ADSORPTION OF MUREXIDE DYE FROM AQUEOUS SOLUTIONS USING PEANUT SHELL

A thesis submitted in partial fulfillment of the

Degree of Master of Philosophy (M.Phil)

By

Poonkodi. A
(16MPZOF002)

Department of Zoology

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

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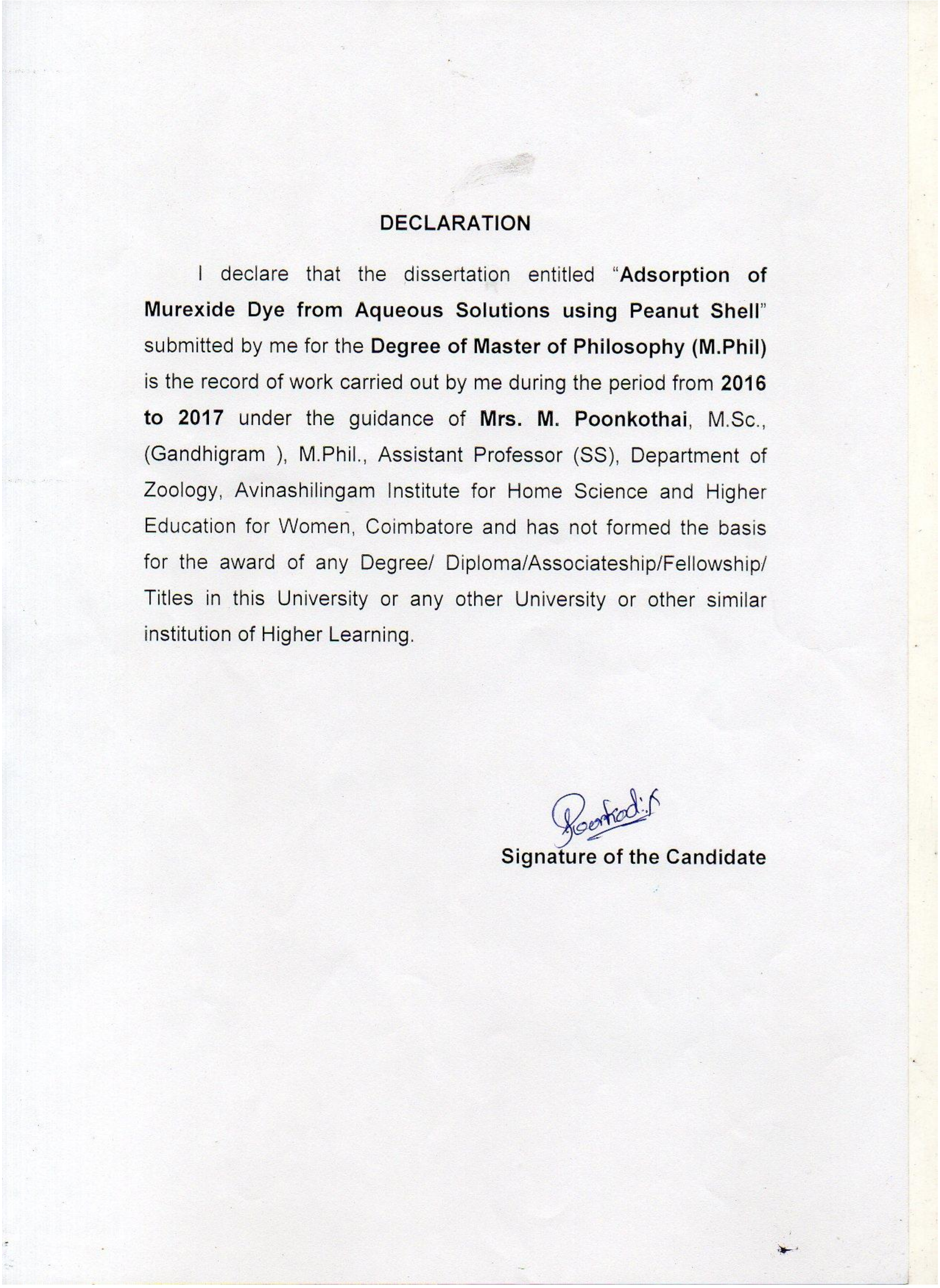


DECLARATION

I declare that the dissertation entitled "**Adsorption of Murexide Dye from Aqueous Solutions using Peanut Shell**" submitted by me for the **Degree of Master of Philosophy (M.Phil)** is the record of work carried out by me during the period from **2016 to 2017** under the guidance of **Mrs. M. Poonkothai**, M.Sc., (Gandhigram), M.Phil., Assistant Professor (SS), Department of Zoology, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore and has not formed the basis for the award of any Degree/ Diploma/Associateship/Fellowship/ Titles in this University or any other University or other similar institution of Higher Learning.

Poonkodi.S

Signature of the Candidate

CERTIFICATE FROM THE SUPERVISOR

I certify that the dissertation entitled **"Adsorption of Murexide Dye from Aqueous Solutions using Peanut Shell"** submitted by me for the **Degree of Master of Philosophy (M.Phil)** by **Poonkodi. A** is the record of research work carried out by her during the period from **2016 to 2017** under my guidance and supervision, and that this work has not formed the basis for the award of any Degree/Diploma/Associateship/ Fellowship/Title in this University or any other University or Institution of Higher Learning.

31.7.17.

Signature of HOD

M.Poonkothai 31/7/17

Signature of Supervisor with designation

M.POONKOTHAI
Assistant Professor

INTRODUCTION

1. INTRODUCTION

Increased population and modernized civilization gave rise to blooming of textile sector in India. Textile manufacturing industries are established in most part of the world and their numbers have been increasing in recent days. In India, textile is one of the oldest establishments with nearly thirty million people. India is the second largest exports of dye stuffs where 80,000 tons of dyes and pigments are produced annually (Saraswathi and Balakumar, 2009).

One of the major problems that humans are facing is the restoration of the contaminated environment. Textile dyes contribute the most important polluting agents of the ecosystem. Several classes of such contaminants have been synthesized, and still new products are being synthesized now and then. The textile industry consumes large amount of water and produces huge volumes of contaminated water. The textile industry generally has difficulty in meeting waste water discharge limits, particularly with regard to dissolved solids, ionic salt, pH, COD, color and heavy metal. Treatment of dye contaminated waste water discharged from the textile and other dye stuff industries is necessary to prevent of soil, surface and ground water (Arulazhagan, 2016).

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

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

Synthetic dyes and heavy metals are widely used textiles, leather, paper, plastics, electroplating, cement, metal processing, wood preservatives, paints, pigments and steel fabricating industries (Ponnusami *et al.,* 2008). These industries discharge large quantities of toxic wastes, and the untreated effluents from these industries cause soil and water pollution, which results in the accumulation of heavy metals and colour to the water. Heavy metals are toxic even at very low concentrations and pose serious problems due to their possible entry into the food chain (Vasanthy *et al.,* 2004). Colour is a visible pollutant and presence of very minute concentration of colouring substances in water makes it unsuitable for domestic purposes like drinking and recreational purposes due to its anaesthetic appearance (Kumar *et al.*, 2003).

Colour is considered as the first pollutant to be identified in wastewater and it is mostly caused by the effluents discharged from dyeing industries such as paper, rubber, cosmetics, textile and plastics. Approximately 10,000 different dyes and pigments are used for industries and over 7×10^5 tons of these dyes are annually produced worldwide (Mane, 2007).

Majority of dyes are visually detected even at the concentration of less than 1 mg/l. The discharge of dyes in the environment is worrying for both toxicological and esthetical reasons. Most of which are difficult to biodegrade due to their complex aromatic molecular structure and synthetic origin (Seshadri, 1994).

In recent decades, waste disposal has become an increasing worldwide concern. The use of waste materials for different purposes can play a significant role in helping to solve disposal problems. In addition, utilization of waste materials can contribute to the wise and efficient use of materials, and to protect our environment. Many efforts, however, have been made to investigate the use of various techniques to remove dyes from waste water.

A wide range of physical and chemical techniques are available for removal of toxic organic compounds from waste water such as filtration, coagulation/ flocculation, ion exchange, adsorption, fenton reagent technique, ozonisation, photocatalytic methods, aerobic degradation and anaerobic degradation methods. Chemical and biological methods found to be limited as they are often involve high investment and functional costs. On the other hand physical methods like ion exchange and reverse osmosis are interesting methods because of their effective removal process of pollutants from industrial waste water but these ion exchange and reverse osmosis methods restricts the use in large scale industries due to their high capital and operational costs. Among all the methods available for separation of pollutants from waste waters, the adsorption shows possible method for treatment and removal of organic pollutants in waste water treatment. Adsorption follows surface phenomenon and more advantageous over the other available methods because of its low capital, operation costs and simple design. As per the researchers the adsorption is most commonly used method for the removal of both organic and inorganic pollutants from industrial waste water. Adsorption material available from various sources such as natural sources, agricultural, and industrial wastes. Dye removal from wastewater using activated carbon is effective method but in industrial processes it was restricted due to its high operational and investment costs. In the adsorption method various other natural sources are available for removal of dyes from industrial wastewater (Kandisa *et al.,* 2016).

In recent years agricultural and industrial wastes are used to removel hazardous contaminants from wastewater (Moghadam, 2010). In China, peanut shell is an abundantly available by product of the peanut blanching or oil extracting industries. The annual generation of peanut shell is estimated to be around 4.5 million tonnes, accounting about one third of the annual gross production throughout the world (Xu, 2008).

However, as low- value agriculture waste materials, most of peanut shells are either burned for energy or abandoned, resulting in a tremendous waste of natural resources and environmental pollution. Therefore, any possible usage of peanut shells, especially on an industrial scale, will yield economic as well as environmental dividends (Sudha *et al*., 2008).

Adsorption has been observed to be an effective process for colour removal from dye wastewater. Use of commercial activated carbon has been found to be effective, but it is too expensive. Many studies have been undertaken to investigate the use of low-cost adsorbents such as peat, betonite, steel-plant slag, fly ash, china clay, maize cob, wood shavings and silica for colour removal. However, these low-cost adsorbents have generally low adsorption capacity and it requires large amount of adsorbents. Therefore, there is a need to find new, economical, easily available and highly effective adsorbents.

With this background, an attempt has been made to study the "Adsorption of Murexide Dye from Aqueous Solutions using Peanut Shell" with the following objectives:

- To find out the adsorption capacity of peanut shell to remove murexide dye from aqueous solutions.
- To optimize parameters for dye decolourization such as dye concentration, adsorbent dose, pH, temperature and contact time using peanut shell.
- To determine the adsorption capacity of murexide dye by the selected peanut shell with isothermal data.
- To analyse the FT-IR spectrum of the peanut shell before and after bioadsorption.
- To characterize the dye – adsorbent interaction and surface structure by SEM (Scanning Electron Microscope) analysis.
- To analyse the phytotoxicity study of adsorbent treated dye solution.

The following chapter outlines the review to literature relevant to the present study.

2. REVIEW OF LITERATURE

The review of literature pertaining to the present investigation is organized and presented under the following headings.

- 2.1. Pollution: A threat to human
- 2.2. Sources of textile dyeing effluent
- 2.3. Toxicity of textile dyeing effluent
- 2.4. Treatment of textile dyeing effluent
- 2.5. Bioadsorption –A green approach for dye removal
  - 2.5.1. Adsorption
  - 2.5.2. Process of adsorption
  - 2.5.3. Mechanism of adsorption
  - 2.5.4. Factors affecting adsorption of dye
  - 2.5.5. Adsorbent – A boon to environment
- 2.6. Removal of synthetic dyes using bioadsorption
- 2.7. Candidate dyes and adsorbent used in the study
  - 2.7.1. Murexide dye
  - 2.7.2. Peanut shell
- 2.8. Regeneration of adsorbent
- 2.9. Isotherm modelling studies
- 2.10. Phytotoxicity studies

2.1. POLLUTION: A THREAT TO HUMAN

The total world colorant production is estimated to be 80,000 tons/year, and generally 20% of the used dyestuff enters the environment through wastes. Most of these dyes are toxic, potentially carcinogenic, hence their removal from industrial effluents is a major environmental problem (Golka *et al.,* 2004).

In recent decades environmental pollution has become one of the major problems in the industrial society. Among the pollutants, dyes have serious effects on both humans and the environment. Their release has continuously increased as effluents due to the growing industrial activities (Chojnacka, 2010). One of the major problems concerning textile industry is dye effluent (Hamed *et al*., 2006).

