STUDIES ON ADSORPTION OF THIONINE DYE FROM IT'S AQUEOUS SOLUTION OVER LOW COST BIOSORBENTS

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CERTIFICATE

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ABSTRACT

Pollution of water is due to the presence of colorants. It is a severe socio-environmental problem caused by the discharge of industrial wastewater. In view of their toxicity, non-biodegradability and persistent nature, their removal becomes an absolute necessity. The aim of the present study is to remove Thionine dye from aqueous solution using peanut hull and walnut hull, under optimized conditions. The concentration of dyes, amount of adsorbent and agitation time was optimized over different biosorbents. Natural Walnut Hull was found to show better dye removal efficiency than the Peanut hull. The removal efficiency increased with increasing the Peanut Hull concentration significantly and reached a value as high as 91.3% at lower concentrations (up to 10 mg/L) there as no significant change was observed at higher concentrations, on the other hand the removal efficiency reached 100% in case of walnut hull.

Spectrophotometric technique was adopted for the measurement of concentration of dyes before and after adsorption. The adsorption data was fitted to various kinetic Models and various adsorption isotherm equations. The characterization of adsorbent was done by using Scanning Electron Microscopy (SEM) in order to study the surface morphology. Fourier transform infrared (FT-IR) was done to study the bands which gives indication about the functional groups responsible for dye biosorption.

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CHAPTER-1

INTRODUCTION

The release of dyes into wastewaters from textile, biomedical, cosmetic and paper industries poses serious environmental problems. The coloration of the water by the dyes causes inhibitory effect on photosynthesis affecting aquatic ecosystems. The role of dyes in connection with variety of skin, lung and other respiratory disorders has been reported worldwide. Color removal from textile effluents is a major environmental problem and the most popular treatment methods are electro flocculation, ultra filtration, reverse osmosis and adsorption.(Thievarsu et al 2011)

Among these methods, adsorption is widely used method because of its ease of operation. Adsorption with activated carbon is very popular, but its high cost restricted its use. There is a constant search for cheaper substitutes. Many efforts have been made to use low cost agro-waste materials as a substitute for commercial activated carbon. For removal of dyes some agro waste materials were used such as Peanut Shell (Punnusami al., 2009), coir pith (Namasivayam and Kavitha, 2002), tamarind fruit shell (Somasekhara, 2006), rice hull (Sadon et al., 2012), orange peel (H. Benaïssa, 2005), wall nut shell (Sumanjit et al., 2008) etc.

Thionine is a strongly staining metachromatic dye that is widely used for biological staining of DNA. Thionin is useful for the staining of acid mucopolysaccharides. It is also a common nuclear stain and can be used for the demonstration of Nissl substance in nerve cells of the CNS (central nervous system). (Budavari,1996; Gurr.E, 1971). It can also be used to mediate electron transfer in microbial fuel cells (biosensors) and used for studying kinetics of heavy metals (Bagheri et al., 2011). Mostly it is used in the biomedical laboratories all over the world. The waste water containing thionine coming out from the medical and microbial laboratories and hospitals causes several harmful effects to the environment. When it is in touch with the human skin can cause nausea, vomiting, diarrhea and gastritis. It also affects photosynthesis of the aquatic plants and thus disrupts the ecosystem. As it has strong affinity (10^5 mol) with double strandes(ds) and single stranded (ss) - DNA and RNA (Begonaet al., 2012), so aquatic animals which consume thionine containing waste water may have thionine intercalation (Paul et al.,2012) in their genetic sequence and as a result may further produce genetically altered DNA to successive generation.

Thionine molecules have an ability for self association, thus it form dimers in an aquous solution with a dimerization constant of 6.60 $\times 10^{-5}$M in the temperature range of 25-75^{o}C. A tendency of forming aggregates or dimers even in dilute solutions strongly affects the photosynthesis and biological processes of aquatic organisms. (Ghasemi and Kubista et al. 2005). It's COD has been experimentally determined by an open reflux system and is found to be 640(mg/L) and BOD =768(mg/L)

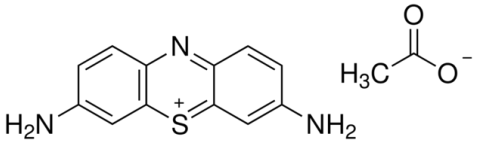


Figure 1:Thionine 3,7-Diamino-5-phenothiazinium acetate

Consequently, many investigators have studied the feasibility of using low cost substances, such as cocoa shell (Mylsamy et al.,2011) chitin (Cheung et al., 2003), peat(Ho and Porter et al., 2003), ash (Djordjevic et al.,2011), banana pseudostem fibers(Mas et al., 2009), Gulmohar leaves (Ponnusami et al.,2009), Bael leaf powder (Senthil et al.,2009) ,Pinecone(Askari and Hadi et al 2009), Coconut Copra Meal(Yuh-Shan and Ofomaja et al., 2006), mango peel (Olugben and Ahmad et al., 2011), Saw dust Oak (Etsuyankpa et al.,2012) etc as adsorbents for the removal of dyes from wastewater. The feasibility of low cost adsorbents for wastewater treatment have been shown in these papers.

The present investigation is an attempt to remove thionine dye from its solution by adsorption using a low cost adsorbents made from peanut-shell and walnut shell. Peanut shell and Walnut shell which otherwise are agricultural wastes thus can be used as a potential low cost biosorbent.

CHAPTER-2

LITERATURE REIEW

It has been found from many literatures that biosorbents have the potential to remove a wide variety of dyes. There is a need to develop biosorbents in a simple, inexpensive way and have a high biosorption capacity. The effectiveness of biosorption depends on the characteristics of the adsorbent, adsorbate, process variables and solution chemistry. The differences in the physical and chemical characteristics of the adsorbent and their dependence on process variables and solution chemistry make it difficult to compare between one another.

2.1. Literature Survey

Abbas et al., (2012) studied adsorptive removal of Congo Red and Brilliant Green dyes from water using Peanut Shell. They studied the effect of various factors on biosorption process such as contact time, pH, agitation speed, biosorption dose, particle size was studied. Study revealed that peanut shell adsorbs dyes by both chemisorptions and physiorption. Removal efficiency of congo red was found to be 15.09 mg/g and that of brilliant green 19.92 mg/g.

Alau et al., (2010) studied the adsorption of xylenol orange, remazole turquoise blue and procion red by neem (Azadirachta indica) husk carbon treated with $ZnCl_2$, H_3PO_4 and KOH at different concentrations, particle size, shaking time and adsorbent dosage. Adsorption studies were carried out using carbonized neem carbon, activated neem carbon and commercial adsorbent from coconut shell on xylenol orange, remazole turquoise blue and procion red. The study showed a high adsorption for remazol turquoise blue.

Altul et al., (2012) studied walnut shell adsorbent for the removal of Cr(VI) ions from aqueous solutions after treatment with citric acid. The modification reaction variables, such as citric acid level (5–10 g), reaction time (0–24 h), and temperature (110–130^oC) were studied in batch experiments. The rate of adsorption was studied under a variety of conditions, including initial Cr(VI) concentration (0.1–1.0 mM), amount of adsorbent (0.02–0.20 g), pH (2–9), temperature

and contact time (10–240 min). The isotherm Langmuir, Freundlich and D–R adsorption isotherms found equilibrium vales as q_e.=596(mg/g) and C_e=0.154 mmol/g for Cr(VI) ions, respectively.

Atay et al., (2006) studied the mechanism of methylene blue adsorption on biosolid. The effects of various experimental parameters, such as pH, biosolid dosage, contact time and initial dye concentration were investigated. The results showed that the dye removal increased with increase in the initial concentration of the dye and also increased in amount of biosolid used and initial pH. Adsorption data was modeled using the Freundlich adsorption isotherm.

Atkinson et al., (2004) investigated the application of biosorption technology to remediate metal-contaminated industrial effluents. It described the factors that must be considered when selecting bioremediation as a cleanup technology for inorganics. Biosorption technology, utilizing any natural form of biomass to passively adsorb and immobilize solubilised heavy metals or radionuclides, offers such an alternative.

Bian and Hu et al., (2011) described adsorption of methylene blue (MB) by peanut husk in batch and fixed-bed column modes at 293 K. The kinetic and equilibrium of adsorption in batch mode were studied. Nonlinear regressive method was used to obtain relative parameters of adsorption models. The kinetic process was better described by a pseudo-second-order kinetic model. The equilibrium adsorption was effectively described by Temkin adsorption isotherm. The value of q_m from the Langmuir model was 72.13±3.03 $mg.g^{-1}$ and the diffusion coefficient value was in the order of 10^{-8} cm^2 s^{-1}. The results were implied that peanut husk may be suitable as an adsorbent material for adsorption of MB from an aqueous solution.

Bhatnagar et al., (2004) studied the comparative adsorption with different industrial wastes as adsorbents for removal of cationic dyes from water. They carried the experiments over four adsorbents prepared from industrial wastes for removal of cationic dyes. This study showed that the adsorbents prepared from carbonaceous slurry are of good porosity and appreciable surface area and also adsorbs dyes to a good extent. The adsorption of two cationic dyes, viz., rhodamine B and Bismark Brown R on carbonaceous adsorbent conforms to Langmuir equation, is a first-order process and pore diffusion controlled. It was found that prepared carbonaceous adsorbent

exhibits dye removal efficiency that is about 80-90% of that observed with standard activated charcoal samples. Thus, it can be fruitfully used for the removal of dyes and is a suitable alternative to standard activated charcoal in view of its cheaper cost.

Brown et al., 2000 in their study assessed the potential of peanut hull pellets to capture metal ions from wastewater and compared their performance to that of raw peanut hulls and a commercial grade ion-exchange resin. The uptake of $Cu2^{+}$, $Cd2^{+}$, $Zn2^{+}$, and $Pb2^{+}$ onto these media was investigated using a system of standardized batch adsorbers under steady state and transient rate conditions. It was found that raw peanut hulls and peanut hull pellets are effective adsorbents for metal ion removal. Kinetic study showed that over 90% of metal ion removal occurs within the first 20 min of contact.

Çelekli et al., (2012) In their study reported that walnut hull had a great potential to remove LR G from aqueous solution at different initial pH values, dye concentrations, and contact time. ANN was found to be excellent model because higher determination of coefficient values between the network prediction and corresponding experimental data. Results of this model showed that pH was the most efficient parameter (43%), followed by initial dye concentration 40%) for the sorption process. As a result, ANN model can be used in design and scale-up for removing of LR G on the walnut hull.

Goetz et al., (2008) investigated the techniques and their effects on the environment. It showed different classes of dyes and their use on different textiles, and their potential effects on the environment was studied. Additionally, experiments with natural dyes were conducted and documented. Natural berries, roots, and other dyestuffs were collected and used to dye both natural and synthetic textiles. Each type of dye has benefits and disadvantages. Every system of dyeing produces waste along with the finished product.

Ho et al., (2006) investigated coconut copra meal, a waste product of coconut oil production for its potential use as a biosorbent for cadmium ions from an aqueous solution. A comparison of three widely used isotherms, Langmuir, Freundlich, and Redlich–Peterson, were examined. Langmuir isotherm parameters obtained from the four Langmuir linear equations by using linear method were not similar, but were the same when non-linear method was used. The best-fitting

isotherms were Langmuir and Redlich–Peterson isotherms. Langmuir isotherm is a special case of Redlich–Peterson isotherm when constant g is unity. In addition, various thermodynamic parameters, such as ΔG°, ΔH°, and ΔS°, were calculated.

