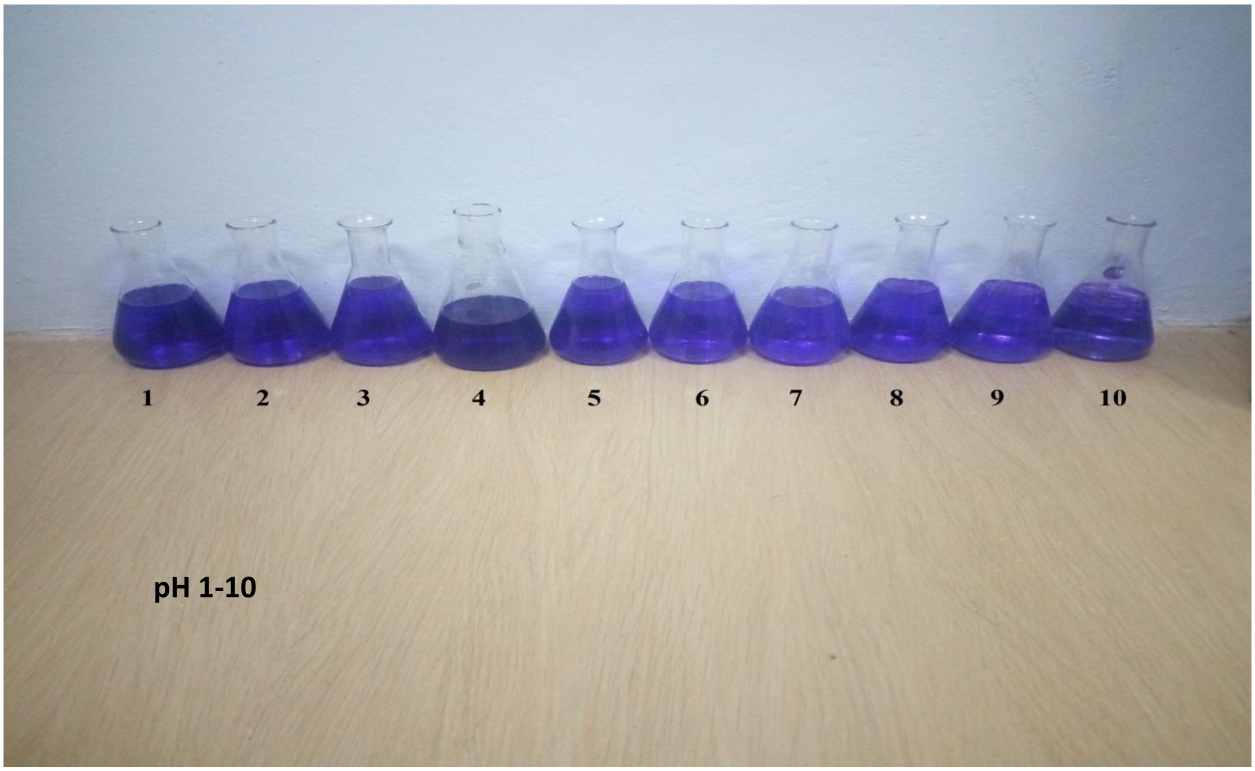

Fig.3.EXPERIMENTAL SET UP TO STUDY THE EFFECT OF pH

4. RESULT AND DISCUSSION

Every industrial process is characterized by the use of inputs asraw materials, water and energy that undergo transformation giving rise to products, byproducts and waste. The wastes produced at all stages of the various types of human activity, both in terms of composition and volume, vary according to the consumption practices and production methods. The main concerns are focused on the impact that these can have on human health and the environment. Hazardous waste, produced mainly by industry, is particularly worrying, because when incorrectly managed, it becomes a serious threat to the environment and human health Thus the study of new alternatives for the treatment of different types of industrial effluent continues to be a challenge to combat anthropogenic contamination.(Chequer *et.al.,*2013).

Dyes are an important class of synthetic organic compounds used in many industries, especially textiles. Consequently, they have become common industrial environmental pollutants during their synthesis and later during fiber dyeing. Textile industries are facing a challenge in the field of quality and productivity due to the globalization of the world market. The large-scale production and extensive application of synthetic dyes cause considerable environmental pollution, making it a serious public concern. Legislation on the limits of colour discharge has become increasingly rigid. There is a considerable urgent need to develop treatment methods that are effective in eliminating dyes from their waste. Physicochemical and biological methods have been studied and applied.Some industrial-scale wastewater treatment systems are now available; however, these are neither fully effective for complete colour removal nor do they address water recycling(Pereira and alves 2012)

Adsorption-based water treatment process is very popular for dye-house wastewater treatment. Among many decolorization procedures, the adsorption technique gives good results because it can be used for the removal of various types of colored matter. Commercial systems use mostly activated carbon as the sorbent for decolorization of waste waters because of its excellent absorption ability. Although activated carbon has an advantage as a sorbent, its massive employment is restricted due to its high price. To reduce the treatment costs, cheap alternative adsorbents are being sought. Natural materials and wastes provide a complete collection of cheap adsorbents and they are environmentally friendly (George *et.al*.,2013)

Hence the present study was undertaken to evaluate the suitabilityof groundnut shell as an adsorbent for the decolourizationof the textile dye, acid violet from aqueous solution.