The textile industries are the greatest generators of liquid effluent, due to high quality of water used in the dyeing process (Selen *et al*., 2008). Although use of different dyes, especially the textile dyes makes the world beautiful and colourful, they pose serious pollution problems, as the waste water from the textile industry is not only coloured but it has high fluctuating pH, large amount of suspended solids along with high chemical oxygen demand (COD) (Phugare *et al*., 2010).

The problems of environmental pollution caused by the industrial waste have become more serious year by year. The development of practical waste treatment systems or recycling systems is gathering global interest (Han *et al.,* 2006)

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

Discharge of the coloured waste water into water sources damages the environment as they disturb human health and they may be toxic to the flora and fauna and significantly reduce photosynthetic activity of autotrophic organism (Saratale *et al*., 2010).

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

Saving water to save the planet and to make the future of mankind safe is what we need now with the growth of mankind, society, science and technology. Our world is reaching to new high horizons but the cost which we are paying or will pay in near future is surely going to be too high. Among the consequences of this rapid growth is environmental disorder with a big pollution problem (Gupta and Suhas, 2009).

Hence the society should obey the Government legislations and if so, the threat of pollution can be minimized.

2.2. SOURCES OF TEXTILE DYEING EFFLUENT

Textile industries are the major sources of effluent discharged into the environment due to the nature of their operations. These require high volumes of water that eventually results in large waste water generation (Ghorishi and Haghigh, 2003).

Wastewater from printing and dyeing units are rich in colour, containing residues of dyes and chemicals and needs proper treatment before being released into the environment (Babu *et al*., 2007).

The textile industry is the largest consumer of dye stuffs. During the colouration process a large percentage of the synthetic dye does not bind to the clothes and is lost to the waste stream (Weber and Adams, 1995).

Approximately 10-15% of dyes were released into the environment during dyeing process making the effluent highly coloured and aesthetically unpleasant. The effluent from textile industries thus carries a large number of dyes and other additives which are added during the colouring process (Wang *et al*., 2002).

Textile industry is one of the greatest generators of liquid effluent pollutants due to high quantities of water used in the dyeing processes. There are more than 10^5 kinds of commercially available dyes with over $7X10^5$ tonnes of dyestuff produced annually and it is estimated the 2,80,000 tonnes of textile dyes are discharged from such industrial effluent every year worldwide (Jin *et al*., 2007).

2.3. TOXICITY OF TEXTILE DYEING EFFLUENT

The toxicity of dyes is of serious environmental concern because the effluents coming from dye processing and manufacturing industries are known to be carcinogenic as well as mutagenic to various organisms (Mathur and Bhatnagar, 2007).

The problem associated with the release of textile wastewater is the presence of the synthetic dyes. These dyes are problematic due to the visibility and their recalcitrance. Many dyes and their degradation products are associated with toxicity and mutagenicity (Weisburger, 2002).

Improper textile dye effluent disposal in aqueous ecosystem leads to the reduction in sunlight penetration, which decreases the activity of photosynthesis, dissolved oxygen concentration, water quality and depicts acute toxic effect on aquatic flora and fauna causing severe environmental problems worldwide (Saratale *et al*., 2009).

Textile dyes and effluents have toxic effects on the germination rates and biomass of several plants species, which have important ecological functions, such as providing habitat for wildlife, protective soil from erosion and providing the organic matter that is significant to soil fertility (Ghodake *et al*., 2009).

Dyeing industry effluent alters the colour and quality of the water bodies which has been proved to be hazardous to aquatic ecosystem. It may also reduce the sunlight penetration which is essential for photosynthesis and leads to toxicity of fish and mammals and also inhibit the activity and growth of microorganisms (Ramachandran *et al*., 2013).

The release of wide range of compounds form industries are creating disturbance to the ecosystem causing climate changes, reduction of water levels in the global warming, ozone layer depletion mostly due to photochemical oxidation, etc (Varsha *et al*., 2011).

Untreated industrial effluents sample being a potential source of pollution load are also toxic to plants (Mehta and Bharadwaj, 2012).

2.4. TREATMENT OF TEXTILE DYE EFFLUENT

Treatment of waste containing dyes and decolourization is very difficult due to wide range of pH, salt concentration and chemicals. The majority of colour removal techniques work either by concentrating the colour into a sludge, or by partial to complete breakdown of the coloured molecule. Effluent treatment methods may be classified into three main categories: physical, chemical and biological. The physical and chemical methods are limited due to excessive use of chemicals, sludge generation with subsequent disposal problems, high installation as well as operating costs and sensitivity to a variable waste-water input.

Bioadsorbent constitutes an alternative to conventional physicochemical methods. Biological systems are recognized by their capacity to reduce biological and chemical oxygen demand by aerobic biodegradation. Biological treatment of textile effluents may be either aerobic, anaerobic or a combination of both depending on the type of adsorbent being employed (Keharia and Madamwar, 2004).

2.5. BIOADSORPTION –A GREEN APPROACH FOR DYE REMOVAL

2.5.1. Adsorption

Adsorption is used as top quality treatment procedure for the removal of dissolved organic pollutants like dyes from industrial waste water. Adsorption is defined as concentration of materials on the surface of solid bodies. It is a surface phenomenon which deals primarily with the utilization of surface forces. When a solution having absorbable solute, also called as adsorbate, comes into contact with a solid, called as adsorbent, with highly porous surface structure liquid-solid intermolecular forces of attraction causes the solute to be concentrated at the solid surface. Adsorption is one of the unit operations in the chemical engineering processes used for the separation of industrial wastewater pollutants.

2.5.2. Process of adsorption

Over the last few years, a sizeable research investigation have been undertaken by various researchers for wastewater treatment using adsorption process. The adsorption process is utilised as a stage of integrated chemical-physical-biological process for the treatment of wastewater (Morawe, 1995 and Geeneus, 2001) or simultaneously with a biological process (Karfi, 2003). Adsorption is a surface phenomenon in which a multi-components fluid (gas or liquid) mixture is attached to the surface of a solid adsorbent to form attachments via physical or chemical bond (Sasaki *et al*., 2014).

The adsorption process of dye molecules usually consists of four consecutive steps (Al-Godah, 2000). The first step involves the diffusion or convection of dye molecules through the bulk solution. In the next stage, the dye molecules will diffuse through a diffusional boundary layer (film diffusion). This is followed by the diffusion of dye molecules from the surface into the interior of the adsorbent materials. Lastly, the dye molecules will attach to the surface of the materials through molecular interactions. The dye concentration and agitation force may affect step 2. Step 3 is the rate determining stage which will affect the adsorption of dye molecules on the substrate. While step 4 is dependent on the nature of the dye molecules, such as anionic and cationic structures. It is important to highlight that step 3 could involve two different phenomena. The first is porous diffusion (the adsorbate first diffuse in the liquid filling the pores and then is adsorbed), another is surface diffusion (the adsorbate is first adsorbed then diffuses from one site to another) (Noroozi, 2013). Adsorption can be divided into two types i.e. chemical sorption and physical sorption. For chemical sorption or chemisorption, it is defined by the formation of strong chemical association between molecules or ions of adsorbate, which is generally due to the exchange of electrons where the process generally is irreversible. Whereas physical sorption or physisorption involves the weak vander Waals intraparticle bonds between adsorbate and adsorbent and thus physisorption generally is reversible in most cases (Allen, 2005).

2.5.3. Mechanism of adsorbent

In order to further understand the adsorption process and select desorption approach, adsorption mechanism of organic pollutants removal onto agricultural waste was discussed. As usual the adsorption on adsorbent is controlled by physical forces with some exception of chemisorptions. Physical adsorption is carried through Vander Waals force, hydrophobicity, hydrogen bonds, polarity and steric interaction, dipole induced dipole interaction, π–π interaction, or their combine. While, chemical adsorption involves the sharing of electrons between the pollutants and the surface of adsorbent form a chemical bond. In addition, film diffusion and particle diffusion models have been often used for investigating their diffusion mechanism.In the physical adsorption, pollutants accumulated on adsorbent surfaces by the above mentioned interactions. For example, the adsorption of dye onto the surface of NMRH, may be due to the formation of surface hydrogen bonds between the hydroxyl groups on the NMRH surface and the nitrogen atoms of CV as given as Fig. 1(Chakarborty, 2011). The surface hydrogen bonds were formed between the hydroxyl groups of adsorbent surface and O/N-containing groups of the adsorbate (Nasuha, 20011 and Chowdhury, 2011). Villaescusa et al. (2011) investigated themechanismof adsorption by modeling calculations. The results indicated that π-stacking interactions between the aromatic ring of paracetamol and lignin syringyl and guaiacyl moieties of grape stalk, along with hydrogen bonding, were likely the responsible for paracetamol adsorption. Another probably the most relevant adsorption mechanism that may occur in the case of solutes containing conjugated systems is π–π dispersive interaction, which can take place between the aromatic rings and –N-C–C-C– system for MB (Ahmad, 2012).

For the chemical adsorption, some researchers also study the electrostatic interaction between adsorbate and adsorbent in the process of adsorption. For example, (Xu *et al*., 2011) selected three different raw materials (i.e. canola straw, peanut straw, or soybean straw) to prepare biochars. Some characterization methods such as zeta potentials, Fourier transform infrared spectroscopy, combined with the effect of ionic strength, indicated that the adsorption of methyl violet on biocharsinvolved in electrostatic attraction, specific interaction between the dye and carboxylate and phenolic hydroxyl groups on the biochars, and surface precipitation. Similarly, chemically modified straw (MWS) adsorbed anionic dye and its adsorption behavior was a monolayer chemical adsorption by an ion-exchange process. The adsorption mechanism of adsorption process was summarized (Zhnag, *et al.,* 201). In addition, Kumar *et al.* (2011) assumed that there were many factors that might affect the biosorption behavior such as (i) hydrogen bonding, (ii) hydrophobic–hydrophobic interaction, and (iii) electrostatic interaction between the cationic dye (the presence of $+N(CH_3)_2$ group) and negatively charged TWG surface in basic medium. According to the FT-IR spectrum and active site analysis, a proposed mechanism for the biosorption of CV onto TGW was shown in (Kumar, 2011).

For a solid–liquid adsorption system, the solute transfer is usually characterized by boundary layer diffusion, intra-particle diffusion or both, and the controlling step of the adsorption could be intraparticle and/or external diffusion process. In order to understand the adsorption mechanism, some researchers use intraparticle diffusion model and Boyd's equation for further elucidation the diffusion mechanism. For example, the study of Feng et al. (2012) indicated that the mechanism of MB adsorptions onto SRSTA is formed a complex and both the surface adsorption and intraparticle diffusion contributed to the actual adsorption process Feng *et al*. (2012).

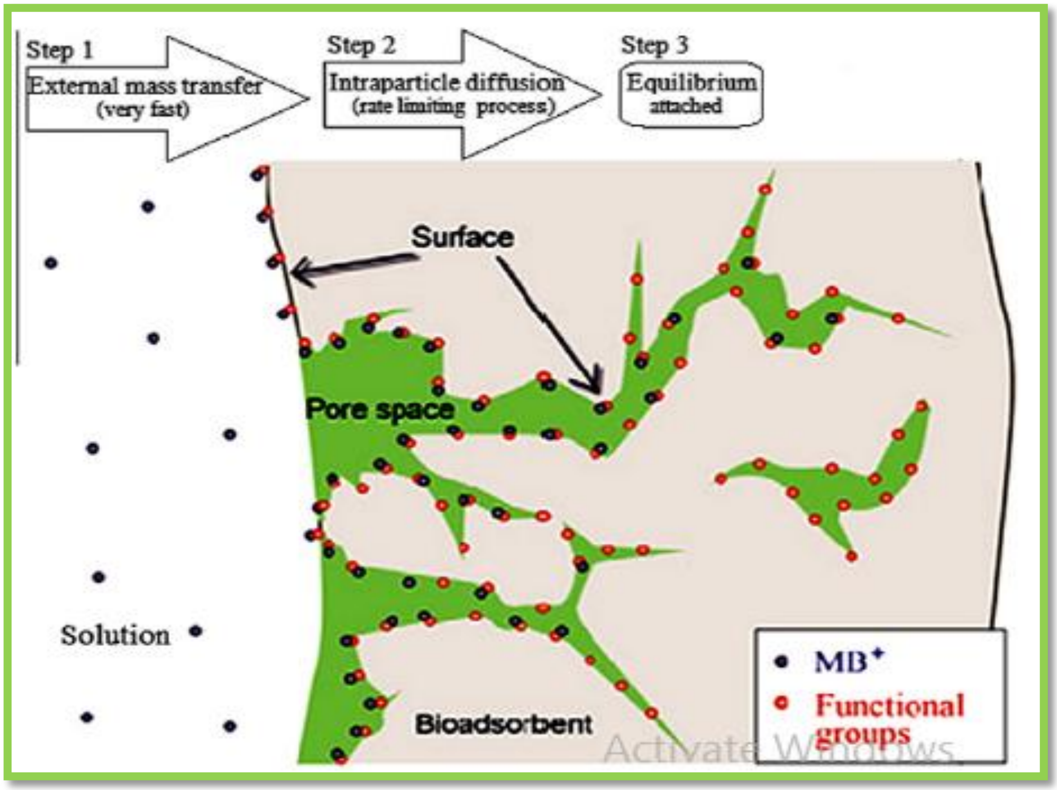


Fig 1 Mechanisms of adsorption process

2.5.4. Factors affecting adsorption of dye

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

pH

The pH of the solution is a very important parameter in the dye adsorption process. The magnitude of electrostatic charges which are imparted by the ionised dye molecules is controlled by the solution pH. As a result the rate of adsorption will vary with the pH of the medium used (Onal *et al,.* 2006). In general, at low solution pH, the percentage of dye removal will decrease for cationic dye adsorption, while for ionic dyes the percentage of removal will increase. In contrast, high solution pH is preferable for cationic dye adsorption but shows a lower efficiency for anionic dye adsorption (Salleh *et al*., 2011). At high solution pH, the positive charge at the solution interface will decrease while the adsorbent surface appears negatively charged (Ozcan *et al,*. 2007). As a result, the cationic dye adsorption will show an increase and the anionic dye adsorption will decrease. At low pH solution, the positive charge on the solution interface will increase and the adsorbent surface will appear positively charged, which results in the decrease of cationic dye adsorption and an increase in anionic dye adsorption (Salleh *et al*., 2011).