Benaïssa et al., (2005) studied the removal of acid dye from aqueous solutions using orange peel as a sorbent material. In laboratory-scale studies, the data showed that orange peel has a considerable potential for the removal of dye from aqueous solutions over a wide range of concentrations. The dye sorption performances are strongly affected by parameters such as contact time, initial dye concentration and type of dye. The amount of dye sorbed by this material increased with the increase of these parameters at a specific time. The results also showed that the kinetics of dye sorption was described by a pseudo-second order rate model. A good fitting of dye sorption equilibrium data was obtained with Langmuir model in all the range of dye concentrations studied. From these results, maximum dye adsorption capacities are observed using this material. It may be concluded that orange peel may be used as a low-cost, natural and abundant source for the removal of dye and it may be an alternative to more costly materials. For Nylosane Blue, a maximum sorption capacity about 65.88 mg/g was obtained followed by Erionyl Yellow (64.14 mg/g), Nylomine Red (62.07 mg/g) and Erionyl Red (40.72 mg/g), respectively.

Krowiak et al., 2011 studied the biosorption of Cu(II) and Cr(III) ions from aqueous solutions by peanut shell biomass. The optimum sorption conditions were studied for each metal separately. Four kinetic models (pseudo-first order, pseudo-second order, power function equation, and Elovich model) were used to correlate the experimental data and to determine the kinetic parameters. Four adsorption isotherms were chosen to describe the biosorption equilibrium. The experimental data were analyzed using two two-parameter models (Langmuir and Freundlich) and two three-parameter models (Redlich– peterson and Sips). The equilibrium biosorption isotherms showed that peanut shells possess high affinity and sorption capacity for Cu(II) and Cr(III) ions, with monolayer sorption capacities of 25.39 mg $Cu2^{+}$ and 27.86 mg $Cr3^{+}$ per 1g biomass, respectively. In their results they showed that peanut shells biomass is an attractive, alternative low-cost biosorbent for removal of heavy metal ions from aqueous media.

Overah et al., (2011) studied the biosorption of Cr (III) from aqueous solution by the leaf biomass of Calotropis procera – Bom bom. The reaction conditions such as biomass dosage, initial metal ion concentration and temperature were found to influence the biosorption process. However, Langmuir gave a better fit with an R-Squared value of 0.967 (closer to unity than that of Freundlich), FT-IR studies of the biosorbent before and after the biosorption process indicated that carboxylate, amino and nitro functional groups were involved in the sorption of Cr (III) onto Calotropis procera leaf biomass. These findings indicate that the leaf of biomass of Calotropis procera could be employed in the removal of Cr (III) from aqueous solutions and industrial effluents.

Ozakar et al., (2005) studied adsorption of metal complex dyes from aqueous solutions by pine saw dust. They made an attempt to alleviate the problem caused by the presence of metal complex dyes, in the textile effluents. The effects of adsorbent particle size, pH, adsorbent dose, contact time and initial dye concentrations on the adsorption of metal complex dyes by pine sawdust was investigated. The experimental isotherm data were analyzed using the Langmuir, Freundlich and Temkin equations. The equilibrium data fit well the Langmuir isotherm. The monolayer adsorption capacities are 280.3 and 398.8 mg dye per g of pine sawdust for Metal Complex Blue and Metal Complex Yellow, respectively.

Ponnusami et al., (2009) carried out **a**dsorption of methylene blue onto gulmohar plant leaf powder. The effects of pH, initial dye concentration, particle size, dosage, agitation speed, and temperature were studied. Langmuir and Freundlich isotherm models were used to test the equilibrium data. The reported adsorbance was found to be 25.3 mg/g.

Safarikova et al., (2010) studied the removal of organic dye using magnetic fluid modified peanut husks as an adsorbent. The maximum adsorption capacity of Bismarck brown was found to be 95.3mg/g, followed by Safranin 86.1mg/g and Crystal violet 80.9mg/g and Acridine orange 71.4mg/g. And thus concluded that Ferrofluid modified biological waste (peanut husks) has been successfully used for the separation and removal of water soluble organic dyes and thus this low cost adsorbent could be potentially used for waste water treatment.

Sharma et al., (2012) carried over adsorption for the removal of methylene blue dye from an aqueous solution using water hyacinth root powder as a low cost adsorbent. In this study adsorbent prepared from roots of water hyacinth was used to remove the Methylene Blue from an aqueous solution. The batch adsorption study was carried out by varying the parameters such as pH, adsorbent dose, initial concentration of dye, and contact time to obtain removal kinetic data. At optimum experimental condition, maximum 95% removal of dye was achieved. Equilibrium data were best represented by both Langmuir and Freundlich isotherms. The maximum dye uptake was found to be 8.04 mg/g. The adsorption kinetic data are adequately fitted to the pseudo second order kinetic model. On the basis of experimental results, it is found to be an excellent adsorbent for the MB removal from wastewater.

Sumanjit et al.,(2008) studied the removal of Rhodamine-B from its aqueous solutions by adsorption on walnut shell charcoal using batch technique. The effects of various experimental parameters on adsorption like contact time, temperature, initial pH, initial dye concentration, sorbent dosage and ionic strength were examined and the optimal experimental conditions were evaluated. At initial pH of 9, the dye studied was found to be removed effectively in a period of 5 hours. The adsorption data were fitted to Freundlich and Langmuir adsorption isotherms for the calculation of various adsorption parameters. The adsorption results indicated that the dye, Rhodamine-B can be effectively removed from its aqueous solutions by using walnut shell charcoal as an adsorbent.

Taha et al., (2011) studied various kinetic models used to describe the adsorption of peanut husk carbon. The kinetic model according to the reaction rate equation was found to be the most in agreement with this system and also investigated the effect of the other operating conditions are necessary. The adsorption capacity was found to be as 0.62 mg/g. In their study they concluded that peanut husk carbon and economical.

T**heivarasu et al.,** (2011) investigated the adsorption over Cocoa Shell as adsorbent for the removal of methylene blue from aqueous solution. methylene blue (MB) adsorption from an aqueous solution onto activated carbon prepared from cocoa *(Theobroma cacao)* shell has been studied experimentally using batch adsorption method. Adsorption kinetics and equilibrium were investigated as a function of initial dye concentration and contact time, pH and adsorbent

dosage. Pseudo-first order, pseudo-second order and intra-particle diffusion models were used to examine the experimental data of different initial concentrations. On the basis of experimental results and the model parameters, it can be inferred that the activated carbon prepared from cocoa shell was effective for the removal of methylene blue from aqueous solution.

2.2. Gaps in literature

Since the past few decades, with the advent of biosorption techniques several biosorbents and contaminant or dyes have been studied but no work has been done on the removal of thionine dye even though it is a novel contaminant found in waste water coming out from biomedical and microbial industries. Moreover, very scarce literature is available on the use of peanut shell and walnut shell as an adsorbent.

The complex structure of dye molecules influences biosorption and further research is needed to establish the relationships between dye molecule structure and biosorption (Fu &Viraraghavan et al., 2001). Although considerable information is available on biosorption but the nature of mechanism and the extent of competition have been inadequately understood. It is very helpful for the biosorption practical application.The technology needs to effectively compete both on a cost and performance basis with existing methods before industry will accept and implement it. No detailed economic and market analysis are available although advantages of these systems are well established.

2.3. Problems in research

The challenge with biosorption as with many in the biotechnology industry is to move this process to an industrial scale. It is relatively less difficult to demonstrate it in a laboratory; it is a little more challenging to demonstrate it at a pilot scale, but to really scale it up to a large scale would call for a significant financial and technological effort. This mismatch between scientific progress in biosorption research (biosciences) and stagnation in industrial biotechnology innovation needs to be corrected through translational research and technology transfer with a push for commercialization of research. Universities can play an active role in this process through more formalized approach to technology transfer and protection of intellectual property.

2.4. Objective of study

The objectives of the present study are:

- To remove the thionine dyes from its solution using different adsorbent such as peanut hull and wallnut hull
- To carry the adsorption over peanut hull for the removal of thionine dye.
- Characterization of the adsorbents by SEM and FT-IR.
- Thermodynamic study of the adsorption of dye
- Study of adsorption kinetics of thionine dye over the adsorbent
- Fitting of adsorption data into various adsorption isotherms

3. MATERIALS AND METHODS

3.1. Materials

The Thionine dye is obtained from Liechem Laboratories Limited (India) and the Peanut shell and walnut shell are collected from local region.

3.1.1 Preparation of adsorbent

Peanut shells and walnut shells collected from local market were extensively washed in running tap water for 1–2 h to remove colour and dirt, and then washed with distilled water several times. The washed sorbent was transferred to an oven maintained at at 150 °C for 24 h to reduce the moisture content. The dried sorbent was micronized using a kitchen grinder. The powder was sieved to pass throught mesh of 180 µm, those retained were oversize fraction. This size fraction in the range of approx 20µm was used in all the experiments. The powdered biosorbents are then are thoroughly washed with distilled water. The filtrate was washed with distilled water several times as Reddy Somasekharan, 2006 reported in his study. This filtered biomass was first dried, at room temperature and then in an oven at105ºC for 6-8 hrs. The dried biomass was stored in air tight glass bottles to protect it from moisture.

Table 1: Physical Properties of the adsorbents

PARAMETER	PEANUTHULL	WALLNUTHULL
Moisture(w/vol)	8.6	7.6
Ash %	4.2	4.6
BulkDensity(g/cm^3)	3.1	4.0

3.1.2 Preparation of dye solution

Stock solution of thionine dye (Chemical formula: $C1_2H_9N_3S \cdot C_2H_4O_2$, M.W.: 287.34, C. CAS-No.: 78338-22-4) was prepared by dissolving 50mg of dye in 1L of distilled water to give concentration of 50 mg/L. The serial dilutions say 10 20, 30, 40 and 50 mg/L were made by diluting the dye stock solution in accurate proportions. Calibration curve for dyes was prepared by measuring the absorbance of different concentrations of the dyes.

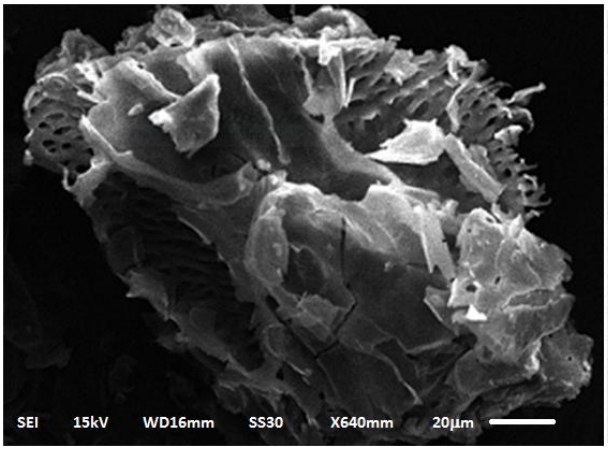
3.2.Methodologies

3.2.1.Batch adsorption experiments

Adsorption experiments were carried out in mechanical stirrer (temperature control) at a constant speed of 200rpm at 25°C, 30°C, 40°C, 50°C using 1000mL beakers containing 250ml of dye 250mL of dye solutions of different concentrations i.e. 10mg/L, 20 mg/L, 30 mg/L, 40 mg/L, 50 mg/L. All the experiments were carried out at optimum pH, specifically determined for the adsorbent systems. After agitating the flasks for predetermined time intervals, samples were withdrawn from the flasks. The adsorbents were separated from the solution by filtration using Allpure membrane filter of size 0.45mm. The absorbance of the supernatant solution was estimated to determine the residual dye concentration, measured at λ_{max} = 598 nm spectrophotometrically using Perkin Elmer UV-Visible spectrophotometer. Adsorption data obtained from the effect of initial concentration and contact time was employed in testing the applicability of isotherm and kinetic equations, respectively.