4.1 CHEMISTRY OF ACID VIOLET DYE

Acid violet dye chosen for the present study is an acid dye commonly used in textile industry

Acid dyes are highly water soluble, and have better light fastness than basic dyes.The textile acid dyes are effective for protein fibers such as silk, wool, nylon and modified acrylics. They contain sulphonic acid groups, which are usually present as sodium sulphonate salts. These increase solubility in water, and give the dye molecules a negative charge. In an acidic solution, the $-NH_2$ functionalities of the fibers are protonated to give a positive charge: $-NH_3^+$.(Abrahart 1997)

These dyes are anionic in nature. The protein and polyamide fibers produce cationic sites in water under acidic conditions. As the acidity of the solution is increased, more cationic sites are produced under these strongly acidic conditions. These cationic sites are thus available for the acid dye anions to combine with through hydrogen bonding, vanderwaals forces or ionic bonding. These linkages are strong enough to break , and thus dyeing produced are fast .

Acid dye is a bright coloured synthetic organic compound whose molecule contains two groups of atoms one acidic, such as a carboxylic group, and one colour producing, such as an azo or nitro group.

4.2 BATCH ADSORPTION STUDIES

Batch adsorption studies were conducted to optimize the parameters for maximum adsorption namely dye concentration, pH , adsorbent dose, temperature and contact time.

4.2.1 EFFECT OF pH

TABLE 1

DYE REMOVAL AT DIFFERENT pH

pH	Decolourization(%)
1	50
2	65
3	75
4	65
5	55
6	53
7	53
8	35
9	30
10	22

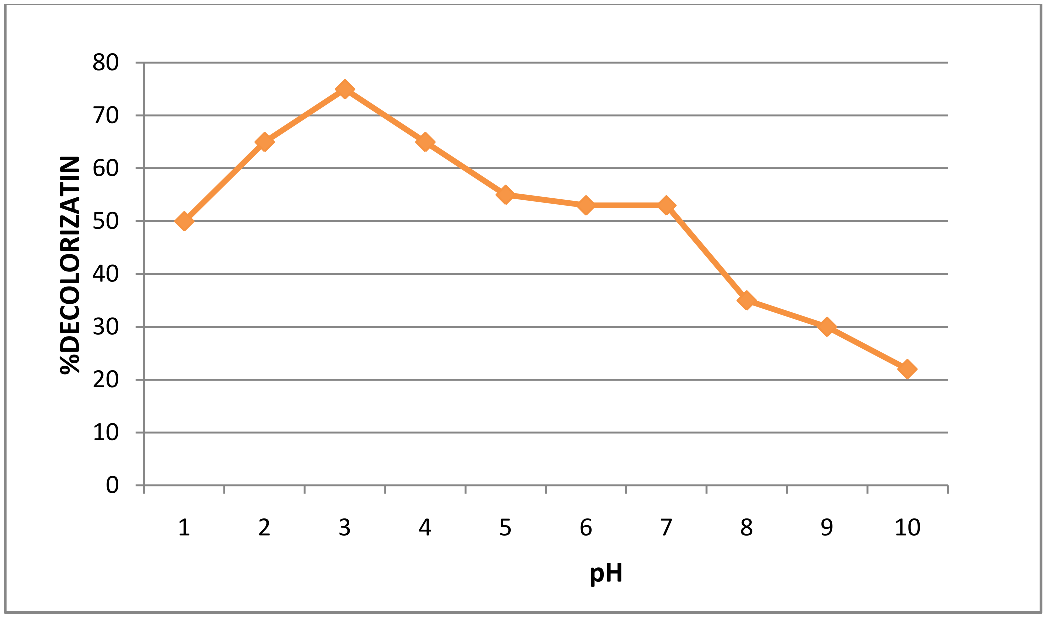

Fig.4.Dye removal at different pH

PH is one of the most important factors in controlling the adsorption process. To evaluate the effect of pH on the adsorption process, the removal of dye from the solution was studied at pH from 1 to 10,keeping all other variables as constant. The result of the study was presented in table 1and fig.6.Its showed that the dye removal was maximum at PH 3 and dye removal achieved was 75%.A slight decrease was observed up to pH 7 and above Ph 7 dye adsorption decreased and reached the minimum of 22% at pH 10(Kavitha *et.al*.,2016).

Similar results were obtained in adsorption studies for acid dyes. The adsorption study of anionic dye tetrazine conducted in the pH range of 2 to12gave the maximum dye adsorption at pH 3(0.19 mg/g) and the lowest at pH12(o.16 mg/g) Banerjee and Chattopadhyaya 2013.The study on the adsorption of Maxilon blue(GRL) and Direct yellow (dy12) on coconut shell activated carbon (CSAC) at a pH of 3 to 10 for 2h showed maximum adsorption at pH 3 and lowest at pH10(Aljeboree *et.al*.,2017)

The above observation showed that the process of adsorption is pH dependent. It controls the degree of ionization of dye molecules in aqueous solution and there by the amount of electrostatic charges imparted by them (Wawrzkiewicz and Hubicki, 2009). It plays an equal role determining the surface charge of the adsorbent and also the dissociation of various functional groups at the active sites of the adsorbent. Adsorbents possess fictional groups which are either protonated or deprotonated in solutions at different pH causing different surface charges on them, resulting in electrostatic attraction or repulsion between charged adsorbate and adsorbent (Alshabana *et.al*.,2013).

From the above it is evident that the initial pH is an important parameter in controlling the adsorption of textile dyes. Percent dye adsorption is more for anionic dyes at lower pH while for cationic dyes it occurs at higher pH. At lower pH three is electrostatic attraction between dye anions and the positively charged surface of the adsorbent. Theoretically, at pH < isoelectric point, the adsorbent surface becomes positively charged which favors the adsorption of negatively charged dye anions through electrostatic forces of attraction (Shanthi *et.al.*, 2016).