The adsorption ability of the surface and the type of surface active centres are indicated by the significant factor which is known as point of zero charge (pH_{pzc}) (Liu *et al,*. 2012). In order to determine the pH_{pzc}, dye solution with different pH should be prepared and considered as pHi_{nitial} and then the fixed amount of adsorbent was added to the dye solution. The dye solution was shaken until the equilibrium is achieved where the pH at equilibrium is regarded as pH_{final}, then plot the pH_{final} values against $pH_{initial}$ where pH_{pzc} is the point when $pH_{initial} = pH_{final}$ (Qadeer, 2007). The value of pH is used to describe pH_{pzc} only for the systems in which H+/OH- are the potential determining ions. Due to the presence of functional groups such as OH^-, COO^- groups, cationic dye adsorption is favoured at $pH > pH_{pzc}$, whereas, anionic dye adsorption is favoured at $pH < pH_{pzc}$ where the surface becomes positively charged (Liu *et al*., 2012).

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

Dawood and Sen (2012) studied the effect of solution pH on the adsorption of Congo red by pine cone and they noticed that the adsorption was maximum at pH 3.5.

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

Temperature

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

Hameed and Ahmad (2009), investigated the adsorption of methylene blue by garlic peel and they found that the adsorption capacity increased from 82.64 to 142.86 mg/g when the temperature increased from 30°C to 50°C indicating that the adsorption is endothermic in nature.

Adsorbent dosage

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

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

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

Initial dye concentration

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

Garg *et al.* (2004) reported the adsorption of methylene blue by sulphuric acid treated sawdust (SDC). It is observed that when methylene blue concentration was increased from 50mg/L to 250mg/L the percentage of dye removal decreased from 99.9% to 82.2% at an adsorbent dose of 0.4g/100mL temperature of 26 ± 1 °C and pH7.

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

2.5.5. Absorbent– A boon to environment

Absorbent, the low cost biomaterial seems to be a good choice for the removal of dyes. Various bioadsorbents are used in the removal of dye. Adsorbents are mainly derived from sources such as zeolites, charcoal, clays, ores, and other waste resources. Adsorbents prepared from waste resources used include coconut shell, rice husk, petroleum wastes, tannin-rich materials, sawdust, fertilizer wastes, fly ash, sugar industry wastes, blast furnace slag, chitosan and seafood processing wastes, seaweed and algae, peat moss, scrap tyres, fruit wastes, etc. (Cameselle, 2013)

Adsorption seems to be a cheap and existed low cost technology used for the removal of dyes from waste water and vinod (2006) reported activated rice husk as a cheap and excellent adsorbent for dye removal from waste water. Hamdaoui (2006) stated that maximum adsorption of methylene blue, a basic dye, onto cedar sawdust and crushed brick was observed as 60 and 40 mg l^{-1}, respectively.

2.6. REMOVAL OF SYNTHETIC DYE USING ADSORBENTS

The feasibility of using diatomite for the removal of the dyes such as methylene blue, Cibacron reactive black and reactive yellow from textile wastewater was investigated. Physical characteristics of diatomite such as $pH_{solution}$, pH_{ZPC}, surface area, Fourier transform infrared and scanning electron microscopy were investigated. The surface area of diatomite was found to be 27.80 m^2 g^{-1} and the pH_{ZPC} occurred around pH of 5.4. The results indicated that the surface charge of diatomite decreased as the pH of the solution increased with the maximum methylene blue removal from aqueous solution occurring at basic pH of around (10–11). Adsorption isotherms of diatomite with methylene blue, hydrolysed reactive black and yellow dyes were constructed at different pH values, initial dye concentrations and particle sizes. The experimental results were fitted to the Langmuir, Freundlich, and Henry models. The study indicated that electrostatic interactions play an important role in the adsorption of dyes onto diatomite. A model of the adsorption mechanism of methylene blue onto diatomite is proposed (Ghouti *et al.,* 2003)

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

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

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

Nadi *et al*. (2012) investigated the ability of peanut shell powder for the removal of reactive dyes such as Green 19, Orange 16, and Yellow 14 from aqueous solutions. Batch adsorption studies showed that the peanut shell powder was able to remove the reactive dyes from aqueous solutions in the concentration range of 25 to 250 mg/L. The highest percent removal for the Green 19, Orange 16 and Yellow 14 dyes was 84%, 87% and 88% respectively. The adsorption was favored with maximum adsorption at pH 2 with adsorbent dose at 0.4g/100 mL. The adsorption isotherm studies clearly indicated that the adsorptive behavior of dyes on peanut shell satisfies only the Freundlich isotherm.

Seey and Kassim (2012) investigated the adsorption character of malachite green (basic dye) and Sunset yellow FCF onto chemically treated mangrove bark. The bark powder was chemically treated in an acidic formaldehyde solution to produce non-soluble adsorbent and used for the adsorption of dyes. Batch experiments were carried out for the adsorption of dyes molecules onto modified barks at room temperature. Various factors such as pH, contact time, initial dyes concentrations, and amount of adsorbent were taken into account, and promising results were obtained. The applicability of the Langmuir as well as Freundlich adsorption isotherms for the present system was tested. The equilibrium data were found to be well represented by the Langmuir isotherm equation.

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

Adsorption is the most appropriate and proficient method for dye removal ineffluents (Anbia and Salehi, 2012 and Zhang *et al*., 2012). A significant role was played by phytoremediation in contaminant removal through filtration, adsorption, cation exchange and throughout plant-induced chemical transformations in rhizosphere (Nouri *et al.,* 2009). Plants generally have optimistic outcome on decontamination and play a promising role in CWs (Kong *et al*., 2009). Rice husk is a key agricultural waste throughout the world; therefore its appropriate management is very indispensable to lessen its effect on environment. Rice husk, rice bran and rice ash was used to destroy a number of dyes including methylene blue, crystal violet, Brilliant Vital Red, Direct Red-31 and Direct Orange-26 and Congo red. So a combination of microbes, plants and constructed wetland would establish itself as an efficient system (Saba *et al*., 2014).

Li *et al.* (2015) investigated the effect of cationic dye sorption from aqueous solution using different peanut shells characterization of different samples is carried out with SEM, FTIR and XRD. SEM and FTIR show that some components of raw peanut shell have been removed during the chemical modification and many cavities of various dimensions are clearly evident on the surface of modified peanut shells. Moreover, there are some especial chemical interactions between raw peanut shell and modifying agents, which lead to significant changes in the groups of raw peanut shell surface. Compared to raw peanut shell, cellulosic crystal style of modified peanut shells is not obviously changed, but the crystallinity of cellulose increased. Maximum sorption capacity of peanut shells for malachite green is obtained by modification of organic solvents (99.99 %), higher than that of raw peanut shells (80.22 %). The base treated peanut shells also enhance the malachite green sorption (94.32 %).

Taha and Azza *et al.* (2016) investigated the potential feasibility of peanut hull particle for removal of cationic dyes (methylene blue) from aqueous solution. The effect of various experimental parameters and optimal experimental conditions were examined. The peanut hulls was characterized by using XRF, FT-IR and SEM. FI-TR analysis showed that there were car-bonyl and hydroxyl groups on the surface of the adsorbent which improve its surface for adsorption and contain capillaries tubes showed by SEM analysis. The equilibrium ad-sorption data of methylene blue on peanut hulls were ana-lyzed using Langmuir, and Freundlich models. The isothermal data for biosorption fitted the Langmuir and Freundlich.

Sharma et al. (2017) evaluated the performance and feasibility of various agro and horticultural waste sorbents such as Petha (*Benincasa hispida*) waste (PW), discarded potato (*Solanum tuberosum*) waste from cold storages (DPWC) and almond seed (*Prunus dulcis*) shell waste (ASSW) to remove chromium (VI) from the aqueous solutions. Impacts of pH, adsorbent dose, initial adsorbate concentration, temperature, contact time, adsorbent grain size and start up agitation speed on chromium removal efficiency were investigated. The highest adsorption was found at pH 4.5-5.0 with initial chromium concentration of 50 mg/L, at startup agitation speed 80 rpm, with adsorbent grain size 1.18 mm with adsorbent doses 10 g/L for petha waste and almond seed shell waste and 20 g/L for DPWC in first 45 - 135 minutes of contact time.

Equilibrium adsorption isotherms and kinetics were analyzed. The adsorption isotherm data were fitted to Langmuir, Freundlich and Tempkin isotherms.

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

2.7. CANDIDATE DYE AND ADSORBENT USED IN THE STUDY

2.7.1. Murexide dye

Murexide is an ammonium salt of purpuric acid. Murexide in its dry state has the appearance of a reddish purple powder and it is slightly soluble in water. In solution, its colour ranges from yellow in strong acidic pH through reddish-purple in weakly acidic solutions to blue-purple in alkaline solutions.

Murexide is used in analytical chemistry as a complexometric indicator for titrations and most often rare used as a colorimetric reagent for measurement of calcium and rare earth metals. Fig 2. gives the structure of murexide dye.

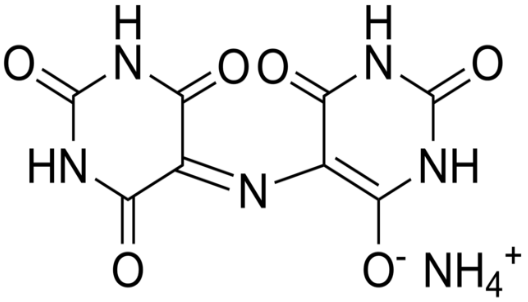


Fig. 2 Structure of Murexide dye

2.7.2. Peanut shell

Native peanut shells mainly consist of cellulose, hemicelluloses, proteins, polyphenols, luteolin and coarse fatness, *etc.* Among them, the amount of cellulose is about 65.7-79.3 %, which is the highest in peanut shells. Cellulose is a carbohydrate homopolymer consisting of β-D-glucopyranose units joined together by β-1 4-glycosidic linkages. The macromolecule contains three reactive hydroxyl groups at C-2, C-3 and C-6 atoms representing a favorable characteristic of peanut shells to be a potential adsorbent material.

2.8. Regeneration of adsorbent

Regeneration of adsorbents is an important process in the wastewater treatment to reduce the processing cost, recover adsorbates, and/or elucidate adsorption mechanism. Different regeneration techniques have been used for desorption study, which include thermal regeneration (steam and hot water) and chemical regeneration. However, for chemical desorption process, it is important to choose suitable pH and desorbents (such as inorganic desorbents: HCl, NaOH, H2SO4; organic desorbents: methanol, ethanol, acetic acid; or combination of both).

Sathishkumar et al. (2014) studied that the remazol brilliant blue Rloaded JCPAC was subjected to desorption under acidic and basic conditions. The results indicated that 1 N NaOH performed very well desorption, it released around 80% of dye molecules fromthe adsorbent.