3.2. 2 Characterization of biosorbents

Characterization of the Un-adsorbed and adsorbed biodsorbent was done. The samples were analyzed by scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR). Characterization of biosorbent for the surface morphology of biosorbents was examined using Jasco Scanning Electron Microscope (SEM). Figure 2 and Figure3 shows SEM results of Peanut hull unloaded and dye loaded respectively. Similarly Figure 4 and Figure 5 shows SEM results of Walnut hull unloaded and dye loaded respectively. The samples covered, with a thin layer of gold and an electron acceleration voltage of 15kV was applied.



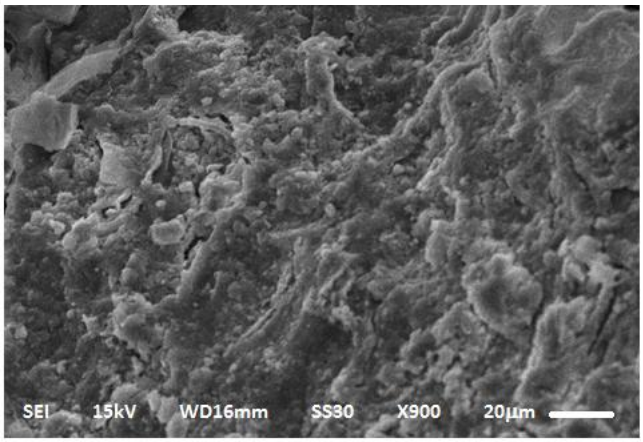
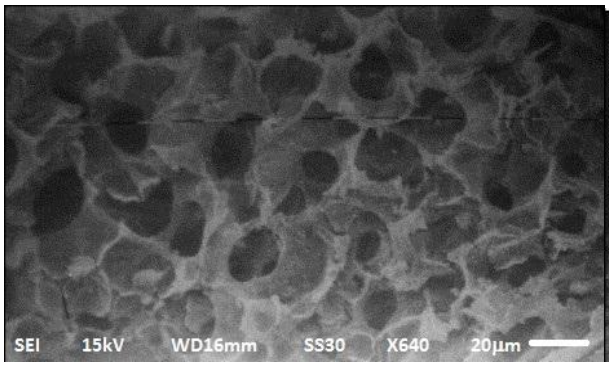


Figure2: SEm of Unadsorbed Peanuthull particle size 20 µm **Figure 3**: SEM of Adsorbed (Dye loaded) Peanut hull particle size20 µm



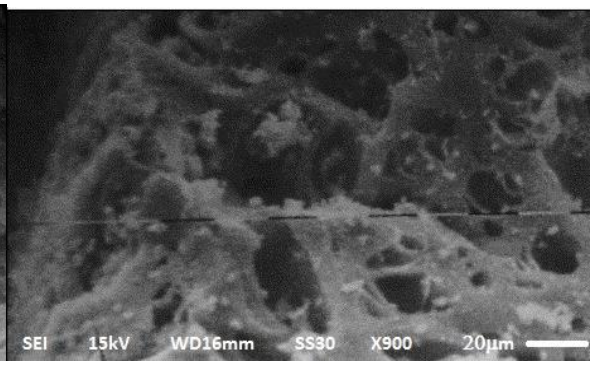


Figure 1:SEM of Unadsorbed walnut hull **Figure 2: SEM of Adsorbed (dye loaded walnut hull)**

Characterization of biosorbent to identify the functional groups present was done by using the Fourier Transform Infrared (FT-IR). Figure 6 and Figure7 shows FT-IR results of Peanut hull unloaded and dye loaded respectively. Similarly Figure 8 and Figure 9 shows FT-IR results of Wallnut hull unloaded and dye loaded respectively. The intensity of an absorption in the IR spectrum is related to the change in dipole that occurs during the vibration. Consequently, vibrations that produce a large change in dipole result in a more intense absorption than those that result in a relatively modest change in dipole .Vibrations that do not result in a change in dipole moment will show little or no absorption for this vibration. The hulls are lignified cell walls making up tissues with very similar compositions; the lignin to cellulose ratio being a critical measurement. The lignin and cellulose appear to be of the same general form despite their different tissues of origin in the tree; secondary xylem or seed pericarp.lignin to cellulose

ratio - % hemicelluloses Peanut 79/100 - 12% (Legume) Like all vegetable biomass, peanut shell nd walnut shells are composed of cellulose, hemi-cellulose and lignin. Nutshells or pericarps are composed of lignin and cellulose so, in that sense, the are woody but not wood. Wood is defined by the interconnections in the vascular growth pattern that nut hulls lack. The lignification is similar between both nut hulls and a tree trunk so the real difference lies in the structural pattern. Wood has a very clear architecture. It is homogenously built in repeating interconnected layers around the circumference of the tree as annual rings.

From elemental analysis, the contents (% of total matter) were obtained for carbon (45.49), hydrogen (5.93), oxygen (34.41) and nitrogen (1.26). Peanut shells and walnut shells are mainly consisted of polysaccharides, proteins, and lipids, offer many polar functional groups such as carboxyl, carbonyl, hydroxyl and amino which can be involved in metal and dye binding. The FT-IR technique was an important tool to identify some important functional groups, which are capable of adsorbing ions. FT-IR spectroscopy was, therefore, done for preliminary quantitative analysis of major functional groups presented in native peanut husk. Figure 6 and Figure 7 showed the FT-IR spectrum of natural peanut hull. It was difficult to assign each peak appearing in the Figures as the structure and composition of peanut husk were complex. The peaks in the FT-IR spectrum of native peanut husk were assigned to various groups and bonds in accordance with their respective wave numbers (cm^{-1}). The broad band around 3398 cm^{-1} was attributed to the surface hydroxyl groups, adsorbed water and amine groups. The O−H stretching vibrations occurred within a broad range of frequencies indicating the presence of “free” hydroxyl groups and bonded O−H bands of carboxylic acids. The peak at 2110 cm^{-1} was assigned to C–H asymmetrical stretching of methyl groups on the surface. These groups were present on the lignin structure The peak located at 1639 cm^{-1} is characteristics of the carbonyl group stretching from carboxylic acids and ketones. They could be conjugated or non-conjugated to aromatic rings (1741 and 1639 cm^{-1} respectively). The peaks associated with the stretching in aromatic rings (from lignin) were verified at 1507 cm^{-1}.

The peak near 1428 cm^{-1} was attributed to the stretch vibration of C–O from the carboxyl group the peak at 1383 cm^{-1} was due to the asymmetric bending vibration of the $-CH_3$ group. The absorption peak at 1255 cm^{-1} could be due to the C−O, C−H or C−C stretching vibrations of the carboxyl groups (−COOH). The wave number observed at 1050 cm^{-1} was due to the C−O group in carboxylic and alcoholic groups. The region below 1000 cm^{-1} was the ‘fingerprint zone’ and the absorption could not clearly be assigned to any particular vibration because they

corresponded to complex interacting vibration systems. The intensity of the peak was a function of the change in electric dipole moment and also the total number of such bonds in the sample. The band of the C−O group in Figure 6 was more intense than that of the C=O group, possibly because of more C−O groups presented in peanut husk. When infrared light interacted with the adsorbent, it caused different types of vibration such as stretching, contraction and bending of its chemical bonds. As a result, the chemical functional group tends to absorb infrared radiation in a specific wavelength range. The analysis of the FT-IR spectrum showed the presence of ionizable groups (carboxyl and hydroxyl) able to interact with protons, metal or positive dye ions. (Bian and Han et al., 2011). .

The Figure 8 and Figure 9 showed the FT-IR spectrum of Unloaded walnut hull and dye loaded walnut hull. Several major intense bands, around 3399, 2927, 1726, 1635,1510, 1424,1383, 1318, and 1265 ,1105, 1055, 1033,669,609 and 560cm^{-1} were observed in unloaded. adsorbent (Figure 7). The peak at 3399 cm^{-1} could be attributed to -OH and -NH_2 groups (Çelekli et al., 2010), while the peak at 2927 cm^{-1}could be assigned to –OH stretching vibrations (Altul et al.,2012). . The appearance a band at 1740 cm^{-1} may be related carbonyl (-C═O) groups (Yang and Qiu, 2010). The peak at 1635 cm^{-1} could be corresponds to the olefinic C═C stretching vibrations (Yang and Qiu, 2010). The C═C vibrations in aromatic rings cause to the peak of 1508 cm^{-1} The variable bands around 1424–1383 cm^{-1} were assigned to bending vibration of the –C–H alkane group. The peak at 1424 cm^{-1} was caused by the CH_2 bending, the peaks at 1383 cm^{-1} are initiated by carboxylate group (–COO) stretching and 1370 cm^{-1} by the -OH bending. The peaks ranging from 1300 to 1000 cm^{-1} are ascribed generally to the C–O stretching vibration in carboxylic acids and alcohols. The peak at 1265 cm^{-1} is an indication of the OH in-plane bending cellulose groups. The bands below 1200 represents as finger print regions for adsorbent. Almost no significant changes of the functional group were visible after dye loading of walnut hull. (Yang and Qiu, 2010). The variable bands around 1424–1383 cm^{-1} were assigned to bending vibration of the –C–H alkane group. The peak at 1424 cm^{-1} was caused by the CH_2 bending, the peaks at 1383 cm^{-1} are initiated by carboxylate group (–COO) stretching and 1370 cm^{-1} by the O–H bending. The peaks ranging from 1300 to 1000 cm^{-1} are ascribed generally to the C–O stretching vibration in carboxylic acids and alcohols. The peak at 1265 cm^{-1} is an indication of the OH in-plane bending cellulose groups. The bands below 1200 represents as finger print regions for adsorbent. Almost no significant changes of the functional group were visible after dye loading of walnut hull.