At high pH, decrease in adsorption may be attributed to the fact that adsorbent surface may become negative resulting in electrostatic repulsion between them and dye anions(Ozcan et.al.,2004)Also at high pH, OH ions compete with dye anions causing a decrease in adsorption from aqueous solutions. Further the change in pH from acidic to basic affects the process of adsorption through dissociation of functional groups on the adsorbent surface which tends to make a shift in equilibrium characteristics of the adsorption process(Dotto *et.al*., 2012).

4.2.2 EFFECT OF INITIAL DYE CONCENTRATION

TABLE 2

DYE REMOVAL AT DIFFERENT DYE CONCENTRATION

Dye concentration (mg)	Decolourization
1	0
2	0
3	22
4	33
5	35
6	55
7	42
8	43
9	42
10	55

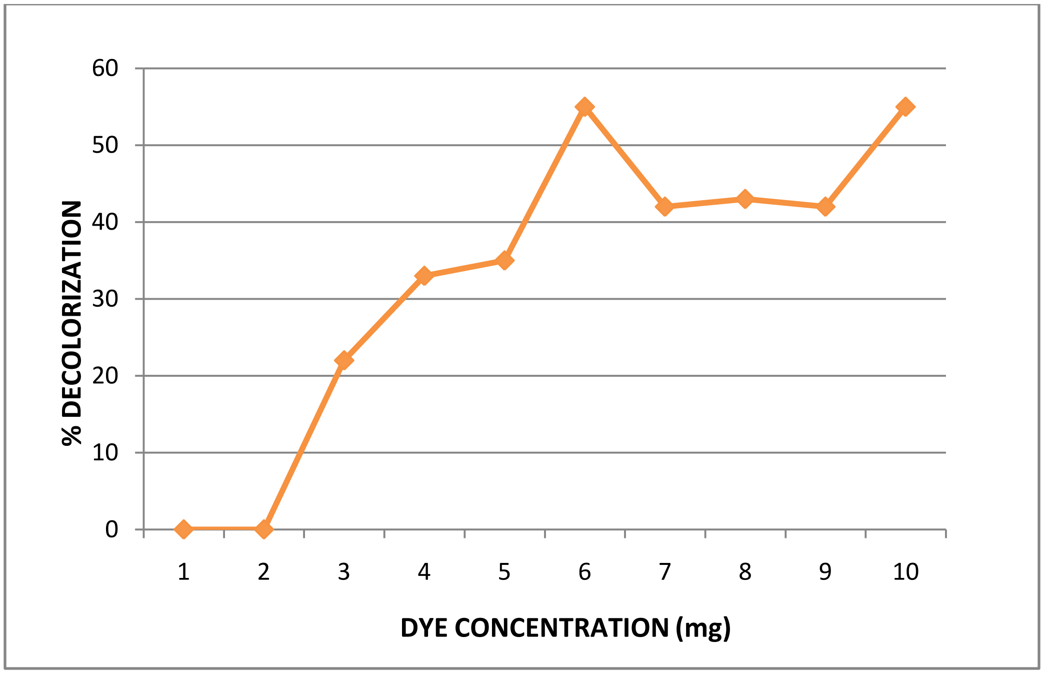

Fig.5. DYE REMOVAL AT DIFFERENT DYE CONCENTRATION

The efficiency of dye adsorption is highly dependent on initial dye concentration and there exists an important relationship between dye concentration and the available binding sites.

The effect of initial dye concentration was studied by changing dye concentration from 1 to 10 mg / 100ml and the result was presented in table 2 and fig.7. the result revealed that dye removal was zero at very low concentration and gradually increased to 50% at a dye concentration of 10mg /100ml. Similar result was cited by Lata *et.al.*,(2007) for a dye concentration in the range of 10 to 100mg /l. cheng *et.al.*,(2015) stated that increase in dye concentration leads to an increase in the mass gradient between the solution and the adsorbent and thus provides a driving force for the transfer of dye molecules from the solution to the surface of adsorbent. Increase in dye concentration can also promote interactions between dye molecule and adsorbent surface.

With further increase there may be a decrease in adsorption due to the saturation of adsorption sites on the adsorbent surface.(Shalleh *et.al.*,2011)

Hence from the study it is show that a given mass of adsorbent can adsorb only a fixed amount of dye and therefore initial dye concentration is one of the important factors for adsorption(Ghaedi *et.al*.,2012)