Similar results were found by the alkaline solution in the desorption study of drimarine black CL-B noto lignocellulosic waste (2013).

The effect of different concentrations of NaOH solution (0.1–0.5 M)were checked on the desorption experiment. It was observed that the maximumdesorptionwas obtained at 0.4MNaOHsolution and showed that the ionic interaction was the primary removal mechanism (2013)

Zhang (2014) and Noreen (2014) also used NaOH solution as desorbent to perform desorption experiments. Malekbala et al. (2012) explored the desorption ability of cationic dyes (methylene blue and safranin) in acid solution (HCl). It was clearly seen that the desorption capacity decreased with increasing the concentration of HCl. This also indicated that the dyes were chemisorbed on the adsorbent.

Salman et al. (2011) investigated the percent desorption efficiencies of bentazon and carbofuran, using ethanol as desorbent. High percent desorption efficiencies were obtained for the pesticides with values of 84.1 and 82.2% after three cycles for bentazon and carbofuran, respectively.

Mhoan et al. (2011) employed methanol as a desorbent to desorb 2,4,6-trinitrophenol-loaded AC. The results showed that almost complete desorption of TNP could be achieved.

Achak et al. (2009) reported that desorption experiments were conducted on 1 g of adsorbent used with 100 mL of neutral pH water, water at pH 12, or water– acetic acid (pH 1.2), which were agitated at 200 rpm/min for 12h. The ability of desorption decreases was in order of acetic acid N neutral pH water (pH 7.3) N alkaline water (pH 12). This indicated that various mechanisms contributed to the adsorption of phenolic compounds on banana peel but chemisorption might be the main mechanism. Moreover, a few researchers used different desorbents to desorb the same spent adsorbent and compared their desorption efficiency.

2.9. Isotherm modelling studies

Equilibrium isotherm equations are used to describe the experimental adsorption data. The parameters obtained from the different models provide important information on the sorption mechanisms and the surface properties and affinities of the adsorbent. The most widely accepted surface adsorption models for single- solute systems are the Langmuir and Freundlich models. The correlation with the amount of adsorption and the liquid phase concentration was tested with the Langmuir and Freundlich isotherm equation.

The adsorption isotherms reveal the specific relation between the concentration of the adsorbate and its adsorption degree onto adsorbent surface at a constant temperature and they are fundamentally important in the design of sorption systems (Rafatullah, 2009).

2.9.1 Langmuir adsorption isotherm

Langmuir adsorption isotherm is based on the assumption that a point of valency exits on the surface of the adsorbent and that each of these sites is capable of adsorbing one molecules. Thus, the adsorbed layer will be one molecule thick. Further, it is assumed that all the adsorption sites have equal affinities for the adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site.

2.9.2 Freundlich adsorption isotherm

The Freundlich isotherm has also been employed to quantity equilibrium biosorption systems. The extent of biosorption is determined as a function of the equilibrium concentration of the metal in solution without reference to pH or other ions in the same aqueous system. The Freundlich isotherm is originally of an empirical nature, but was later interpreted as sorption to heterogeneous surfaces or surfaces supporting sites are occupied first and that the binding strength decreased with increasing degree of sites occupation.

2.10. PHYTOTOXICITY STUDIES

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

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

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

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

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

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

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

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

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

Phytotoxicity test of treated effluent was conducted on maize and sorghum, plants. The results indicated better plant growth in treated effluent (Mahmood *et al.,* 2015).

A detailed description of the methodology adopted for the present study is given in the following chapter.

3. MATERIALS AND METHODS

The methodology adopted for the present study “Adsorption of Murexide Dye from Aqueous Solutions using Peanut Shell” is discussed under the following headings:

3.1. Collection and preparation of peanut shell

3.2. Batch adsorption study

3.3. Decolourisation of murexide dye using peanut shell under optimal conditions

3.4. Desorption of dye

3.5. Isotherm modelling for bioadsorption studies

3.6. Structural characterization of peanut shell powder

- 3.6.1. Surface characterization of the adsorbent by Scanning Electron Microscope (SEM)
- 3.6.2. FT-IR Spectra of dye loaded and unloaded peanut shell

3.7. Phytotoxicity study

- 3.7.1. Selection of the experimental plant
- 3.7.2. Pot culture experiments
- 3.7.3. Germination percentage
- 3.7.4. Growth parameters
    - 3.7.4.1. Shoot length and root length
    - 3.7.4.2. Fresh weight
    - 3.7.4.3. Vigour index

3.8. Statistical analysis

3.1. COLLECTION AND PREPARATION OF PEANUT SHELL

Fresh biomass of peanut shell was collected from the local market of Karamadai, Coimbatore,Tamil Nadu and used as adsorbent for dye removal (Plate 1). The collected biomass was washed thoroughly with tap water to remove soil and dust, followed by distilled water and dried in an oven at 80^{o}C for complete dryness. Dry peanut shell was crushed into powder and sieved through a mesh to get fine particles (Plate 2) and stored in an air tight container for further use.

3.2. BATCH ADSORPTION STUDY

The batch adsorbent experiments were conducted to optimize various parameters namely dye concentration, pH, contact time, temperature and adsorbent dose to obtain optimum colour removal from dye solution. Batch studies were conducted with fixed amounts of adsorbents (100mg- 500mg) which were shaken separately in a rotary orbital shaker at 150 rpm in 100ml of the dye solution (50mg-600mg) at different temperatures (20-60^{o}C) and pH (2-10) for various incubation period (1-6 days) (Plate 3). The pH was adjusted using 0.1N NaOH and 0.1N HCl solutions. At the end of predetermined time intervals, samples were withdrawn from the shaker and the adsorbents were separated from the solution in a centrifuge for a period of 5 minutes. The absorbance of the supernatant was read in a colorimeter at 525nm to estimate the final dye concentration. All experiments were carried out thrice with respect to each condition and the average values were obtained. The percentage decolourization was calculated using the formula

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

PLATE 1

PEANUT SHELL

PLATE 2

PEANUT SHELL POWDER

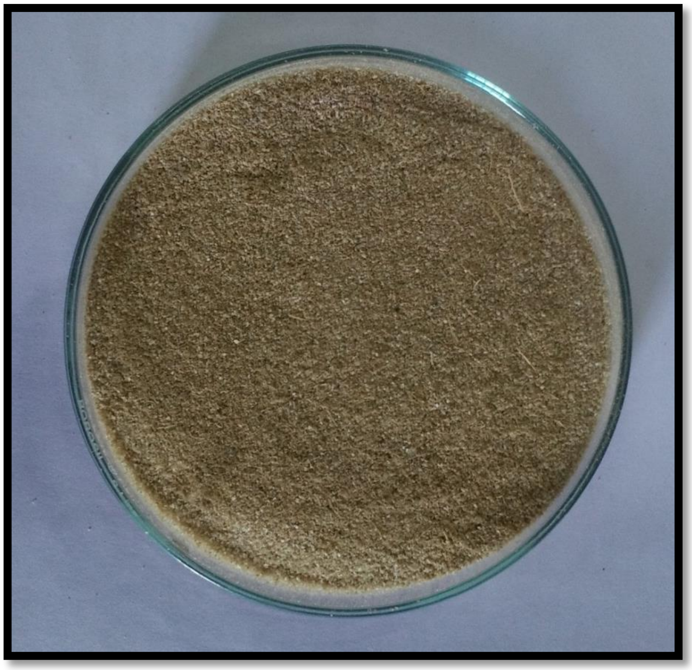


PLATE 3

EEXPERIMENTAL SET UP FOR DECOLOURISATION OF MUREXIDE DYE USING PEANUT SHELL

3.3. DECOLOURIZATION OF MUREXIDE DYE USING PEANUT SHELL UNDER OPTIMAL CONDITION

Under the optimal conditions, the peanut shell was added into murexide dye solution and the percentage decolourization was determined**.**

3.4. DESORPTION OF DYE

The dye adsorbed peanut shell obtained from the decolourization experiments was subjected to desorption using elutants. The peanut shell with dye was harvested, washed twice with distilled water and dried. The eluting reagents such as 0.1 NaOH and 0.1N HCl were used in the present study to examine desorption of dye from the peanut shell. The dried biomass (0.4g) was taken in 250ml Erlenmeyer flasks containing 100ml of each eluting reagent. The flasks were agitated for 30 minutes in shaker at 110 rpm. The liquid samples were withdrawn, centrifuged and analyzed for optical density to determine color intensity in the liquid using UV-VIS spectrophotometer. The desorbed biomass separated from the liquid phase was also mechanically destructed, grinded and washed with distilled water to remove colour from the peanut shell and analyzed for optical density.

3.5. ISOTHERM MODELING FOR BIOADSORPTION STUDIES

The isothermal adsorption study for murexide dye by the peanut shell was performed. In the isothermal studies, 100ml of different concentrations of the murexide dye (50-600 mg/100ml) were prepared in 250ml Erlenmeyer flasks. A fixed quantity of the adsorbent (400mg/ 100ml) was added to each flask and was kept at room temperature to obtain the sorption value before and after adsorption at 525 nm. The pot of Langmuir and Freundlich isotherm were drawn using these absorbance values.

3.6. STRUCTURAL CHARACTERIZATION OF PEANUTSHELL POWDER

3.6.1. Surface characterization of the adsorbent by SEM

In order to understand the mechanism of dye adsorption, the surface structure of untreated as well as peanut shell treated with murexide dye at a concentration of 100mg/100ml was analysed by Scanning Electron Microscope (SEM). The untreated and treatedpeanut shell was washed thoroughly with sterilized Triple Distilled Water (TDW), immersed in Glutaraldelyde (2.5% v/v) for 2 hrs at room temperature and washed thoroughly with sterilized Triple Distilled Water (TDW). The pellet was then subjected to Osmium tetraoxide staining (2% v/v) for 1 hr and washed thoroughly with sterilized TDW. Then, the pellet was dehydrated by transferring it into series of 25, 50, 70, 90 and 100 % (v/v) ethanol for 10 minutes. The dehydrated pellet was then dried overnight in an oven and mounted on a glass slide 120 stab with double – stick carbon tab followed by coating with a thin layer of gold under vaccum to increases the electron conduction and to improve the quality of the micrographs.

3.6.2. FT-IR Spectra of dye loaded and unloaded peanut shell

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

3.7. PHYTOTOXICITY STUDY

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

3.7.1. Selection of the experimental plant

Vigna unguiculata. L (Cow pea) was chosen for the study because of the following reasons: 1. It is very common food crop in Tamil Nadu with good nutritional value. 2. Germination period is very short. 3. Easy cultivation under laboratory conditions.

3.7.2. Pot culture experiments

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

3.7.3. Germination percentage

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

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

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

3.7.4. Growth Parameters

3.7.4.1. Shoot length and root length

The uprooted seedlings were washed in running water to remove soil particles and pressed between filter paper folds to remove water droplets before taking measurements. The maximum length of each shoot and root were recorded in cm.

3.7.4.2. Fresh weight

The seedlings were weighed and weight was expressed in gram per plant.

3.7.4.3. Vigour index

Vigour index was calculated as the product of germination percentage and plant height. The vigour index of each seedling was calculated using the formula

Vigour index = Germination percentage x (root length + shoot length)

3.7.5. Statistical analysis

The data obtained were statistically analysed by one way analysis of variance.

4. RESULTS AND DISCUSSION

The results of the present study are discussed under the following headings.

Phase I

4.1. Optimization studies for murexide decolourisation using peanut shell.

Phase II

4.2. Decolourisation of murexide using peanut shell species under optimal conditions.

PHASE III

4.3. Desorption of murexide dye

Phase IV

4.3. Bioadsorption using isotherm modeling studies.

Phase V

4.4. Structural characterization of peanut shell powder

- 4.4.1. Scanning electron microscope analysis (SEM)
- 4.4.2. FT-IR spectra of dye loaded and unloaded peanut shell

Phase VI

4.5. Phytotoxicity study

PHASE I

4.1. OPTIMIZATION STUDIES FOR MUREXIDE DECOLOURISATION USING PEANUT SHELL

4.1.1. Effect of dye concentration on decolourisation

The murexide at the concentration of 0.1g showed maximum decolourisation of 77 per cent by peanut shell within 4 days of incubation and minimum decolourisation of 31 per cent was observed at 0.6g. From Fig 3 it was clear that by increasing the dye concentration the decolourisation is decreased considerably.

The effect of dye concentration on dye decolourization was presented in Fig 3.