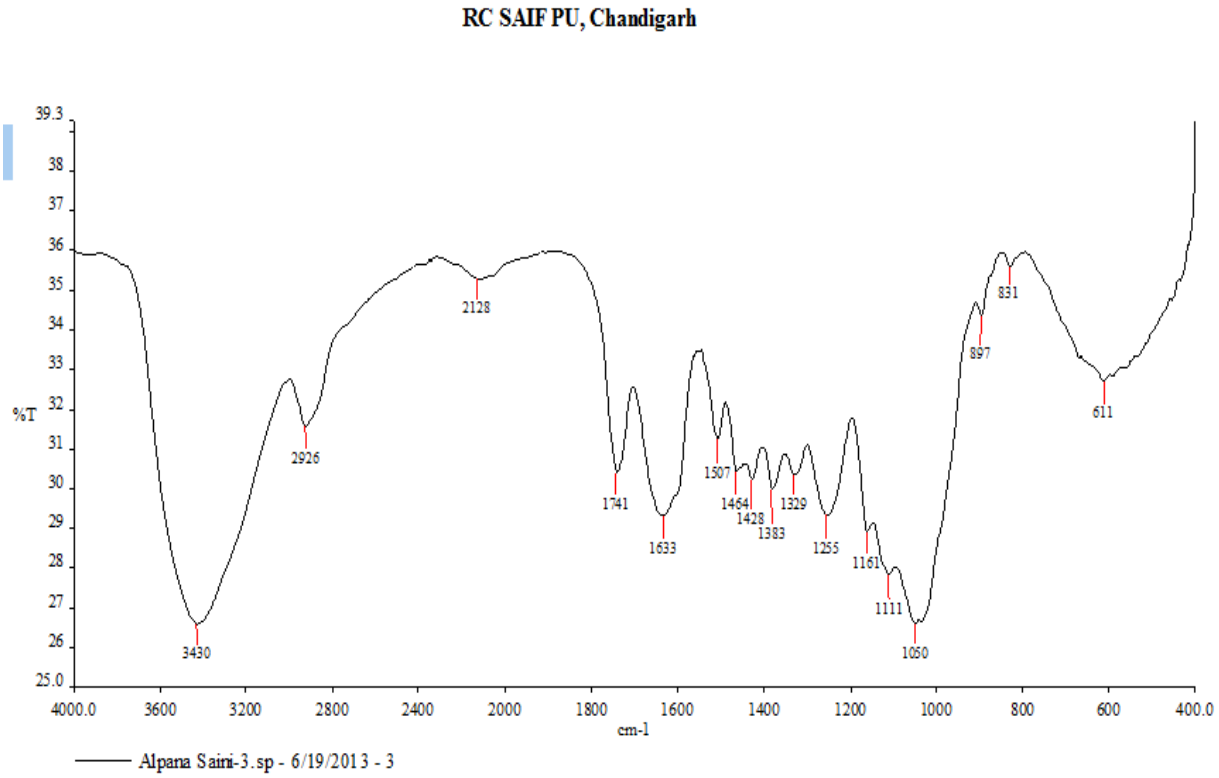


Figure 6 :Unadsorbed (unloaded) FT-IR of Peanut

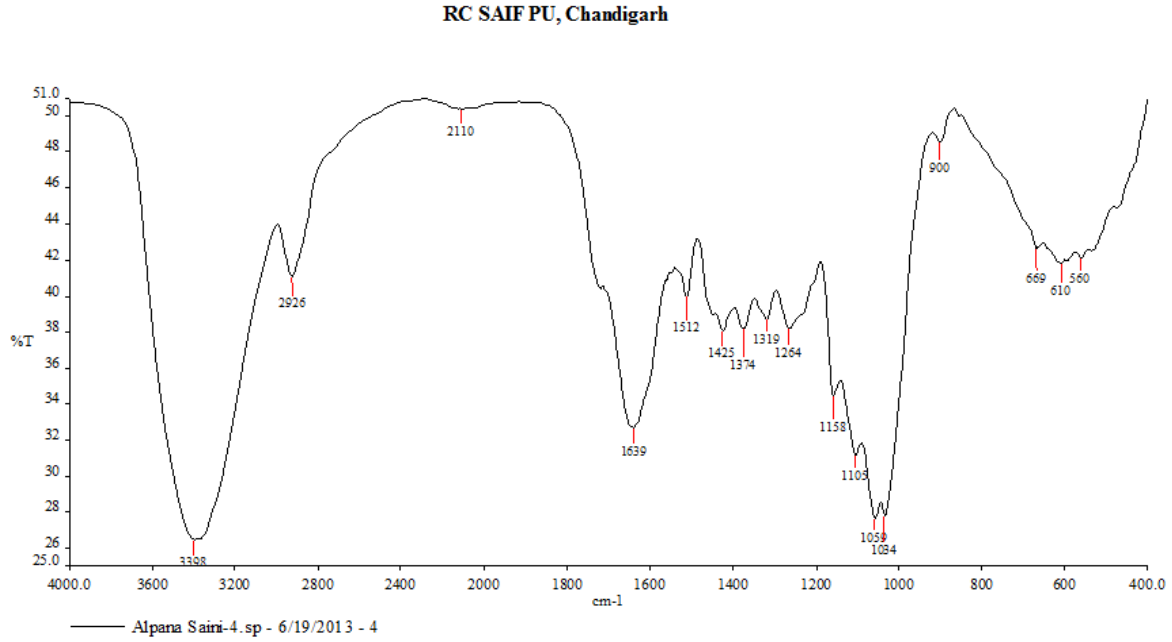


Figure 7: Adsorbed (dye loaded) FT-IR peanut hull

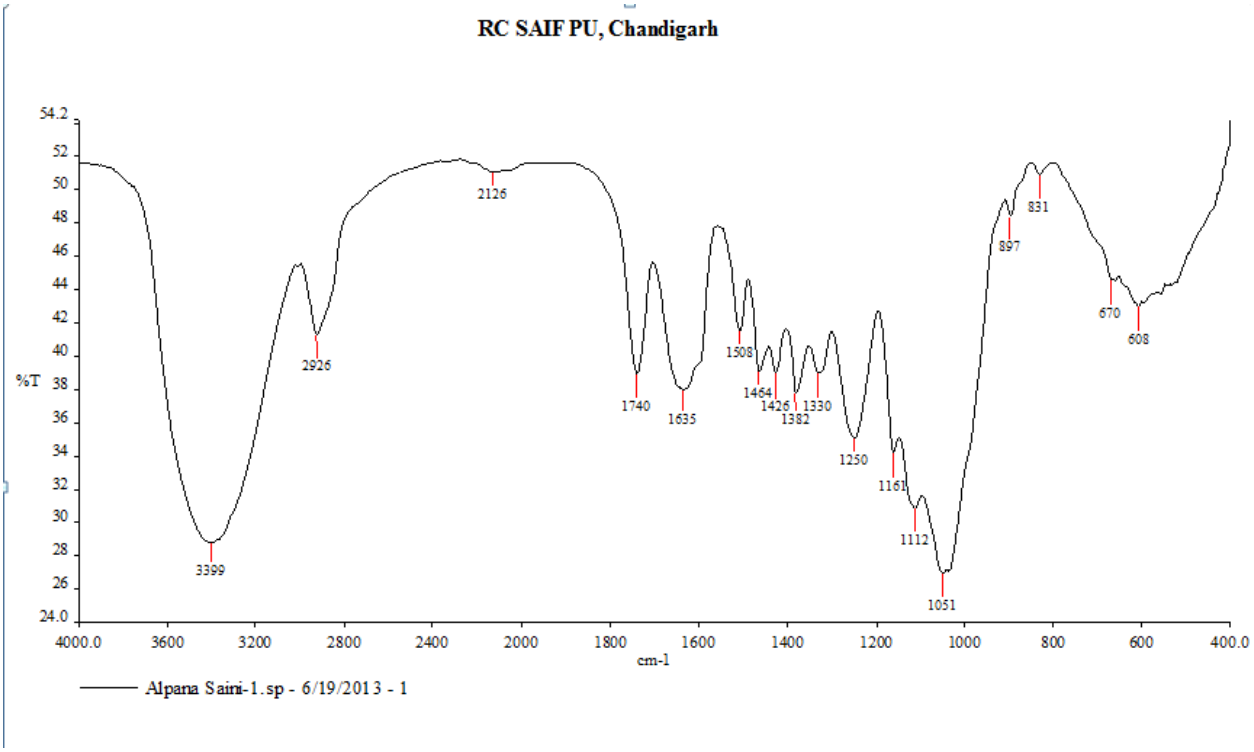


Figure8: Unadsorbed (unloaded) FT-IR walnut hull

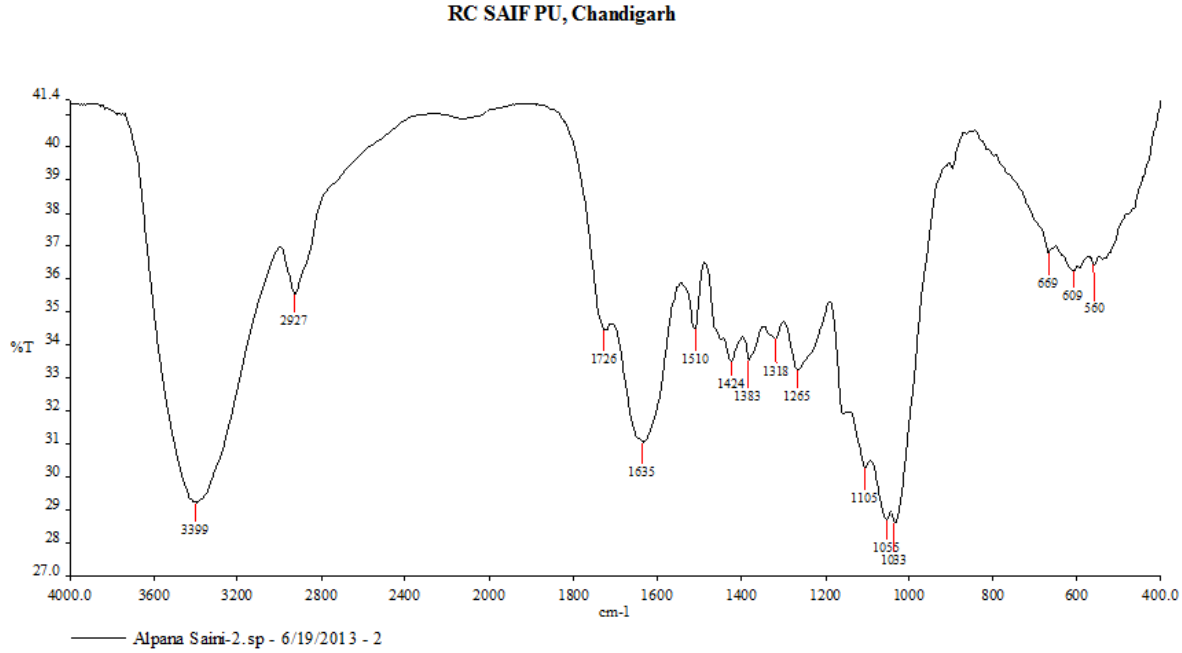


Figure9: Adsorbed (dye loaded)FT-IR walnut hull

CHAPTER-4

4. RESULT AND DISCUSSION

4.1. Concentration measurement and Calibration

In order to calculate the concentration of the sample from each experiment, first and foremost the λ_{max} of the solution was determined (Figue10), which came out as 598nm. Further all the experiments were conducted at 598nm λ_{max}. The calibration curve of dye (Figure11) was first prepared. Five different concentrations of dye solutions were prepared and absorbance was measured using a Perkin–Elmer UV-VIS Spectrophotometer Lambda 18 over a range from 400 to 700 nm. Calibration experiments were carried out in duplicate and the maximum absorbance of each dye was plotted against concentration. From these results, the concentrations of the dye samples were calculated with the following equations and constants as per the Beer Lambert's Law. $A = \epsilon \times b \times c$ (1)

A is the absorbance (no units, since $A = \log_{10}(P_0 / P)$), P is the radiant power. ϵ is the molar absorbtivity with units of L mol^{-1} cm^{-1}, ϵ for thionine dye =54200 L mol^{-1} cm^{-1}

b is the path length of the sample - that is, the path length of the cuvette in which the sample is contained. Here for quartz cuvette path length is 10 mm or 1cm. c is the concentration of the compound in solution, expressed in mol L^{-1}

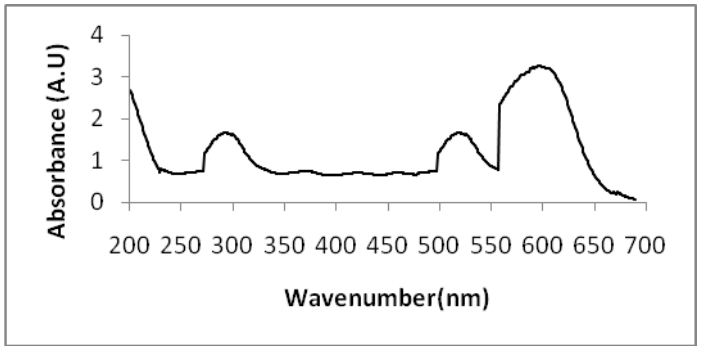


Figure 3: λ_{max} **of Thionine Dye**

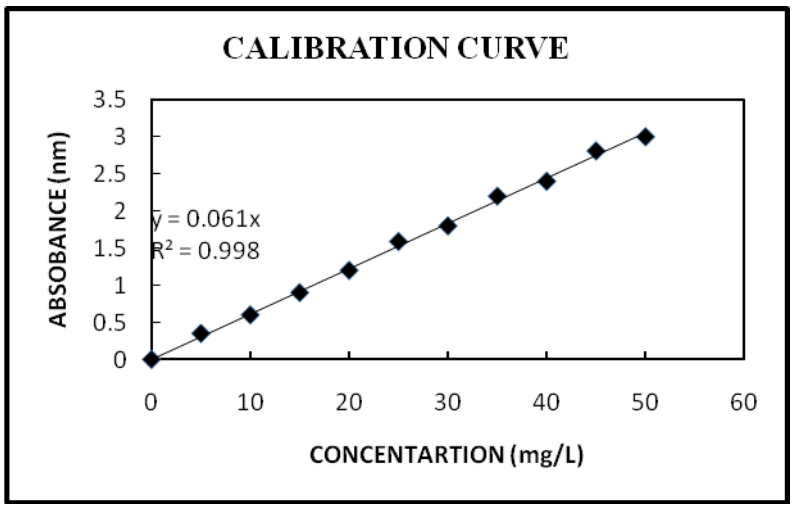


Figure 4: Calibration curve of Thionine Dye

4.2. Effect of Contact Time

Percentage dye sorbed were estimated at different times keeping the other parameters fixed and the. It was observed that the rate of removal of thionine dye increases with increase in contact time. 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 by the adsorbents. The time required to attain this state of equilibrium is termed as the equilibrium time, and the amount of dye adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions. Therefore, further batch experiments were carried out at 5 hours of optimum contact time for peanut hull and 3 hrs of walnut hull.