4.2.3 EFFECT OF TEMPERATURE

TABLE 3

DYE REMOVAL AT DIFFERENT TEMPERATURE

Temperature (^{O} C)	Decolourization(%)
10	12
20	12.5
30	62
40	25
50	12.5
60	12

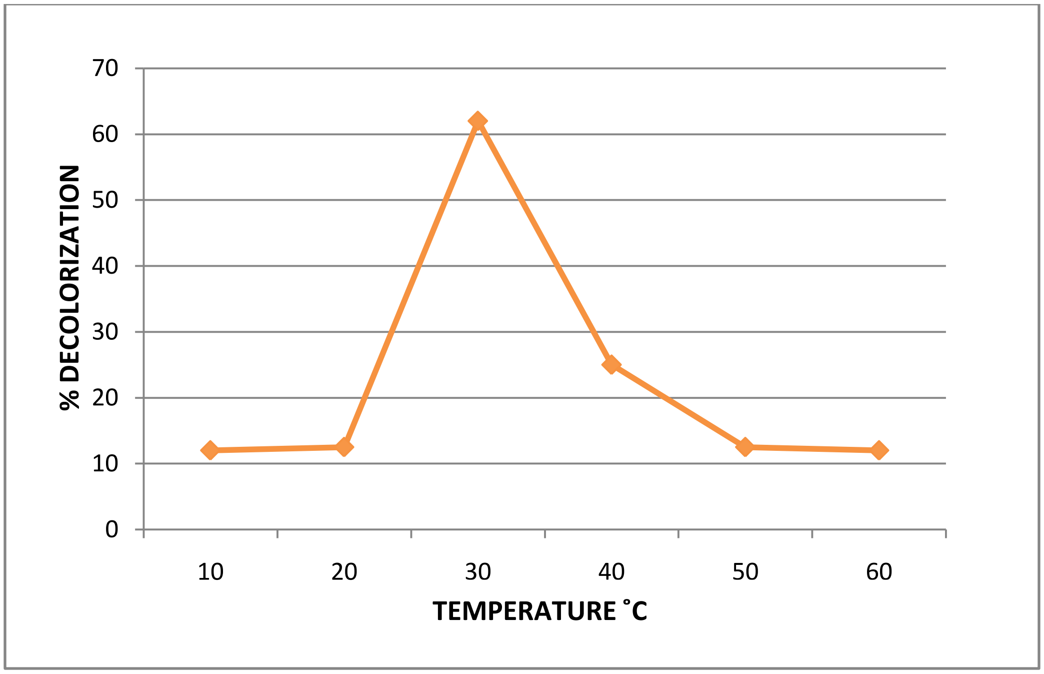

Fig.6. DYE REMOVAL AT DIFFERENT TEMPERATURE

Temperature as a parameter indicates whether adsorption is exothermic or endothermic. The result of the effect of temperature on adsorption was given in table 3and fig.8.The study was conducted in the temperature range of 10 to 60 ^{o}C. With rise in temperature percent dye removal gradually increased up to 30^{o}C(65%) and with further increase, dye removal gradually decreased and at 60^{o} C dye removal was only 30%.

The increase in adsorption capacity with increasing temperature showed that the process of dye adsorption is endothermic. This may probably be due to an increase in the number of active sites and mobility of dye molecules at higher temperature (Senthilkumar *et.al*.,2006)

Similar result was recorded by hameed and ahmad(2009) for a temperature rise from 30^{o}C to 50^{O}C Senthilkumar *et.al*.,(2006) made a similar observation and concluded that higher temperature may cause the swelling of internal structure of the adsorbent, enabling the diffusion of more dye molecules

Fu *et.al*.,(2016) conducted a similar study using polydopamine microspheres as adsorbent for the selective adsorption and separation of organic dyes including acid, neutral and basic dyes. They showed that temperature is an important factor for adsorption and adsorption capacity increases as temperature rises from 15 to 45^{o}C.Also stated that rise in temperature quickens diffusion of dye molecules increasing the opportunity for dye molecules to contact the adsorbent surface.

4.2.4EFFECT OF ADSORBENT DOSE

TABLE 4

DYE REMOVAL AT DIFFERENT ADSORBENT DOSE

Dose adsorbent (mg)	Decolourization(%)
100	0
200	19
300	33
400	43
500	89
600	60
700	60
800	41
900	40
1000	40