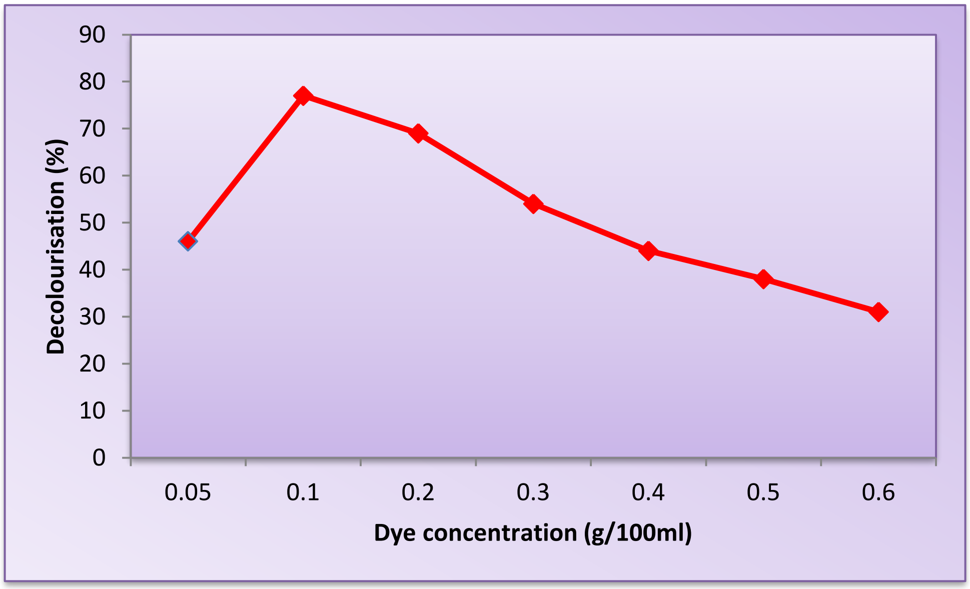


Fig 3- Effect of dye concentration on decolourisation

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

Similar such study was done by the effect of initial Eriochrome Black T (EBT) concentration on the adsorption efficiency at different concentrations (50, 70, 90 and 120 mg/l). It was obvious that the removal percentage of EBT decreased with the increase in initial dye concentration. This can be explained by the fact that the increase in initial dye concentration intensifies the interaction between peanut shell and EBT. Kumar *et al*., (2010) reported that the removal percentage was found to be 85.34% for 50 mgl^{-1} of initial concentration, while at $120mg.L^{-1}$ this value was 62.41%.

Jin (2015) also carried out the bioadsorption study at different dye concentrations ranging from 40mg/L to 240mg/L. The percentage adsorption of crystal violet from aqueous solution onto almond shell decreases with increasing initial dye concentration. The decrease in percentage adsorption with increasing dye concentration is due to the saturation of available active sites of the adsorbents at higher concentration of dye molecules.

Similar such result was observed by Karadge *et al*. (2007) who reported that adsorbent dose at $1gL^{-1}$ exhibited maximum percentage removal of dye. The percentage of congo red removal decreases with increase in its concentration, however actual amount of the dye adsorbed is increased. This is due to increase in congo red concentration, surface area, and active sites of the adsorbent were saturated and hence percentage removal decrease.

4.1.2. Effect of adsorbent dose on murexide decolourisation

In order to find out the optimum adsorbent dose for high percentage decolourisation, peanut shell of varying concentration from 100-500mg was in added into the aqueous solution amended with 100mg of dye.

The effect of adsorption dose on dye decolourisation was presented in Fig 4.

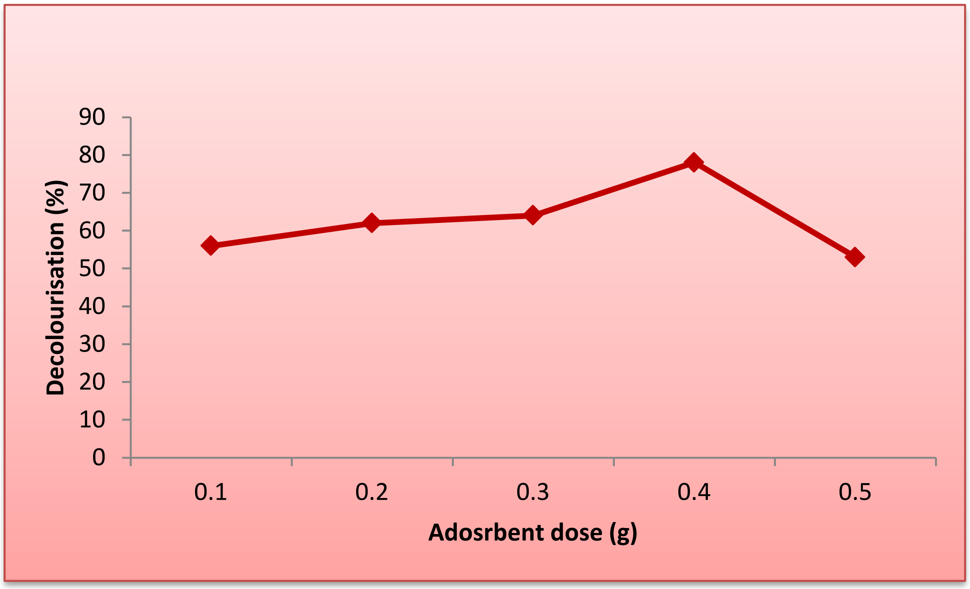


Fig 4- Effect of adsorbent dose on murexide decolourisation

The percentage removal of dyes was studied by varying the adsorbent dose between 0.1 g and 0.5 g at a dye concentration of 100 mg/100ml. An attempt to enhance dyes removal was evaluated by examining the effect of adsorbent dosage. As shown in Fig.4, it is apparent that the removal percentage of dye increases as the adsorbent amount increases and then becomes constant. The removal increased with increased amount of peanut shell up to 0.4g with a maximum efficiency 78% removal after which an increase in adsorbent dosage does not further improve the dye removal, implying that a complete dye removal could not be achieved even though using large amount of the adsorbents (Gode and Pehlivan, 2005). When too much adsorbent was added into the dye solution, the transportation of dye ions to the active adsorption sites will be limited as well, hence reduced the adsorption efficiency (Araujo and Teixeira, 1997).

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

Cao *et al*. (2014) explained that the adsorption capacity of almond shell decreased with increasing adsorbent dose. The decrease in the adsorption capacity of the adsorbent with increasing adsorbent dose may be due to the aggregation of the adsorbent particles on the active surface of the adsorbent. The adsorbent remain unavailable for the binding of dye molecules, and thus it results in the decrease of adsorbent capacity.

The results of the present study coincides with the findings of Karkmaz *et al*. (2014) and Brillas *et al*. (2014), who reported that the treated rice husk showed higher adsorption capacity at 0.8g and 1.2g of adsorbent respectively. The adsorption rate decreased initially and then become constant. Increase in adsorption at lower adsorbent does was attributed to the availability of more adsorption sites, which usually decreases at higher adsorbent dose due to the particle interactive 53ehaviour like aggregation that ultimately lead to decrease in total surface area of the bioadsorbent.

4.1.3. Effect of incubation period on murexide decolourisation

The effect of contact time was observed for a time period ranging from 1 to 6 days and the results were presented in Fig 5. The results of the present study show that the percentage decolourisation of murexide by peanut shell was (84) at 4th day of incubation.

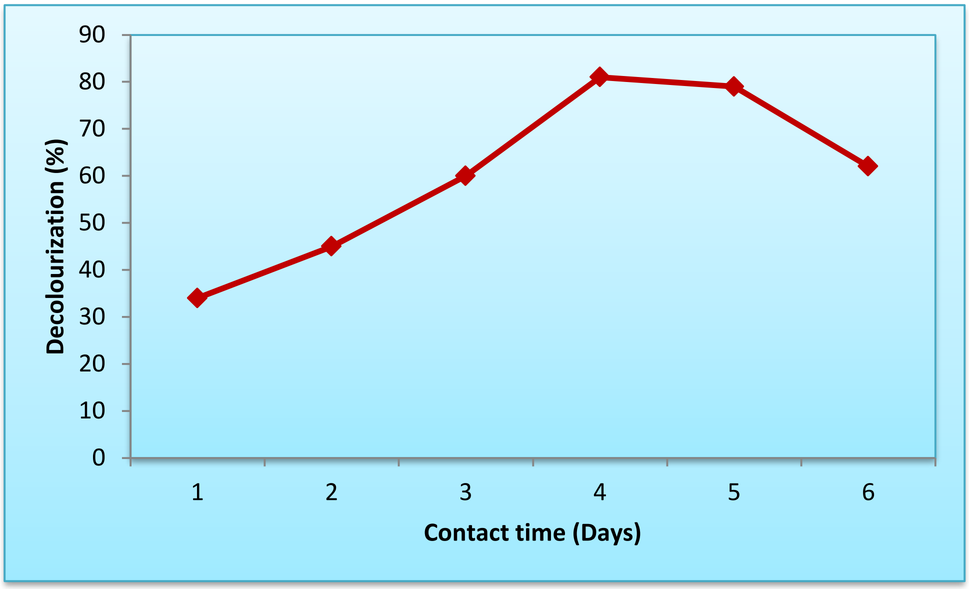


Fig 5- Effect of incubation period on murexide decolourisation

Contact time can be effective on adsorption processes. For a fixed concentration of reactive dyes and a fixed adsorbent mass, the retention reactive dyes increased with increasing contact time.

The rate of removal of the adsorbate is higher in the beginning due to the large surface area of the adsorbent available for the adsorption of dye ions (Hameed and Ahmad, 2009). After a certain period, only a very low increase in the dye uptake was observed because there are few active sites on the surface of sorbent. From the contact time studied, it was revealed that 4 days of incubation time is sufficient to reach equilibrium when 0.1mg/100ml of dye concentration was employed. Therefore, equilibrium time of 4 days was selected for the adsorption of the dye for further studies. It was found that an increase in the dye concentration had caused a decrease in the percentage of dye removal. This is due to the saturation of the sorption sites on the adsorbents as the concentration of the dye increased. A similar observation was reported for the adsorption of malachite green on oil palm trunk fibre (Hameed and Khaiary, 2008).

Brillas *et al.* (2004) reported that the maximum adsorption of Murexide and Brilliant Vital Red dyes occurred when contact time was 30 minutes. After that, adsorption rate decreased first and then become constant because of all available sites on urea modified rice husk.

Tilaki *et al*. (2014) observed that initially the number of surface sites are very large on the adsorbent and that allows rapid adsorption. But as the time period increase, the active sites get saturated, thus slowing down the rate of adsorption.

Generally the rate of removal of dye increases with an increase in contact time to a certain extent. Further increase in contact time does not increase the uptake due to deposition of dyes on the available adsorption site on adsorbent material. At this point, the amount of the dye desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of the dye being adsorbed onto the adsorbent. The time required to attain this state of equilibrium is termed the equilibrium time, and the amount of dye adsorbed at the time reflects the maximum adsorbent capacity of the adsorbent under those operating conditions (Deokar and Sabale 2014 and Bharathi and Ramesh 2013).

4.1.4. Effect of pH on murexide dye decolourisation

The effect of pH on dye adsorption was studied in the range of 2 to 10. The adsorption capacity for the peanut shell was maximum at pH 5, (84%) and further increases in pH gradually decrease the adsorption percentage and minimum of 18% adsorption was recorded at pH 10.The effect of pH on dye decolourisation was presented in Fig 6.