4.3. Effect of initial dye concentration on dye adsorption

The effect of the initial thionine dye concentration on the adsorption over peanut hull and walnut hull at optimum adsorbent dosage of 1 g per 250ml and mixing speed of 200 rpm, pH 7 and temperature 30^{o}C were shown in the Figure 12.

It can be seen that the adsorption at different concentrations is rapid in the initial stages and gradually becoming constant with the progress of adsorption until the equilibrium is reached. The amount of thionine adsorbed at equilibrium (q_e) increased from as the concentration was increased from 10 mg/L to 50mg/L. The optimum dye concentration was found to be 20mg/L of solution in both the adsorbents. The initial concentration provides an important driving force to overcome all mass transfer resistances of the thionine dye between the aqueous and solid phases. Hence a higher initial concentration of dye enhanced the adsorption process. The equilibrium

conditions were reached within 5hrs; also the rate of adsorption was faster for concentrations ranging from 10 to 20 mg/L. But at higher initial concentrations there are no more active sites available for more adsorptions of dyes, as a result removal of dyes decreased at higher concentrations of dyes. The decrease in removal efficiency can be explained by the increased tendency of aggregation formation at higher dye concentration of thionine dye. (Ghasemi and Kubista et al. 2005)

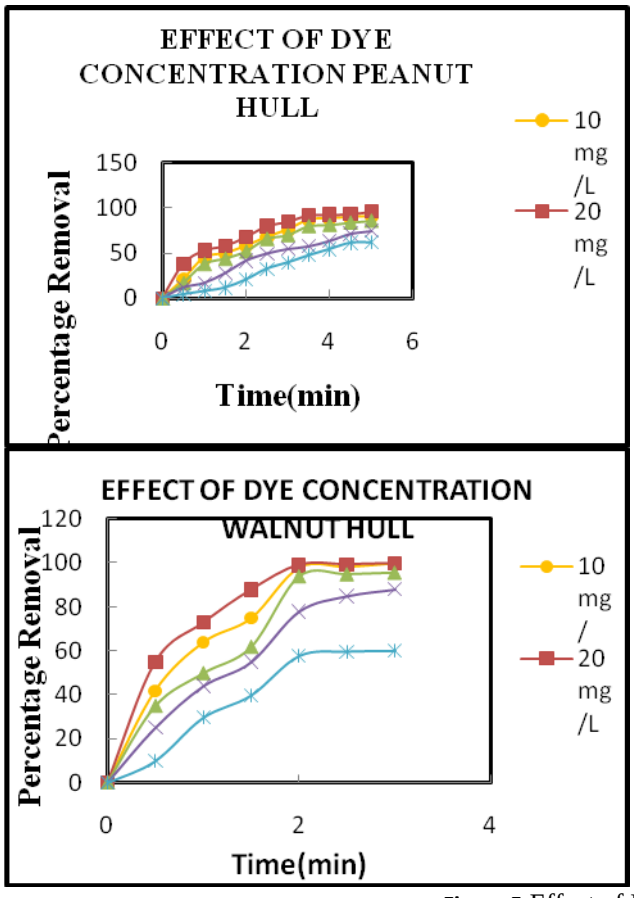


Figure 5:Effect of Dye Concentration

4.4 The Effect of Varying Adsorbent Dosage

The effect of the adsorbent varying dose (shown in Figure 13)was studied at dye concentration 20mg/L, pH 7, 30^{o}C for peanut hull and walnut hull both by varying the sorbent amounts from 0.5g/L, 1g/L, 1.5g/L and 2g/L. For all these runs, initial concentration of dye solution was fixed as 10 mg/L. Figure 13 shows the adsorption of thionine dye increases rapidly with increase in the amount of peanut hull due to greater availability of the surface area at higher concentration of the adsorbent. The significant decrease in uptake was observed when the dose was increased from 0.5g/L to 1g/L. Any further addition of the adsorbent beyond this up to 1.5 g/L did not cause any

significant change in the adsorption. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles. The maximum removal of dye was obtained in the adsorbent dose of 1 g/L. Similarly for walnut hull the optimum dosage was found out to be 1.5g/L, and again any further addition of the adsorbent beyond this up to 1.5g/L did not cause any significant change in the adsorption.

A specific weight of adsorbent has a specific capacity of adsorption, but the decrease in amount of dye adsorbed onto the adsorbent q_e(mg/g) with increasing adsorbent dose is due to split in flux or the concentration between dye concentration in the solution and dye concentration on the surface of adsorbent . Thus with increasing adsorbent dose, the amount of dye adsorbed onto unit weight of asdsorbent gets reduced. Therefore, causing decreasing in q_e(mg/g) value with increasing adsorbent dose.

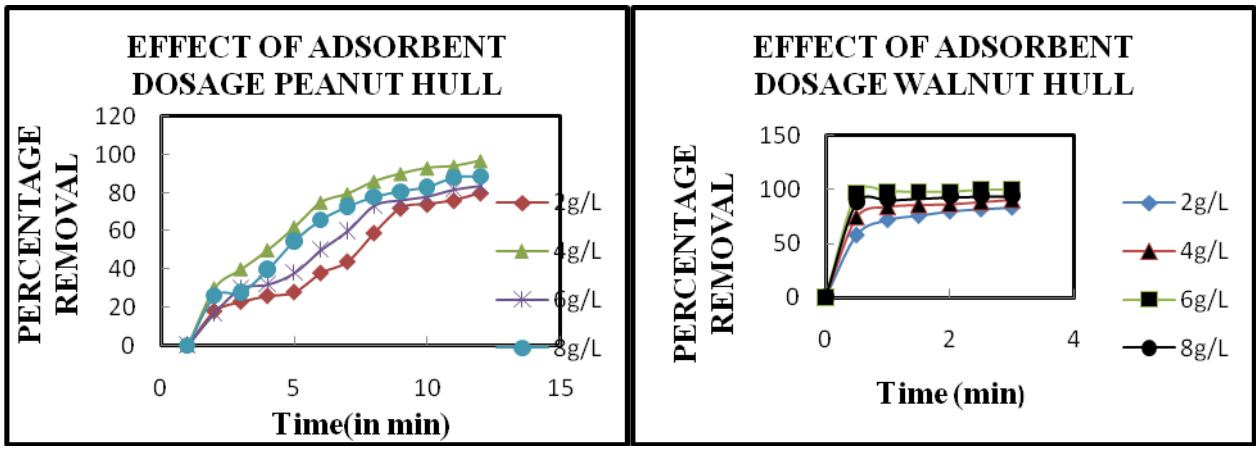


Figure 6: Effect of adsorbent dosage on dye adsorption

4.5 Effect of solution pH on dye adsorption

As shown in Figure 14 effect of pH on adsorption was studied using 10 mg/L dye concentration, pH 2–12 at 40 ˚C. The Figure 14 shows optimum pH 8 for peanut hull and pH 7 for walnut hull. The dye adsorption was significantly changed over the pH value of 2–10. The dye adsorption was nearly constant at pH 10–12. The lowest dye adsorption was recorded at pH 2. The equilibrium adsorption (q_e) was found to increase with increasing pH. The q_e increases from for an increase in pH from 2 to 8. Wang et al., reported that thionine dye adsorption usually increases as the pH is increased. Lower adsorption of thionine dye at acidic pH is probably due to the presence of excess H+ ions competing with the cation groups on the dye for adsorption sites. At higher pH, the surface of Peanut hull and Walnut hull particles may get negatively charged, which enhances the positively charged dye cations through electrostatic forces of

attraction. The complex nature of the adsorbent as shown in Figure 6 and Figure 7 of peanut hull and Figure 8 and Figure 9 of FT-IR may indicate the possible involvement of some functional groups on the surface of Peanut hull in sorption process.

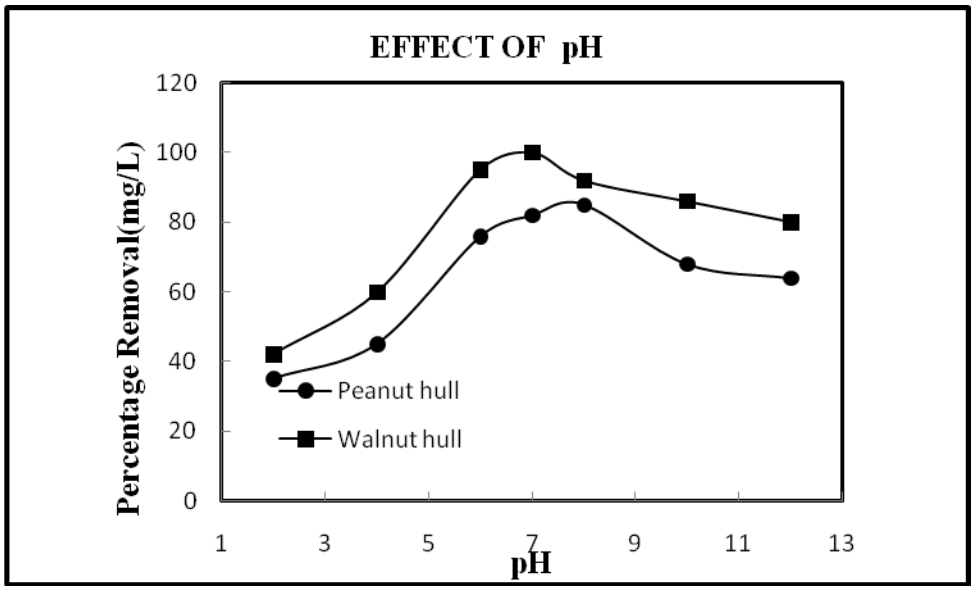


Figure 7:Effect of solution pH on dye adsorption

4.6 Effect of Temperature of dye solution on dye adsorption

Effect of solution temperature on dye adsorption was studied in the temperature range from 25 to 60ºC. The diagrams in this Figure 15 bring the result for the 10mg/L dye concentration and the adsorbent dosage of 1.5g per 250ml of Solution. It is shown that a little higher temperature simplifies dye removal with adsorption on an adsorbent, whereas a higher temperature favors desorption.

The amplification of the adsorption with temperature can be assigned to the increased number of active surface locations that are available for adsorption on the adsorbent, and also the porosity and the overall cubage of the pores of the adsorbent. The intensity of the adsorption also depends on thickness of boundary layer, which surrounds the adsorbent and offers resistance to mass transfer. With the increase in temperature there is a decrease in the boundary layer thickness thus increased mass transfer. This can also be the result of an increase in dye-molecule mobility with an increase of their kinetic energy and increased diffusion speed inside of the particles of adsorbents due to the temperature increase as reported by Djordjevic et al., 2011.