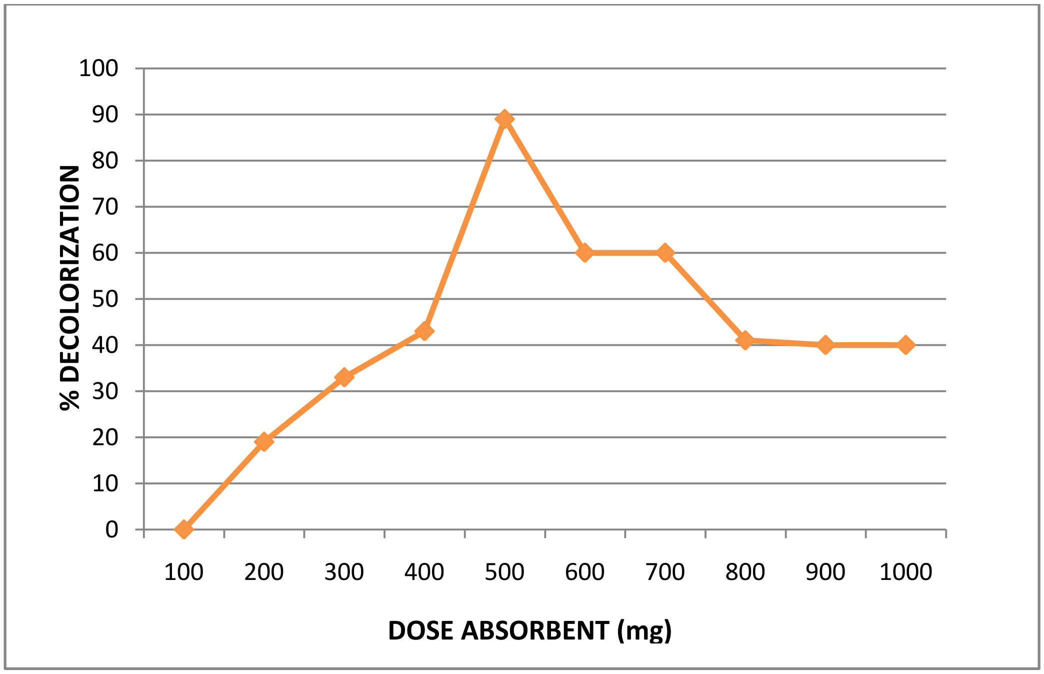

Fig.7. DYE REMOVAL AT DIFFERENT ADSORBENT DOSE

To study the effect of adsorbent dose, batch adsorption study was conducted by preparing adsorbent –adsorbate solution with varying amount of adsorbents added to fixed initial dye concentration (Salleh *et.al*.,2011).It determines the optimal dose of adsorbent for better dye adsorption. The table 4 and fig 9 showed that the increase in percent dye adsorption was rapid when adsorbent dose was increased from 200 to 500mg/100ml of dye solution and the maximum dye removal of 89% was achieved. Beyond this, no further increase was recorded the adsorbent dose of 500mg/100ml of dye solution was consider as the optimum dose.

Kanamadi *et.al*.,(2006) in a similar study noted that an increase in biomass quantity from 1to 6g/l caused a significant augmentation in percent biosorption and a dose < 6g/l was not required this because at lower adsorbent dose the dye solution are more easily accessible, thereby increasing the percent removal of dye per unit weight. After the optimal dose there is no increment in dye removal efficiency because at higher adsorbent dose there is a very fast superficial adsorption onto the adsorbent surface that produces a lower solute concentration in the solution than when adsorbent dose is lower and many sites on the adsorbent remain unsaturated (Salleh *et.al*.,2011).

Form the adsorption studies, the optimal conditions for dye adsorption on to groundnut shell powder were found to be:pH 3.0,Initial dye concentration of 6mg/100ml,temperature of 30^0C and adsorbent dose of 500mg/100ml.

4.3.UV-VIS SPECTRAL ANALYSIS

The dye sample collected before and after decolourization process was filtered and the filtrate was scanned in UV-vis spectrophotometer within the range of 200 to 800nm.The band width was set to 1nm and absorbance noted at the respective characteristic peak was used for the interpretation of result (senthilkumar *et.al*.,2014)

The dye showed the presence of four absorbance peaks at 251,305, 550 and 580nm (fig.8). The peaks at 251 and 305 are due to aromatic rings in the dye (Senthilkumar et.al.,2014)

In the decolourized dye sample decrease in absorbance in this region was noted,(fig.9).indicative of removal of aromatic part of the dye. The peaks at 550 and 580nm may be due to choromophore groups(senthilkumar *et.al,*. 20014 an there removal is indicated by the disappearance of these bands in the decolourized dye sample.