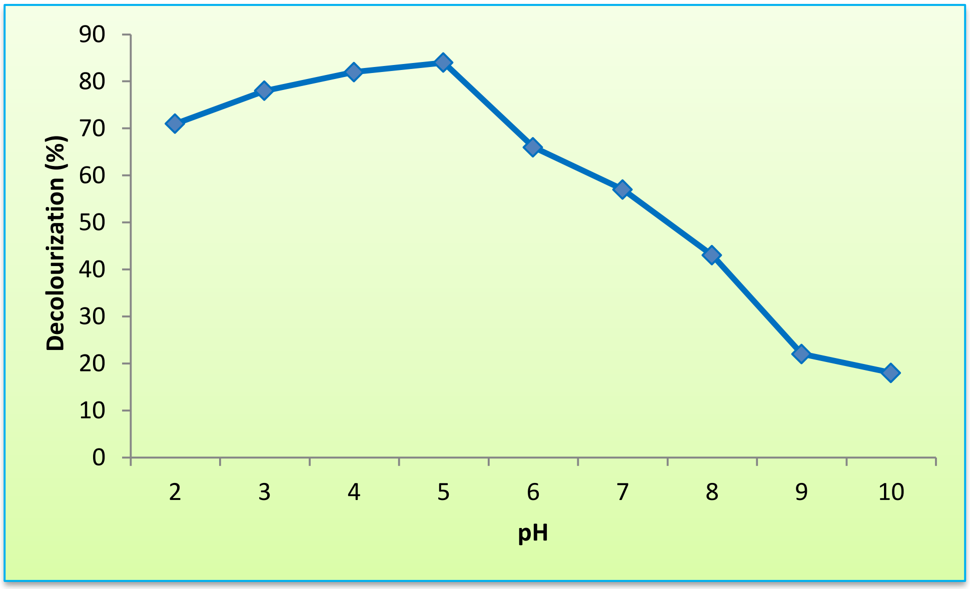


Fig 6- Effect of pH on murexide decolourisation

pH is a key parameter that enhance dye adsorption. The rate of adsorption varies with the pH of an aqueous medium. The pH of a medium controls the magnitude of electrostatic charge which are important by the ionised dye molecules (Onal *et al*. 2006 and Ansari *et al*., 2011).

Solution pH is one of the most critical parameters in the adsorption process and pollutants removal from aqueous solutions (Mahvi *et al*. 2012, Shokoohi 2010 and Nagda 2007).

Several reasons may be attributed to dye adsorption behavior of the adsorbent related to solution pH. The electrostatic attraction as well as the organic properties of the adsorbent and structure of dye molecules play an important role in dye adsorption. Thus a competition between the protons and hydroxyl ions for adsorption occurs. Under acidic condition the dye uptake is higher as compared to the basic and neutral conditions. When pH is raised the charge of the dye becomes negative and the interaction between the dye and adsorbent decrease which in decrease in adsorption of dye. The surface of the adsorption peanutshell has hydroxyl ions (OH^-). Which might have completed with the dye which is acidic in nature when dissolved in water.

Thus the pH value of the solution is an important process controlling parameter in the adsorption of dye. At an acidic pH condition, the hydroxyl groups on the surface of peanut shell gets attracted to the dye and promote the binding of dye.

4.1.5. Effect of temperature on murexide dye decolourisation

The effect of temperature was studied in the range of 20^o C to 60^o C. The percentage dye removal was maximum at 30^oC (72%) and further increases in temperature from 40^o C to 60^o C could not increase the dye removal capacity instead a decrease was observed from 46 % to 11% respectively (Fig 7).The observations showed the optimum temperature for dye removal was noticed to be 30^oC. The effect of temperature on dye decolourisation was depicted in fig 7.

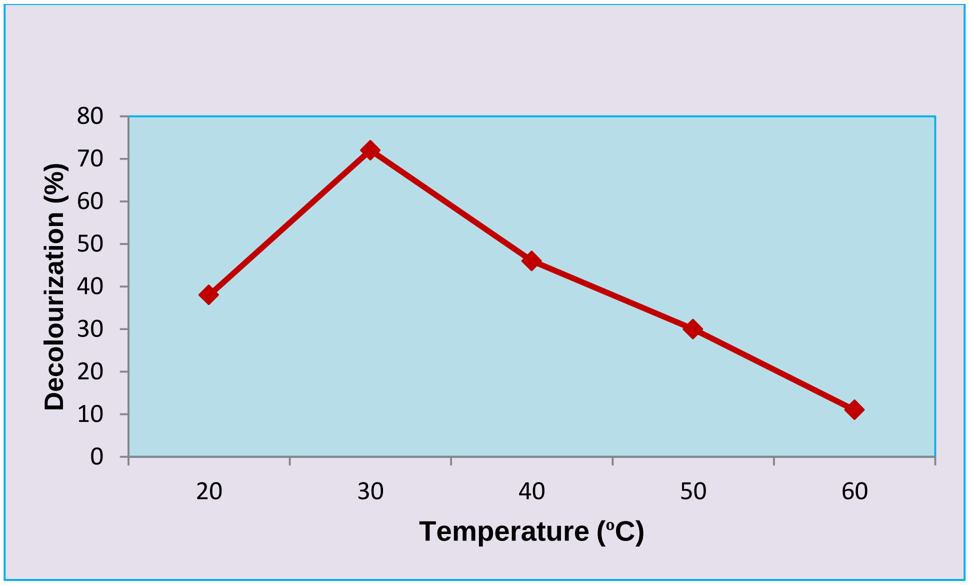


Fig 7- Effect of temperature on murexide decolourisation

Temperature is a significant parameters because it will changes the adsorption capacity of adsorbent (Argun *et al.* 2009). Adsorption is normally exothermic in nature.

The initial increase in the adsorption rate may be due to increase in surface area of the adsorbent. Further increase in temperature could result in the loss of active surface area due to prolonged exposure to high temperatures which have resulted in low dye removal at higher temperature.

Temperature has two significant effects on the adsorption. Increasing the temperature has a known effect to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. In addition, changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate (Alkan *et al.* 2008 and Tekin *et al.* 2005). Therefore, effect of temperature on the removal of dyes was investigated at three different temperatures, i.e. 10°C, 25°C and 40°C.

Rehma *et al. (*2013) also explained that at higher and lower temperature, adsorption efficiency of dye decreases. This decrease in adsorption efficiency was attributed to the fact that at high temperature Murexide and Brilliant Vital Red dyes molecules move with larger speed and less time of interaction was available for the adsorbate with urea modified rice husk.

PHASE II

4.2. DECOLOURISATION Of MUREXIDE USING PEANUT SHELL SPECIES UNDER OPTIMAL CONDITIONS.

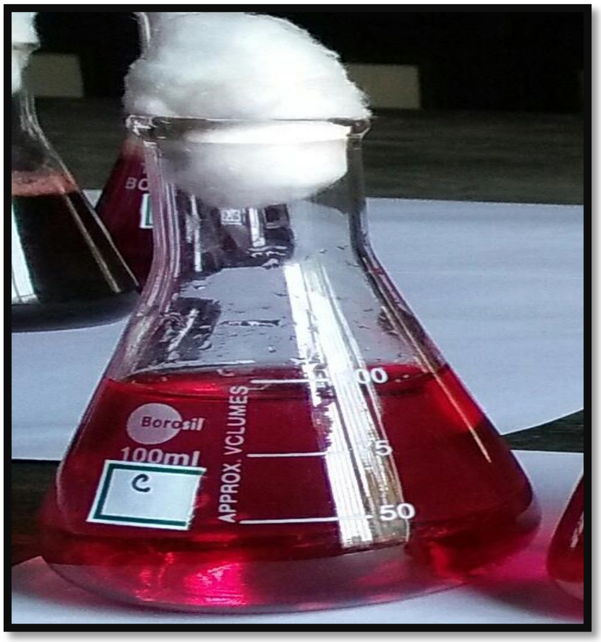
From the batch adsorption studies it can be concludes that the most efficient operational parameters in the current study were found to be, pH of 5, temperature of 30°C, adsorbent dose of 0.4g, and contact time of 4th day (peanut shell) for the decolourisation of 0.1gm of murexide dye solution using peanut shell (Plate 4).

PHASE III

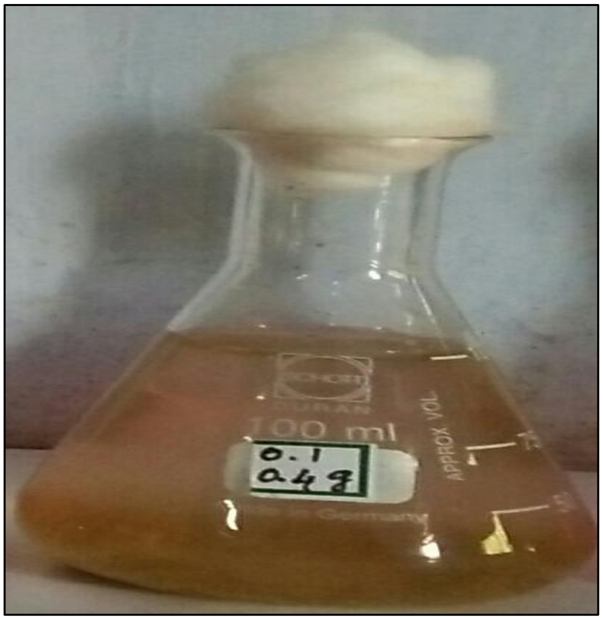
4.3. DESORPTION OF MUREXIDE DYE

The extent of desorption of colour from the adsorbent depends upon the hydration of dyes, functional groups of the cell wall and their respective binding strength. Desorption experiments were conducted with peanut shell using 0.1N HCl and 0.1N NaOH so as not to destruct adsorbent structure. A marginal desorption (10%) of the sorbed colour was observed with distilled water. Maximum desorption of 70% for 30 minutes contact time using 0.1N HCl was observed in peanut shell where as NaOH 0.1N desorbed only 52% of dye from the aqueous

PLATE - 4



Untreated murexide dye



Murexide dye treated using Peanut shell

solution. No significant increase in desorption of color was observed with increased contact time between the bioadsorbent and the eluting agent. This indicates intracellular uptake of dye by the adsorbent. Effective desorption of the color could only be possible after complete destruction of the biomass.

PHASE IV

4.4. BIOSORPTION ISOTHERM MODELING STUDIES

Equilibrium study on adsorption provides information on the capacity of the adsorbent. An adsorbent isotherm is characterized by certain constant values, which express the surface properties and affinity of the adsorbent. It is also been used to compare the adsorptive capacities of the adsorbent for adsorbates.

M – Weight of adsorbent (mg)

C_e – Concentration of dye at equilibrium

$K_1{}'$ and K_1 – are the Langmuir constants which are the measures of adsorption capacity and maximum energy of absorption respectively.

The Langmuir isotherm equation is given as

$$X/m= (K_1{}'C_e/ 1 + K_1{}'C_e)$$

Where,

X – Amount of dye adsorbed (mg/l)

The essential features of Langmuir adsorption isotherms can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter ‘R_L’ which can be used to predict whether a sorption system is favourable or unfavourable in batch adsorption process. R_L was calculated from Langmuir isotherm based on the following equation.

$R_L = 1/(1+bC_i)$

Where, C_i = initial concentration of the dye (mg/l)

b = Langmuir constant ($K_1^{'}$)

R_L Value	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$R_L < 1$	Favourable

The Freundlich adsorption isotherm is used to study the relationship between the magnitude of adsorption and pressure. The Freundlich adsorption isotherm is given by the equation,

$x/m = k_f\, C_e^{\,1/n}$

$\log x/m = \log k_f + 1/n \log C_e$

Where,

x/m is the amount of dye adsorbed on unit weight of adsorben in equilibrium.

C_e is the concentration of solute in aqueous solution

K_f and 1/n are Freundlich constants related to the adsorption capacity and adsorption intensity respectively.

Two isotherm models were used to analyze the equilibrium curve at different initial dye concentration. The linearcorrelation coefficient of determination (*R*2) was used as an error function to evaluate the fitness of each isotherm equation obtained for the two isotherm models Vigneshpriya *et al., (*2017).

In the present study, the calculated values of R_L are observed to be in the range of 0.936076 to 0.861247 at 4 days of incubation period indicating that the adsorption of murexide onto the biosorbent was favourable, for Langmuir model.

The Freundlich model does not fit and R_L value was greater than 1 and found to be unfavourable.

The results of the present study coincides with the findings of Kumari and Abraham (2007) who reported that the non-viable biomass of peanut shell showed an optimal fit to Langmuir.

Thus the present study indicated that peanut shell promising bioadsorption capacity of murexide and highlighted the possible exploitation in dye polluted habitat.