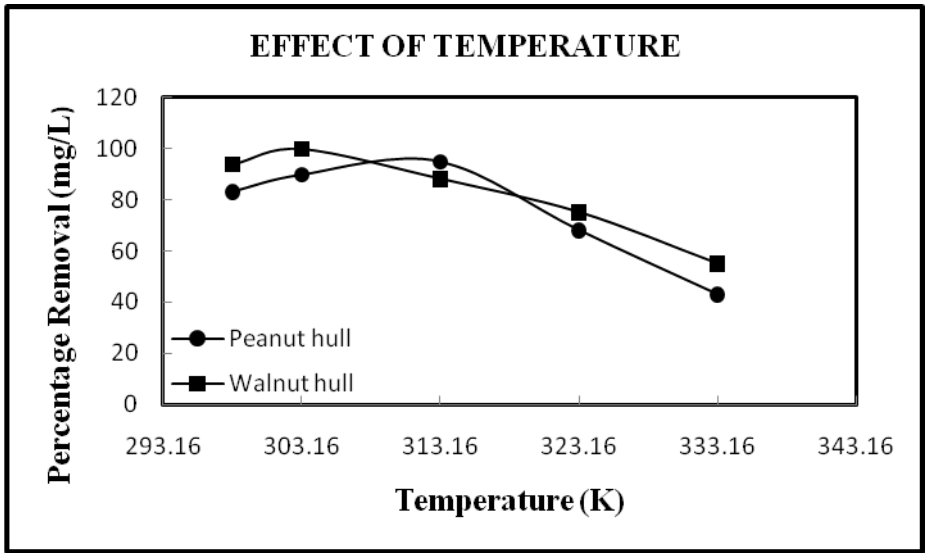


Figure 8: Effect of solution Temperture on dye adsorption

4.7 Effect of agitation on dye adsorption

In a liquid adsorption system, the transfer rate of a solute to a particle is affected by liquid film thickness surrounding the particle and the film thickness depends on agitation speed. A series of experiments at difference of 50 degrees of agitation (from 100 to 300 rpm) were undertaken using blade type impeller for the adsorption of thionine dye on Peanut hull. The Figure16 indicates that the degree of agitation influences the sorption rate as the agitation rate increases from 50, 100, 200 and 300 rpm. At agitation rates higher than 200 rpm the sorption rates only differ to a quite small extent, indicating that the film thickness has insignificant effect when the agitation rate is higher than 300 rpm. Hence, an agitation rate of 200 rpm was selected for all the experiments.

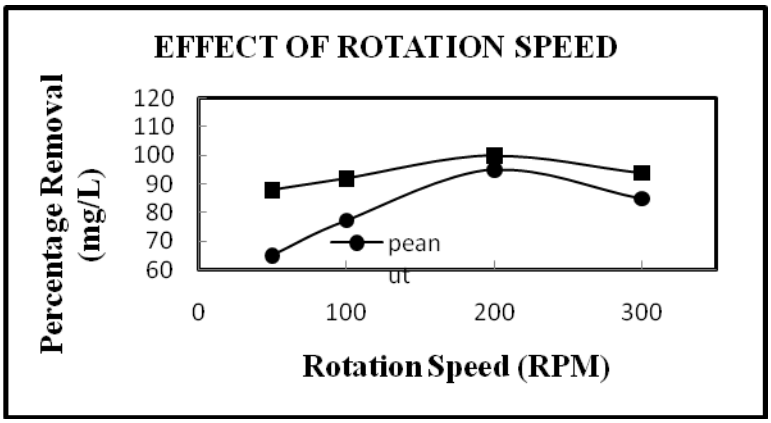


Figure 9: Effect of stirrer speed on dye adsorption

CHAPTER-5

KINETIC MODELS

The study of adsorption kinetics describes the solute uptake rate and this rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetic model which is fits well, describes the mechanism of adsorption by comparing the correlation coefficients (R^2). Also the experimental data and the predicted values are compared.

5.1. Pseudo-First Order Kinetic Model

Pseudo-first order equation or Lagergren's kinetics equation (Lagergren, 1898) is widely used for the adsorption of an adsorbate from an aqueous solution.(Figure 17)

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad \textbf{(2)}$$

After integration and applying boundary conditions $t \rightarrow 0$ to $t \rightarrow t$ and $q_t \rightarrow 0$ to $q_t \rightarrow q_t$, the integrated form of equation (4) becomes:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad \textbf{(3)}$$

$$-\ln(1 - \frac{q_t}{q_e}) = K_1 t \quad \textbf{(4)}$$

where q_t is the amount of solute adsorbed per unit of adsorbent (mg/g) at time t, K_1 is the pseudo-first order rate constant(L/min), and t is the contact time (min). The slope of a straight line fit to the data of $-\ln(1-q_t/q_e)$ versus t (as shown in Figure 17) gives the value of the pseudo first-order rate constant, K_1. The value of the pseudo first-order rate constant, K_1 for peanut hull adsorbent-dye system as obtained from the linear curve fitting is 0.048 min^{-1} and -0.0115 min^{-1} for walnut hull adsorbent-dye system(Table 2). In peanut hull adsorbent-dye system pseudo first order is not showing a satisfactory result (R^2=0.939), whereas it is fitting well in walnut hull adsorbent-dye system (R^2=0.947).

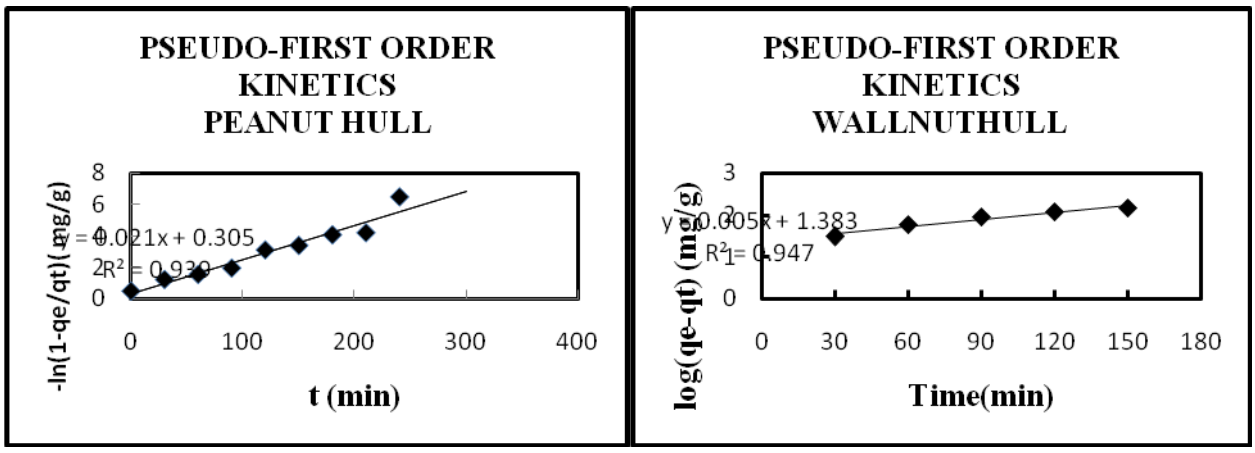


Figure 10: Pseudo- First order Kinetics

Table 2 : Parameters of Pseudo- First order Kinetcs

Adsorbent	$K_1 = -2.303 \times slope$ (min^{-1})	qe(mg/g)	R^2
Peanut hull	-0.048	4.2	0.939
Walnut hull	-0.0115	3.625	0.947

5.2 Pseudo- Second Order Kinetic Model

It is assumed that the sorption capacity is proportional to the number of active sites occupied the sorbent, Ho and McKay, (1998) presented the pseudo-second order kinetic as:

$$\frac{dq_t}{dt} = K_2(qe - qt)^2 \quad \textbf{(5)}$$

For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of Eq. (4) becomes:where K_2 is the pseudo-second order rate constant (g/mg.min). The initial adsorption rate, h (mg/g.min) at $t \rightarrow 0$ is defined as: $h = K_2 q_e^2$ **(6)**

Pseudo second order kinetic plot of (t/q_t) versus (t) (as shown in Figure 18) gave the perfect straight line for the adsorption of dyes onto peanut hull and walnut hull indicating that adsorption reaction can be approximated with pseudo-second order kinetic model. The values of model parameters K_2, h, q_e and correlation coefficients (R^2) are obtained from the plots. The value of the pseudo first-order rate constant, K_2 for peanut hull adsorbent-dye system as obtained from the linear curve fitting is 0.00084 (g.mg^{-1}.min^{-1}) and -0.57176 (g.mg^{-1}.min^{-1}) for walnut hull

adsorbent-dye system and values of h= -5.655×10^{-7} (mg.g^{-1}min^{-1})for peanut hull adsorbent-dye system and h= -0.044641054 (mg.g^{-1}min^{-1}) for walnut hull adsorbent-dye system.(From Table 3) The values of q_e and K_2 can be obtained from the slope and intercept of a straight line fit to the data of t/q_t versus t (as shown in Figure18). The regression coefficient value is close to 1.0. Therefore, the pseudo second-order kinetic model is an appropriate model for the dye–adsorbent system considered in this study. This suggests that this sorption system is pseudo-second order rather than pseudo first order. Based on the assumption that the rate-limiting step, there may be a chemi-sorption, involving valence forces (through sharing or exchange of electrons) between sorbent and sorbate.

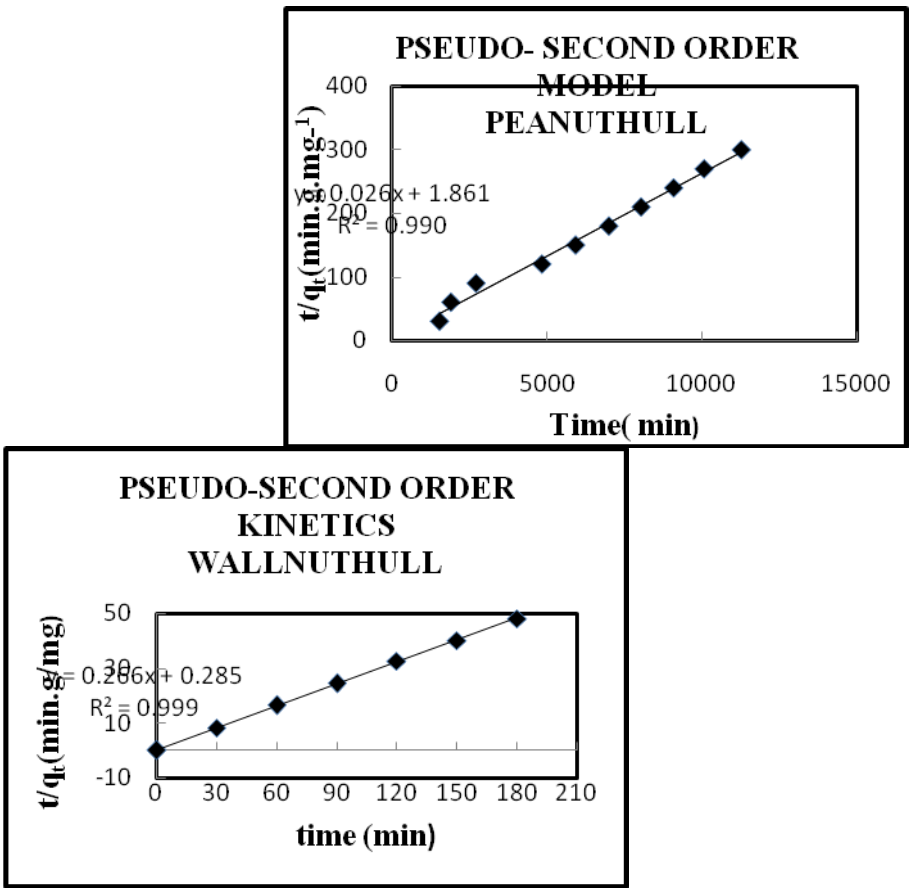


Figure 11:Pseudo Second Order Kinetics

Table 3Paramrters of Pseudo First Order Kinetics

Adsorbent	$K_2 = \frac{slope^2}{\text{int } ercept}$ (g.mg^{-1}.min^{-1})	$qe = \frac{1}{slope}(mg/g)$	$h = K_2 q_e^2$ (mg.g^{-1}min^{-1})	R^2
Peanut hull	3.632×10^{-4}	3.46	5.655×10^{-7}	0.99