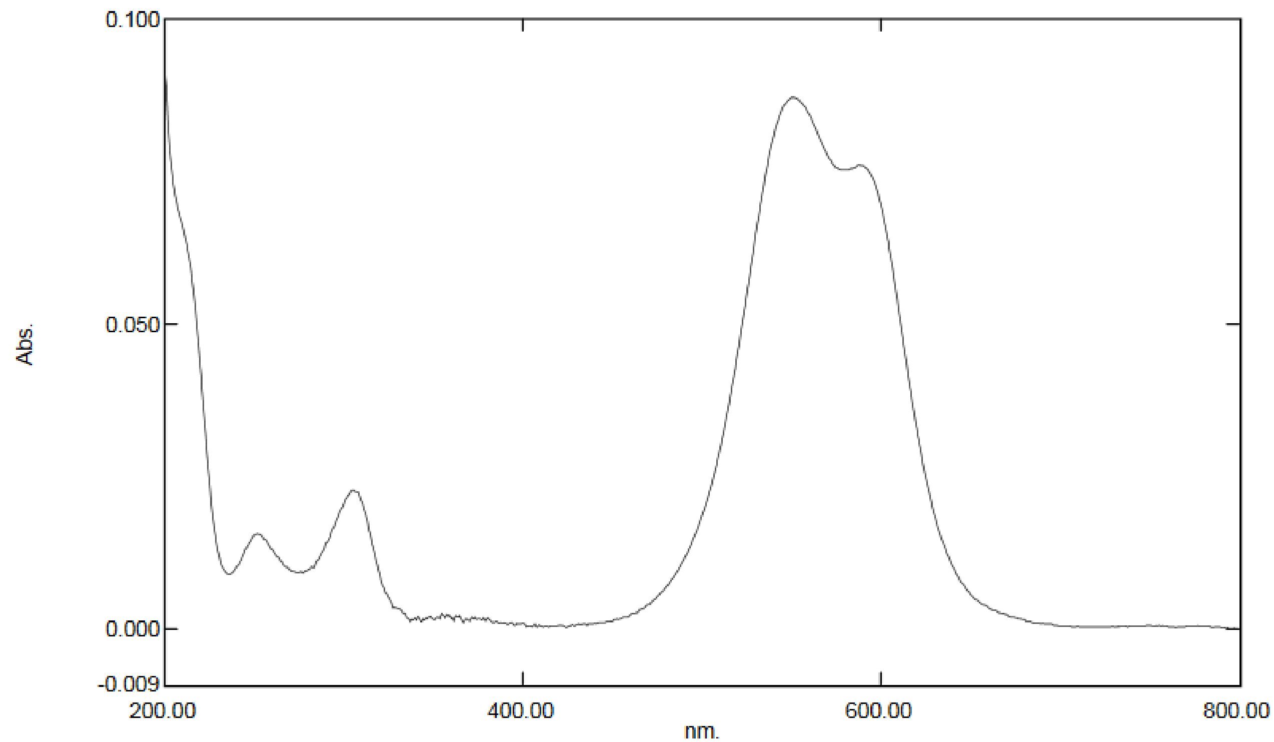

Fig 8. UV-vis spectrum of dye solution before adsorbtion

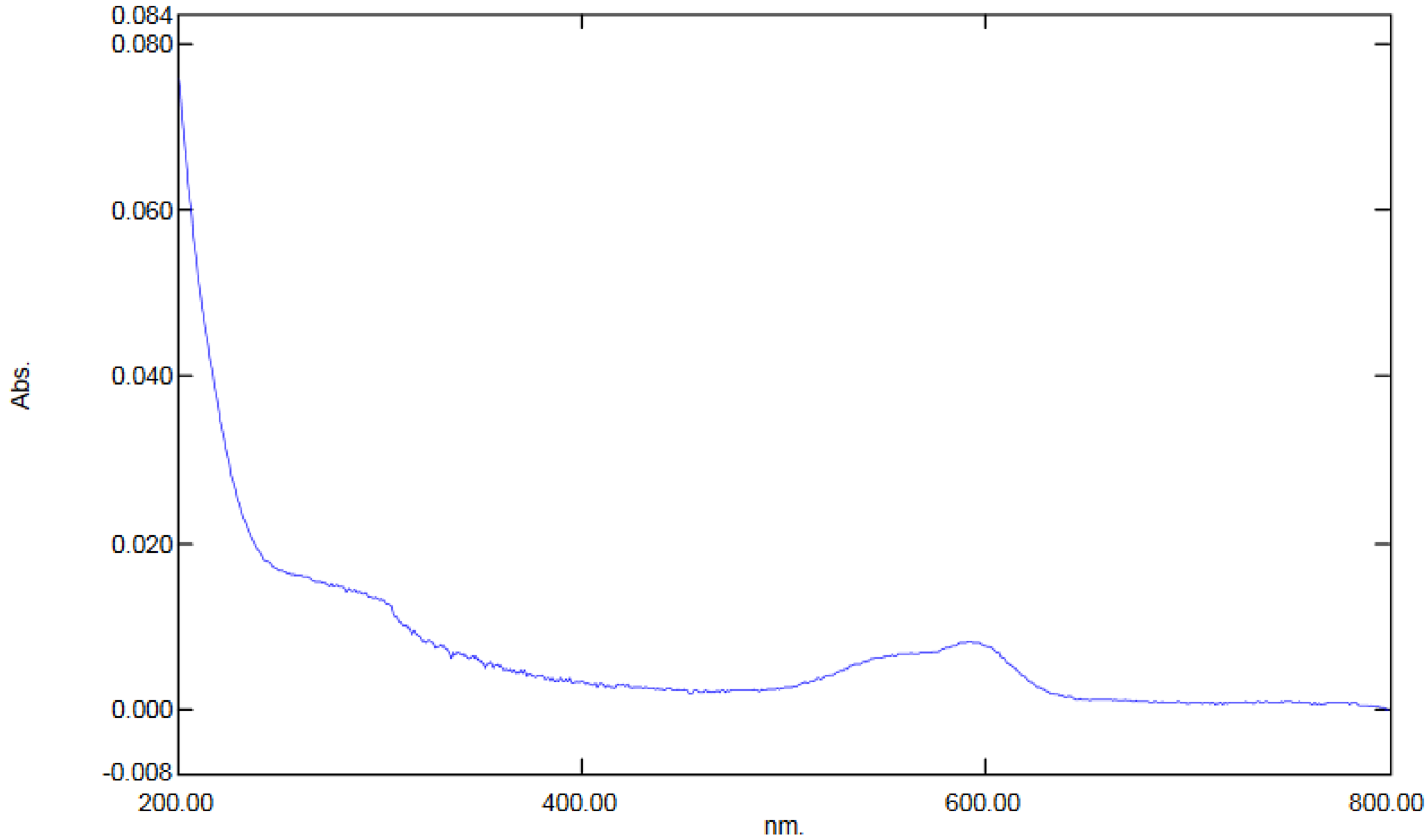

Fig 9. UV-vis spectrum of dye solution after adsorbtion

4.4.FT-IR ANALYIS

FT-IR Spectroscopy is used to study the functional groups present in molecules and for the characterization of covalent bonds within the molecules. FT-IR Spectroscopy is a non destructive, fast and sensitive physical technique for the analysis of organic compounds with minimum sample preparation.

Peak shifiting and changes in peak intensity in FTIR spectra after dye loading indicate their involvement in dye biosorption, which are interpreted based on the standard wave number(Skoog and leary1992)

The FTIR spectra of groundnut shell before and after adsorption of acid violet dye were analysed within the range of 4000 to 500cm^{-1}

FTIR frequencies of groundnut shell before and after dye adsorption were presented in fig.10. fig.11). Major peaks were observed at 3402.43,2927.94,1643.35,1041.56 and 601.79 for groundnut shell before dye adsorption. The broad peak at 3402.43 and 1041.56cm^{-1} became narrower and shaper and shifted to 3414.00 and 1044.42cm^{-1} receptively which indicated the involvement of alcoholic and phenolic groups in the process of adsorption.

The involvement of carboxylic and phenolic groups in adsorption on to coconut shell was reported by(Aljeboree *et.al*.,2017). .They stated that these groups get protonated, become more positively charged which enhance the adsorption of negatively charged dye anions of Maxilon blue (GRL) and Direct yellow (dy12) through electrostatic attraction.