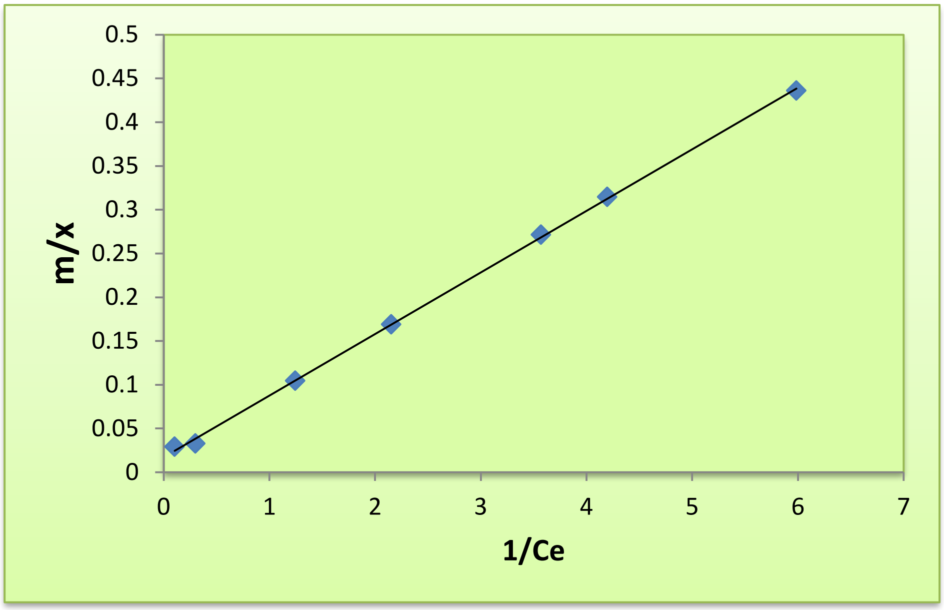


Fig 8 - The linearized Langmuir adsorption isotherm of murexide dye (100mg/100ml)

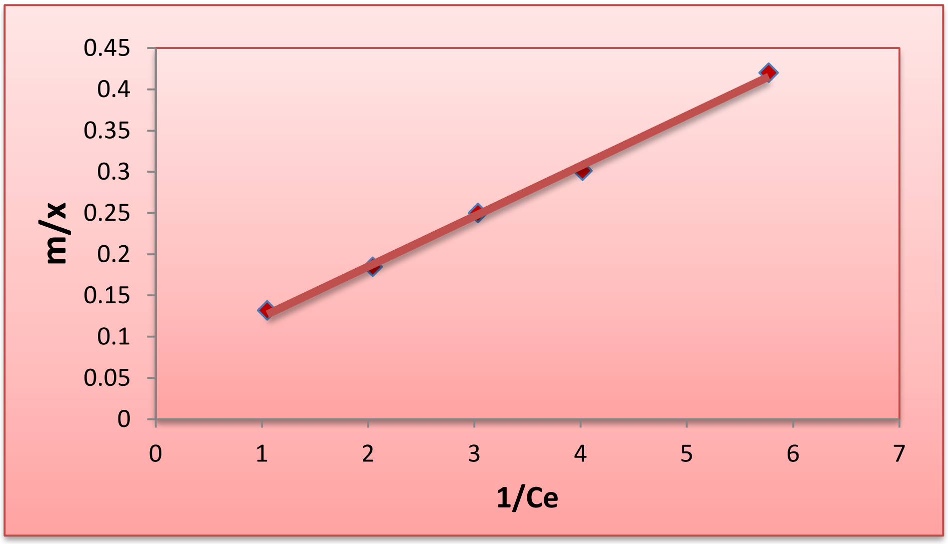


Fig 9 - The linearized Langmuir adsorption isotherm of peanut shell (100mg/100ml)

Table 1

Adsorption of murexide dye concentration Langmuir Adsorption Isotherm

LANGMUIR ADSORBENT ISOTHERM							
Incubation period (Days)	**Adsorbent dose (mg)**	**Amount of dose left (Ce)**	**1/Ce**	**m/x**	**Separation factor (R_L)**	**Intercept K_1/K_1**	**Slope $1/K_1$**
4	50	7.56	0.1046	0.029	0.936076	0.15752	1.7656
	100	9.05	0.3021	0.0328	0.851750		
	200	8.70	1.2458	0.1045	0.765031		
	300	8.23	2.1538	0.1689	0.732740		
	400	7.52	3.5710	0.2715	0.693274		
	500	6.7	4.1987	0.3145	0.725431		
	600	6.5	5.9871	0.4358	0.861247		

Table 2

Adsorption does of murexide dye by peanut shell in terms of Langmuir Adsorption Isotherm

LANGMUIR ADSORBENT ISOTHERM							
Incubation period (Days)	**Adsorbent dose (mg)**	**Amount of dose left (Ce)**	**1/Ce**	**m/x**	**Separation factor (R_L)**	**Intercept K_1/K_1**	**Slope $1/K_1$**
4	100	6.17	0.1053	0.1104	0.951861	0.02922	0.94431
	200	7.32	0.7692	0.7632	0.842860		
	300	8.23	0.1213	0.1215	0.774031		
	400	9.15	0.1327	0.1328	0.735244		
	500	7.52	0.0303	0.1125	0.68374		

PHASE V

4.4. STRUCTURAL CHARACTERIZATION OF PEANUT SHELL

4.4.1. Scanning Electron Microscope analysis (SEM)

Scanning Electron Microscopy was done to observe the surface characteristics of the adsorbents well before and after adsorption. The scanning electron microscopy of the adsorbents at specific resolution and magnification was depicted in Plate 6a and Plate 6b.

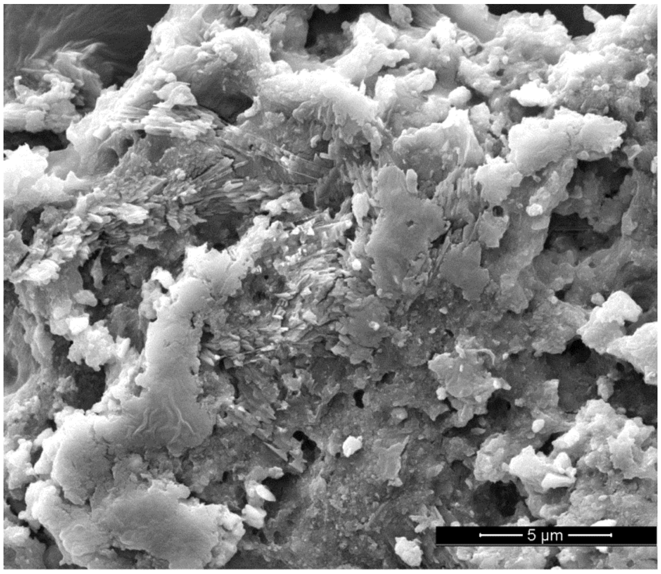
SEM is widely used to study the morphological features and surface characteristics of the adsorbent materials. It also reveals the surface texture and porosity of adsorbent. SEM provides high magnified image of the surface of the material. It images the electrons that are reflected from a sample.

The presence of cavities in plate 5a shows that there are large irregular fragments on the surface morphology of raw peanut shell. While Plate 5b illustrates that the surface of the peanut shell becomes smooth due to the adsorption of murexide which plays and important role in determining the adsorption of dyes on adsorbents.

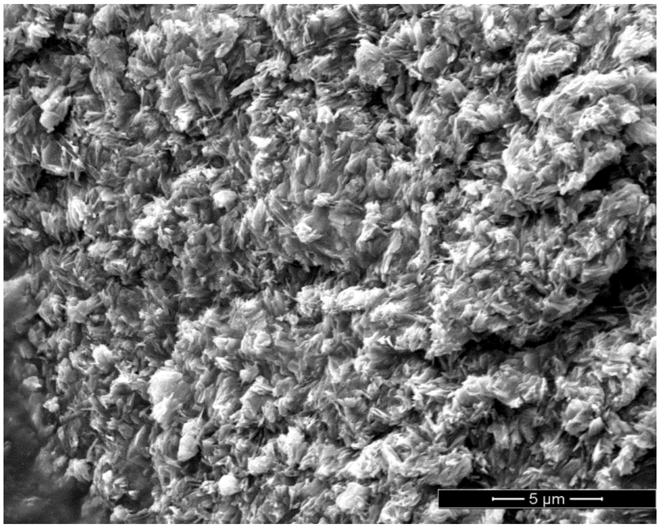
Sharma, et al. (2016) reported that the porous structure found in adsorbent surface collapses to some extent which may be due to the fact that adsorbent being a natural biological material changes its characteristic.

PLATE 5

SCANNING ELECTRON MICROGRAPHS DEPICTING THE EFFECT OF MUREXIDE DYE ON THE PEANUT SHELL



(a) PEANUT SHELL BEFORE ADSORPTION OF MUREXIDE DYE



(b)PEANUT SHELL AFTER ADSORPTION OF MUREXIDE DYE

4.4.2. FT-IR Spectra of dye loaded and unloaded peanut isolates

Fourier Transform Infra Red is the preferred method of infra red spectroscopy. In infra red spectroscopy, IR radiation is passed through a sample. Some of the infra red radiation is absorbed by the sample. The resulting spectrum represents the molecules absorption and transmission creating a molecular fingerprint of the sample.

The dry powdered samples of peanut shell were subjected to Fourier Transform Infra Red analysis which resulted in many functional groups based on the wavelength and percentage of transmittance. Surface characterization of peanut shell by FT-IR analysis without and with adsorbed murexide was shown in plate 6a and 6b. The complex nature of the biomass examined is indicated by a number of absorption peaks in the control sample. The spectra of decolourised sampled reveals shifting of some characteristic bands, which depict changes in functional group after decolourisation compared to untreated dye sample.

FT-IR frequencies of peanut shell before and after dye adsorption were presented in plate 6a and 6b. The band at 3410.15 cm^{-1} was shifted to 3433.29 cm^{-1} due to O-H stretching vibration, which indicates the presence of alcohols and phenols The peak shift from 1257.59 cm^{-1} to 1265.30 cm^{-1} is due to C-O stretching and 1153.43 cm^{-1} to 1157.29 cm^{-1} represents the C=O stretching vibrations and the presence of amide groups. Minor peaks at a 509.21 cm^{-1} to 478.35 cm^{-1} indicate the involvement of S-O groups in the decolourisation of the dye. New peaks (2337.72, 2291.43, 2167.99, 2086.98, 2067.69, 2032.97, 1994.40, 1978.97, 1724.36, 1724.36, 1265.30cm^{-1}) were noted in the dye treated solution with peanut shell indicating the decolourisation of the dye.

On the basis of the change in the band, it was reasonable to assume that the peak value suggested the coordination of the dye with hydroxyl or carboxyl or amino groups, which may increase the hydrogen bodings or forms ligands between the dye and the cell wall.

Considerable difference between the FT-IR spectrum of control murexide and the metabolites obtained after complete decolourization by peanut shell confirmed the biodegradation of dye into different metabolites.

The peak results in the sample give the functional group this analysis had eventually confirmed the difference between functional groups in relation to biosorption of murexide dye.

PHASE VI

4.5. PHYTOTOXICITY STUDY

The results of germination percentage, root length, shoot length, fresh weight, dry weight and vigour index of cow pea seedlings grown with tap water (T_1), untreated murexide (T_2), and treated murexide (T_3), on 7th day favoured the growth of the experimental plant and the results were depicted in table 2. Plate shows the growth of cow pea on 7th day.

Germination percentage and vigour index

A maximum of 85 percent germination was recorded in cow pea seeds grown with tap water (T_1) followed by 52 percent in treated dye solution (T_3). A minimum of 6 percent germination was recorded in seeds grown with untreated dyesolution(T_1)