Walnut hull	2.4×10^{-9}	3.75	0.044641054	0.999

5.3. The intra-particle Diffusion Model

Several steps are involved in the sorption of sorbate by a sorbent. These involve transport of the solute molecules from the aqueous phase to the surface of the solid particulates and diffusion of the solute molecules into the interior of the pores, which is usually a slow process. The Weber and Morris model or intra-particle diffusion model (shown in Figure 18) is of major interest because the internal diffusion determines the adsorption rate in most of the liquid systems. Eq. (9) is a general representation of the kinetics, where the intercept is related to the mass transfer across the boundary layer and the expected value of the exponent is 0.5 (for Fickian diffusion and plate geometry). The intra-particle diffusion rate constant (K_{in}) is given by the following equation: $q_t = K_{in}t^{0.5}$

$$q = k_{in}t^{0.5} + c \quad . \qquad \textbf{(7)}$$

When intra-particle diffusion plays a significant role in controlling the kinetics of the sorption process, the plots of qt versus $t^{0.5}$yield straight lines passing through the origin and the slope gives the rate constant K_{in}

The Weber and Morris model (eq. 9) describes the time evolution of the concentration in adsorbed state, where the rate constant (k_{in}) is obtained from the plot of q versus $t^{0.5}$ and is related to the respectively. (shown in Table 4)

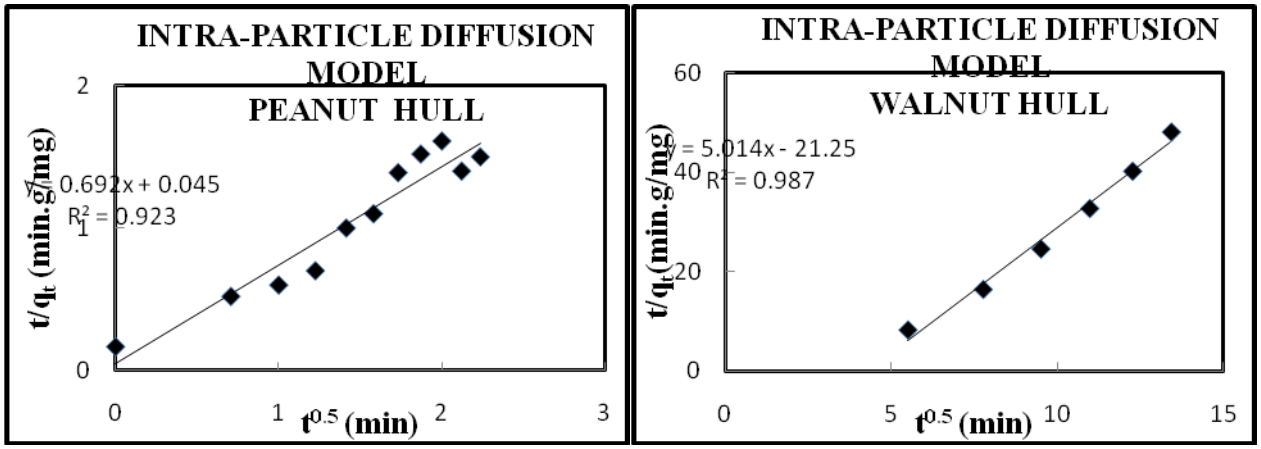


Figure 19:Intra-particle diffusion Model

Table 4: Parameters of Intra-particle diffusion Model

Adsorbent	K_{in}	Intercept=c	$t_{1/2} = \frac{1}{K_2 \times q_e}$ (min)	$D = \frac{0.03r^2}{t_{1/2}}$ (cm^2/min)	R^2
Peanut hull	0.692	0.045	238.0952381	5.04×10^{-10}	0.923
Walnut hull	5.014	21.25	1.071428571	1.12×10^{-7}	0.987

5.4. Liquid Diffusion Model

It is also known as Boyd's model. This model is often used to obtain insight into the mechanism of the adsorption kinetics. Originally proposed for intraparticle diffusion in a spherical particle, it is better known as the Boyd's film-diffusion model. When applied to external mass transfer, it supposes a linear dependence through the origin between (1-F) . where F is q (the fractional approach to equilibrium i.e. (qe/qt) and t (time): ln(1_ F) kt . Here k denotes the external mass transfer coefficient. It states that a model can either be defined by liquid diffusion model or intra-particle diffusion model, not both at the same time.

For better application the intercept should be zero with a straight line passing through origin. Apparently, from Figure 19(a), this model is not fitting into the data.

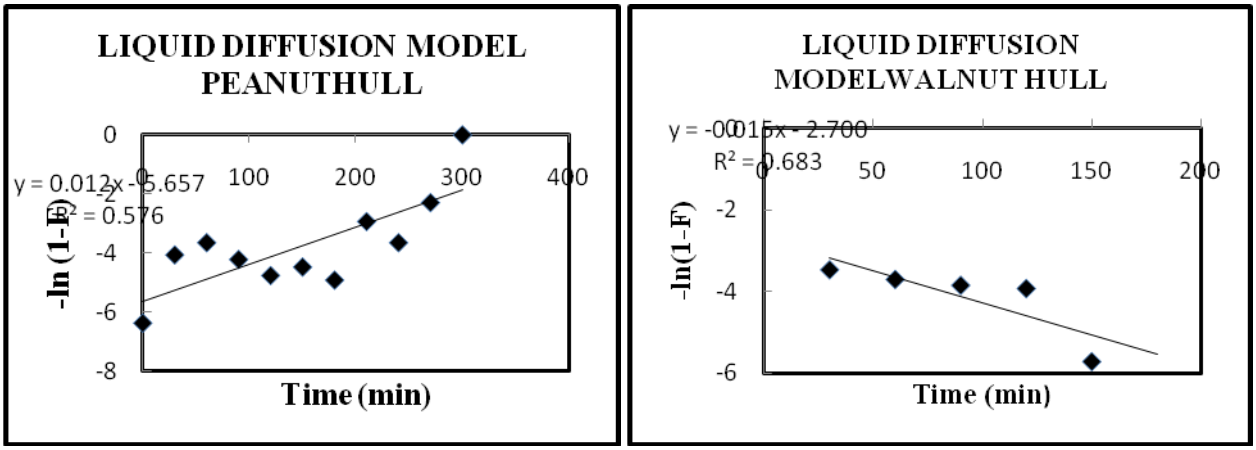


Figure 19(a)**:Liquid Diffusin Model**

CHAPTER-6

ADSORPTION THERMODYNAMICS

6.1. Gibb's Free Energy Model

The change in standard free energy (ΔG^o) at various temperatures can be estimated as follows

$$\Delta G^o = -RT \ln K_d = -RT \ln\left(\frac{q_e}{C_e}\right) \quad \textbf{(8)}$$

Here, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the temperature in K. The relation among the thermodynamic parameters mentioned above is given by the following equation. $\Delta G^o = \Delta H^o - T\Delta S^o$ **(9)**

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad \textbf{(10)}$$

A plot of ΔG^o versus T yields a straight line with the slope of $-\Delta S^o$ and intercept of ΔH^o, shown in Figure 20 .Where;

T – temperature [K],

ΔS^o - change in entropy [J/K·mol],

R - universal gas constant (8.314 J/K×mol),

ΔH^o – change of enthalpy [J/mol],

ΔG^o - change of Gibbs free energy [J/mol].

Also, alternatively the graph of $\ln(k_2/T)$ versus 1/T gives a straight line with a slope is - $\Delta H^o/R$ and intercept $[\ln(k_b/h) + \Delta S^o/R]$,

Where $K_{2=}$ pseudo second order rate constant

h= plank's constant

k_b=boltzman constant

from which the change in enthalpy and entropy was calculated. Figure 20 is based on slope and intercept which are determined the basic thermodynamic parameters, enthalpy and entropy of adsorption, and based on those determined the change of Gibbs's free energies.(Table 5)

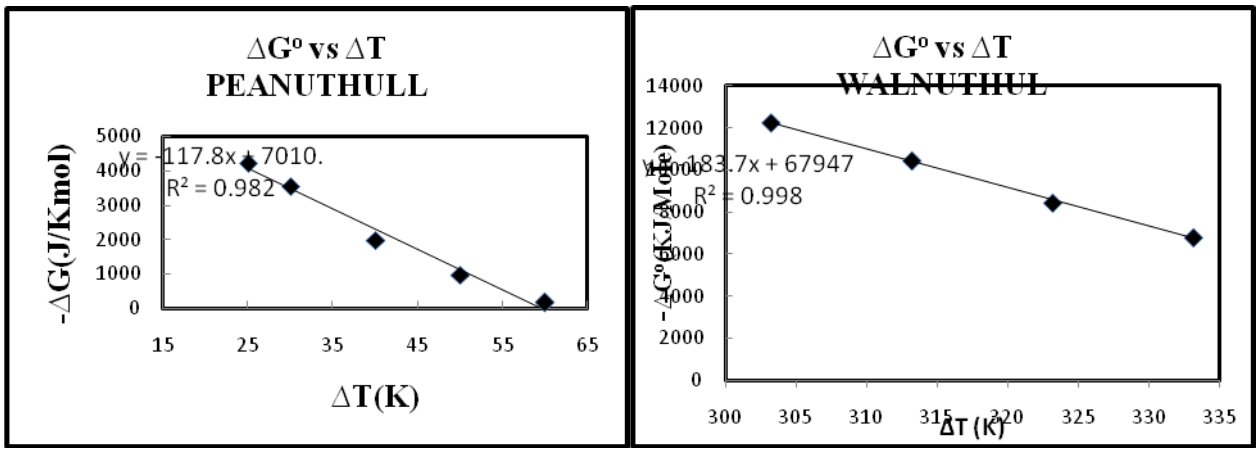


Figure20: Plot of change in Gibbs free energy with temperature

Table 5: Gibb's Free Energy for Peanut Hull Adsorption

Adsorbent	ΔH^o(J/kmol)	ΔG^o(J/kmol)	ΔS^o((J/kmol)	R^2
Peanut Hull	7010	11143	117.8	0.971
Walnut Hull	67947	7395	1837	0.916

The entropy increased with increasing initial concentration of adsorbate and is generally decreased with increasing amount of adsorbent. Energy released during the adsorption process compensates for the loss of entropy of adsorbed molecules, the stronger the forces, the more energy is released In general, the extent of aggregation depends reciprocally on the temperature

of the solution and is fully reversible. The observed relationship between entropy and enthalpy reflects an electrostatic nature of the dimerization phenomenon of this ionic dye.
(Ghasemi and Kubista et al. 2005)

Most of the sorption/desorption transformation processes of various solid phases are time-dependent. To understand the dynamic interactions of pollutants with solid phases and to predict their fate with time, knowledge of the kinetics of these processes is important (Ho et al., 2010). Various kinetic models have been used by various researchers, whereas in this study the pseudo-first-order and pseudo-second-order models were studied.

CHAPTER-7

ADSORPTION ISOTHERMS

The amount of dye sorbed at equilibrium, q_e (mg/g) which represents the dye uptake, was calculated from the difference in dye concentration in the aqueous phase before and after biosorption.

The uptake of dye by unit mass of biosorbent at any time (q) was determined from the following equation: $q_e = (C_o - C_e)/ C_o$ **(11)**

where; C_o is the initial dye concentration (mg/l),

C_e is the residual (unadsorbed) dye concentration at any time (mg/l).