From the study it can be concluded that groundnut shell can be used as a low cost adsorbent for the decolourization of textile acid dyes like acid violet.

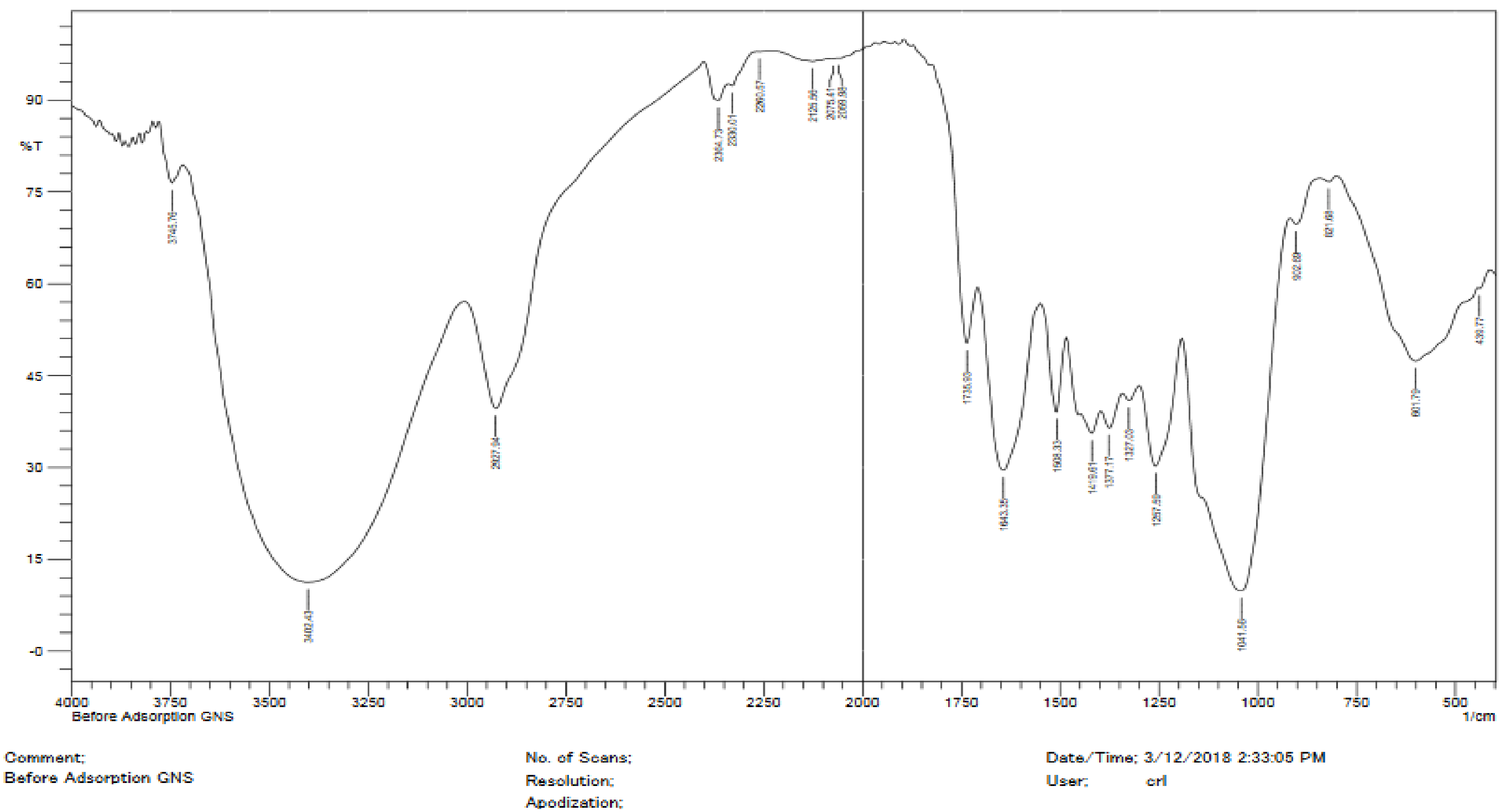

Fig .10. FT-IR spectra of groundnut shell before adsorbtion

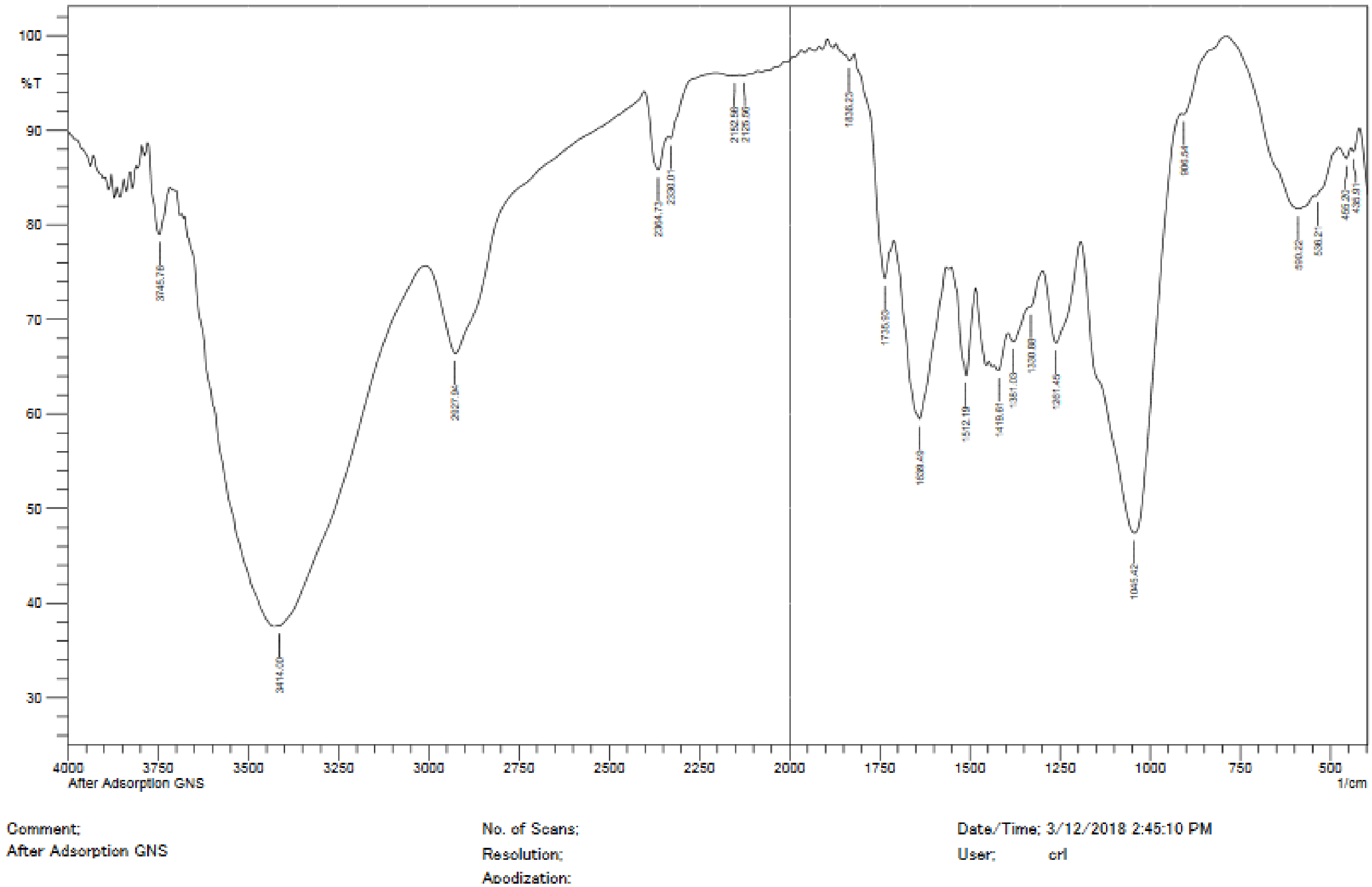

Fig 11. FT-IR spectra of groundnut shell after adsorbtion

5.SUMMARY AND CONCLUSION

The study was conducted to evaluate the potential of groundnut shell as an adsorbent for the decolourization of acid violet dye.

Groundnut shell was collected from the local market and washed in tap water to remove soil particles.

It was sun dried to remove moisture content, crushed well and ground into a fine powder in an electric mixture cum grinder. The powder was sifted to get particles of uniform size and stored for use in the study.

Acid violet dye was purchased from a local distributer. 100mg of the dye was dissolved in 100ml of distilled water. Each 1ml contained 1mg of the dye. The required concentrations of dye solution (1-10mg)were prepared from the above stock solution.

Batch experiments were conducted to get optimum conditions for dye removal namely optimum dye concentration, pH, temperature and adsorbent dose.

Fixed amounts of adsorbent(100mg-1.0g)were added to dye solution of varying concentrations (1mg-10mg)and maintained at different temperatures(10-60^0 C)and pH(1-10)for time periods from 24 -90 hours(Fig.3).For adjusting the pH of dye solution diluted NaOH and HCL were used.

At the end of each experiment the absorbance of the dye solution was read in a colorimeter at 420nm to estimate final dye concentration. Initial absorbance of each dye solution was also read in the colorimeter and % decolourization was calculated.

All experiment were conducted thrice for each parameter to get average values for calculation