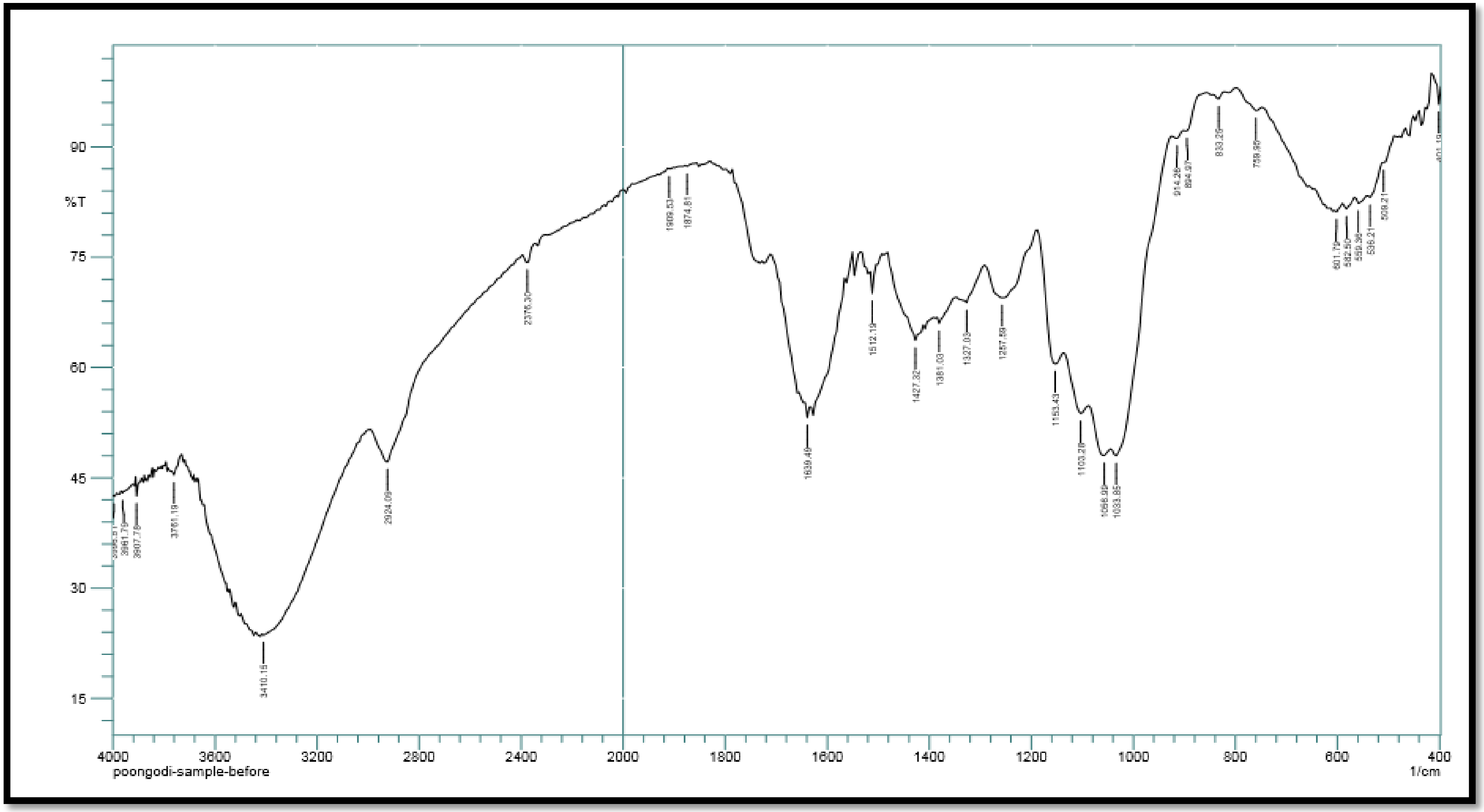


PLATE 6a - FT-IR SPECRTUM OF PEANUT SHELL BEFORE ADSORPTION

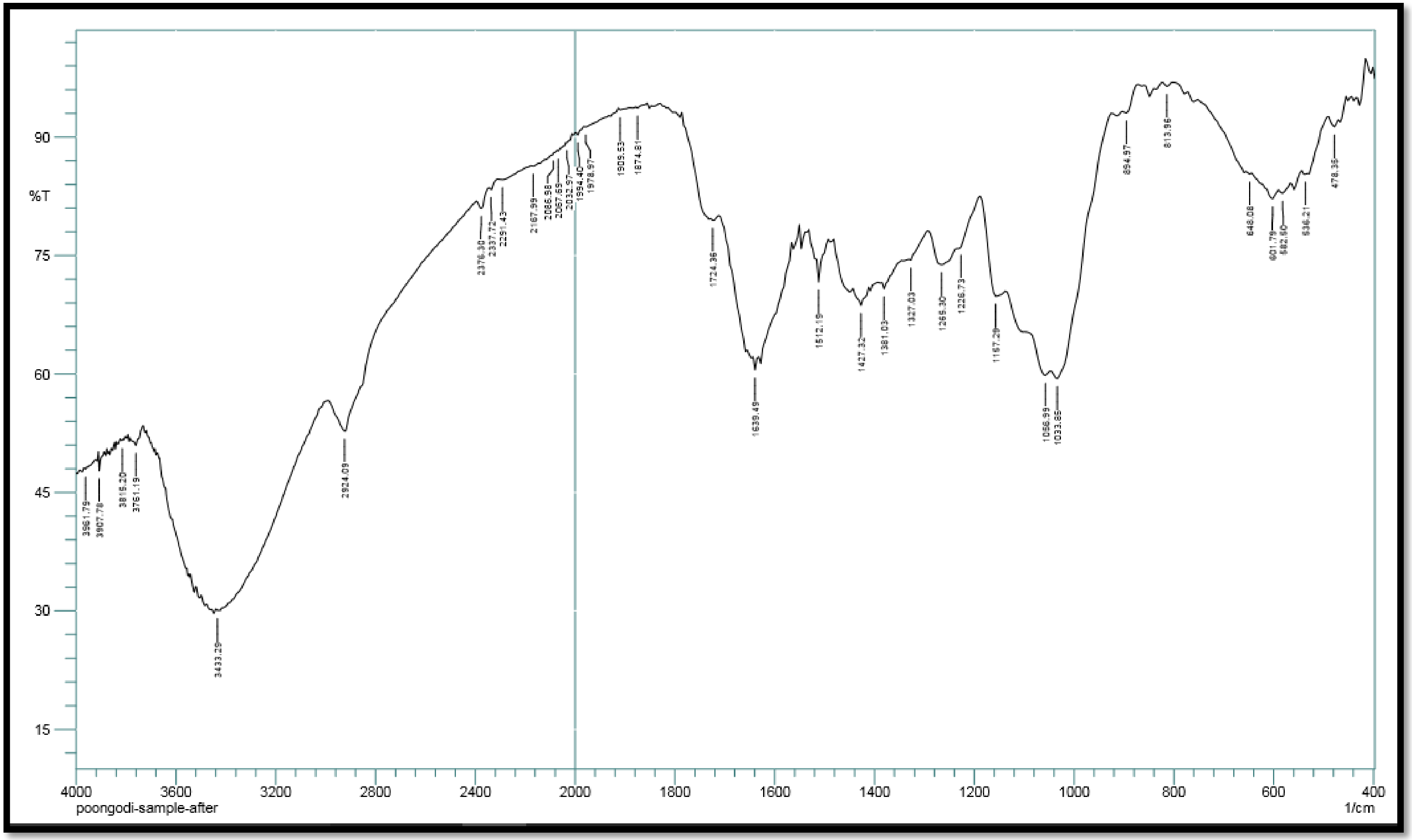


PLATE 6b - FT-IR SPECRTUM OF PEANUT SHELL AFTER ADSORPTION

The reduction in seed germination was also observed by several researches in various agriculture crops grown in dyeing (Kumar and Bishwas, 2005 and Rajeswari, *et al*., 2005), distillery (Virendra and Dhar, 2002 and Surendra *et al*., 2005), tannery (Thangavel and Balagurunathan, 2002) and pulp mill (Medhi *et al.*, 2008) effluents which supports the findings of present study.

The vigour index was maximum in T_1 (1752) followed by T_3 (764) and minimum was observed in T_2 (25) as shown in table 2. Decrease in the vigour of seeds irrigated with untreated murexide observed in the present study might be due to the interaction of different pollutants with the developing radical. Seed vigour may also be correlated with physiological and chemical properties of axes than with those of whole seeds (Andersan and Abdhul Baki, 1971).

Shoot length and root length

Shoot length of seven days old cow pea seedlings after treatment with tap water (T_1), untreated murexide dye (T_2), and treated dye (T_3) were recorded in Plate 7 shows the shoot length and root length of 7 days old cow pea.

The values recorded for the shoot lengths of cow pea seedlings were 12.2, 1.0 and 9.83 cm in T_1, T_2 and T_3 respectively. The values recorded for the seedlings grown in treated dye (T_3) were highly significant when compared with untreated dye (T_2). The root length of cow pea was maximum (7.6cm) in T_1, followed by T_3 (3cm) and minimum (0.22 cm) in T_2. T_1 showed an increase in root length when compared to T_2 and T_3 plants.

PLATE 7 – POT CULTURE SUPPORTING THE GROWTH OF 7 DAYS OLD COW PEA

T_1 T_2 T_3

T_1 T_2 T_3

PLATE 8 – ROOT LENGTH AND SHOOT LENGTH OF 7 DAYS OLD COW PEA

T_1 – Tap water

T_2 - Untreated murexide dye solution

T_3 – Treated dye solution

Table 3

Biometric parameters in 7 days old seedlings of cow pea grown with different treatments

Treatments	**Germination percentage**	**Shoot length (cm)**	**Root length (cm)**	**Fresh weight (g)**	**Dry weight (g)**	**Vignour index**
T_1	85	12.2	7.60	0.42	0.210	1752
T_2	6	1.0	0.22	0.05	0.030	25
T_3	52	9.83	3.0	0.20	0.135	764
SED		0.7524	0.7824	0.0308	0.0175	
CD (5 %)		2.1545	2.0121	0.1126	0.0412	

The values are mean of triplicates

T_1 – Tap water

T_2 – Untreated murexide dye solution

T_3 _ Treated murexide dye solution

From the above results it was observed that the reduction in shoot and root length of seedlings grown using T_1 might be due to the presence of higher dye concentration of dye which exhibited the uptake of micro and macro elements by plant system. Murexide treated with peanut shell has been reported to favour root and shoot length due to the translocation of nutrients to the plants (Jothumani and Elayarajan, 2003).

Fresh weight and dry weight

The fresh weight of cow pea seedlings treated with different treatments were depicted in table 7. The highest fresh weight (0.42 g) was observed in T_1, followed by treated dye T_3 (0.20 g) and least value (0.20 g) was recorded in T_2. The dry weight of cow pea was maximum (0.21 g) in T_1 and minimum (0.030 g) in T_2 and T_3 recorded (0.136 cm). There was an increase in the fresh and dry weight of T_1 plants when compared with treated dye and T_2 plants.

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

5. SUMMARY AND CONCLUSION

Synthetic dyes released into the environment cause considerable water and soil pollution because they may be toxic carcinogenic, mutagenic and clastrogenic to living organisms. Over the last two decades, awareness and concern about the environmental and health hazards of synthetic dyes is increasing in the global community. Consequently, environmental and government legislations are becoming more and more stringent regarding the removal of these pullutants from industrial waste waters.

Different physical and chemical methods have been employed for the treatment of effluent released from the textile industries. These methods mostly suffer from serious limitations like high cost, low efficiency, limited versatility and production of secondary pollution.

In contrast bioadsorption is a cost effective, efficient, biofriendly and environmentally benign method for the removal of dyes from industrial waste waters. It is the application of adsorbents for the removal of xenobiotics from polluted environment in which harmful synthetic substances are converted into simple, less toxic or completely benign products.

An attempt to highlight the potential of adsorption process for the elimination of dye molecules from industrial wastewater is carried out. Peanut shell was collected from Karamadai, Coimbatore. The effect of various physico-chemical experimental conditions that affect the dye adsorption such as solution pH, initial dye concentration, contact time, adsorbent dose and temperature were studied in the present work. Under optimized condition peanut shell was subjected for effective decolourisation of murexide by the selected sample. The peanut shell were subjected to FT-IR spectral and SEM analysis before and after treatment with murexide dye. The untreated and treated murexide dye on the biometric parameters such as germination percentage, shoot length, root length, fresh weight and vigour index of cow pea was studied on 7th day after sowing.

Findings of the study,

- The study showed that dye concentration, adsorbent dose, temperature, pH, and contact time played a major role in adsorption.
- The percent decolourization was maximum in 0.1g of dye amended aqueous solution in concentration for peanut shell (78 %).
- The effect of adsorbent dose on decolourization of dye indicated maximum dye removal (78%) at 0.4gm of peanut shell. Adsorption efficiency decreased with further increase in adsorbent dose.
- An increase in temperature showed an initial increase in adsorption percentage and maximum adsorption was recorded at 30°C for peanut shell (72 %).
- The adsorption capacity for adsorbent peanut shell was maximum at pH 5, (84%). With further increase in pH, the adsorption percentage was gradually decreased.
- The effect of contact time on colour removal was observed from 1 to 6 days maximum dye removal was observed on 4th day of incubation.
- The experimental data fitted well in Langmuir and Freundlich adsorption isotherms.

- FT-IR analysis showed vibration frequency changes in the spectrum after dye adsorption. Peak shifting and intensification were observed which indicates the involvements of functional group in bioadsorption.
- The scanning electron microscopic study proved the accumulation of dye within the adsorbent surface.
- *Vigna unguiculata.*L grown with peanut treated dye solution exhibited significant germination percentage and growth parameters such as shoot length, root length, fresh weight and vigour index when compared with untreated dye solution. The plants grown with untreated dye recorded minimum growth when compared with treated and tap water plants on 7th day after sowing.

From the study it can be concluded that the low cost adsorbent like peanut shell have the potential for the decolourization of murexide dye. The phytotoxicity study also revealed that the treated dye solution is non-toxic and can be utilized for agricultural purpose.

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