The structural characterization of groundnut shell was done by FTIR analysis and dye decolurization by adsorbent by UV-vis spectral analysis.

Dye decolourization by the adsorbent was evaluated by subjecting the dye solution before and after adsorption to spectral analysis in the UV and visual region

FTIR analysis was done in the spectral range of 4000-500cm^{-1} to study the functional groups available on the absorbent surface for adsorbtion.

The study showed that pH, dye concentration, temperature, adsorbent dose play major role in adsorption.

The adsorption capacity for groundnut shell was maximum at pH 3.0 (75%) . With further increase in pH, the adsorption percentage was gradually decreased and recorded 22% at pH10.

The percent decolourization was maximum in initial dye concentration of 6mg (55%) which on higher concentration has decreased to 22%.

An increase in temperature showed an initial increase in adsorption percentage and maximum adsorption was recorded at 30^{o}C (62%).

The effect of adsorbent dose on decolourization of dye indicate maximum dye removal at 500 mg of adsorbent (89%).Adsorption efficiency decreased with further increase in adsorbent dose.

UV-vis analysis of the treated dye solution showed absence of peaks at 251,305, 550 and 580nm.The absence of peak indicated removal of dye from the solution by adsorption on to adsorbent.

FT-IR analysis showed vibration frequency changes in the spectrum after dye adsorption. Peak shifting and intensification were observed which indicated the involvement of functional groups such as carboxyl, alcoholic and phenolic groups.

From the study it was concluded that the groundnut shell can be used as an adsorbent for the removal of acid violet dye from aqueous solutions.

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6.REFERENCE

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