Equilibrium data commonly known as adsorption isotherms are basic requirements for the design of adsorption systems. Langmuir, Freundlich, Temkin, Dubinin-Radushkevich Isotherm were used to describe the equilibrium characteristics of adsorption in the present study.

7.1. Langmuir Isotherm

The Langmuir isotherm basically assumes homogenous surface energy distribution. The Langmuir isotherm assumes that the adsorption rate is proportional to the number of vacant sites

on the adsorbent and fluid phase concentration, while the desorption rate is proportional to the number of sites covered with adsorbate molecules.

Langmuir proposed a theory to describe the adsorption of gas molecules onto metal surfaces. The Langmuir adsorption isotherm has found successful applications in many other real sorption processes of monolayer adsorption. Langmuir's model of adsorption depends on the assumption that intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The isotherm equation further assumes that adsorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a dye molecule occupies a site, no further adsorption can take place at that site. Moreover, the Langmuir equation is based on the assumption of a structurally homogeneous adsorbent where all sorption sites are identical and energetically equivalent. Theoretically, the sorbent has a finite capacity for the sorbate. Therefore, a saturation value is reached beyond which no further sorption can take place. The saturated or monolayer (as $Ct \rightarrow \infty$) capacity can be represented by the expression:

$$q_m = \frac{K_L C_e}{1 + a_L C_e} \quad \textbf{(12)}$$

where q_e is solid phase sorbate concentration at equilibrium (mg/g), Ce is aqueous phase sorbate concentration at equilibrium (mg/L), K_L is Langmuir isotherm constant (L/g), L is Langmuir isotherm constant (L/mg).Therefore, a plot of Ce/qe versus Ce gives a straight line of slope a_L/K_L and intercept $1/K_L$, where K_L/a_L gives the theoretical monolayer saturation capacity, q_m(mg/g). The Langmuir equation is applicable to homogeneous sorption where the sorption of each sorbate molecule onto the surface has equal sorption activation energy. The Langmuir equation obeys Henry's Law at low concentration; when the concentration is very low, $a_L C_e$ is far smaller than unity, it implies $q_e = K_L C_e$, **(13)**

hence, it is analogous to Henry's Law. Therefore, a linear expression of Langmuir equation is:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \quad \textbf{(14)}$$

Figure 21 describes the Langmuir isotherm.The sorption data were analyzed according to the linear form plots of specific sorption C_e/q_e against the equilibrium concentration C_e. The isotherms were found to be linear over the whole concentration range studies and the correlation coefficients were extremely high. These values of the correlation coefficients strongly support

the fact that the dyes- sorption data closely follow the Langmuir model of sorption. The isotherm constants, a_L, K_L and equilibrium monolayer capacities q_m(mg/g).

The plots in Figure 21 demonstrate that the Langmuir equation that provides an accurate description of the experimental data, (shown in Table 6) which is further confirmed by the extremely high values of the correlation coefficient in case of both peanut hull and walnut.

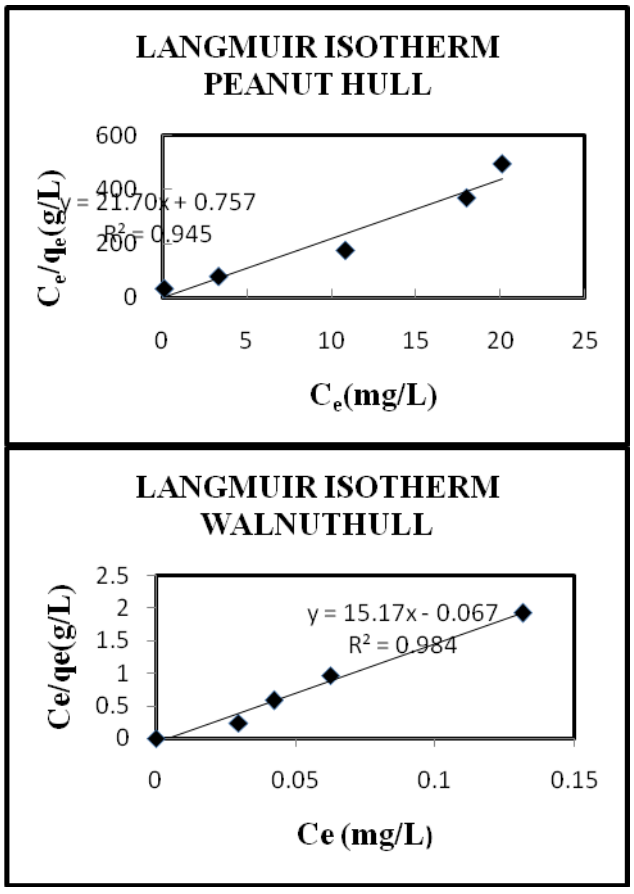


Figure 121: Langmuir Isotherm

Table 6: Parameters of Langmuir Isotherm

Adsorbent	$K_L = \frac{1}{Inercept}(L/g)$	$a_L = Slope * K_L$ (L/mg)	$K_L C_e = q_e$ (mg/g)	R^2
Peanut Hull	1.321	28.66	4.40	0.945
Walnut Hull	14.92537	226.4179	4.28	0.984

There is one more essential feature of Langmuir isotherm which is expressed in terms of equilibrium parameter R_L, It is a dimensionless constant referred to as separation factor or

equilibrium parameter further, the equilibrium adsorption intensity (R_L), which indicates the type of adsorption, is defined as follows: $R_L = \frac{1}{1 + K_L Co}$ **(15)**

Here, C_o is the initial dye concentration (mg/L) in the solution. R_L value indicates the adsorption nature to be either unfavourable if R_L>1), linear if R_L =1, favourable if 0< R_L <1 and irreversible if R_L =0. If the R_L is greater than 0 but less than 1 indicates that Langmuir isotherm is favourable.(Samarghandi et al.,2009).

A plot of R_L versus C_o is shown in Figure 22. From this figure, it can be observed that the adsorption process is more favorable at higher lower concentration of dye solution.

R_L for peanut hull was determined to be R_L<1(favourable) at optimum dye concentration of 10mg/L. and for walnut hull R_L=0.59 for optimum dye concentration of 20 mg/L (R_L < 1, indicating favorable adsorption) for the dye concentration. The Langmuir IsothermParameters are shown in Table 6.

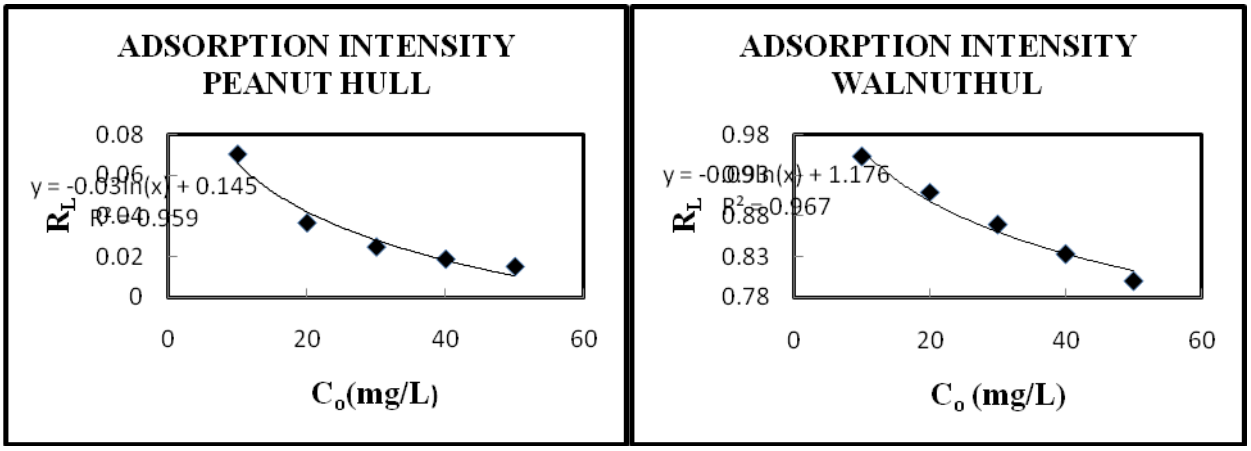


Figure 23: Equilibrium Adsorption Intensity

7.2. Freundlich Isotherm

The Freundlich equation is an empirical equation employed to describe heterogeneous systems, in which it is characterized by the heterogeneity factor 1/*n*. Hence, the empirical equation can be written: $q_e = K_F C_e^{1/n}$ **(16)**

where q_e is solid phase sorbate concentration in equilibrium (mg/g), C_e is liquid phase sorbate concentration in equilibrium (mg/L), K_F is Freundlich constant (L/g) and 1/*n* is the heterogeneity factor.The constant K_F is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process .If n = 1 then the partition between the two

phases are independent of the concentration. If value of 1/n is below one it indicates a normal adsorption. On the other hand, 1/n being above one indicates cooperative adsorption, If n lies between one and ten, this indicates a favorable sorption process. A linear form of the Freundlich expression can also be obtained by taking logarithms of Equation (16).

$$\ln q_e = \ln K_F + 1/n(\ln Ce) \quad \textbf{(17)}$$

Therefore, a plot of q_e versus C_e (Figure 23)enables the constant K_F and exponent $1/n$ to be determined. The Freundlich isotherm describes reversible adsorption and is not restricted to the formation of the monolayer. The Freundlich Isotherm Parameters are shown in Table 7.

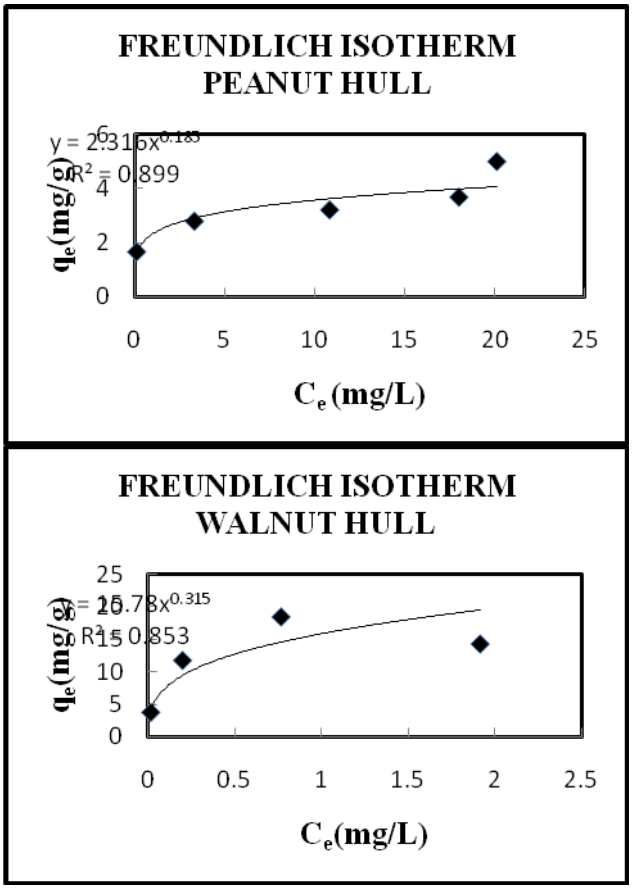


Figure 133: Freundlich Isotherm

Table 7: Parameters of Freundlich Isotherm

Adsorbent	K_F=slope (L/g)	1/n	N	$q_e=K_F C_e^{1/n}$	R^2
Peanut Hull	2.316	0.185	5.40	3.6	0.899
Wallnut Hull	15.78	0.315	3.17	9.5	0.853

7.3. Redlich–Peterson Isotherm

Redlich and Peterson incorporate three parameters into an empirical isotherm (shown in Figure 24).The R–P isotherm model combines elements from both the Langmuir and Freundlich equation and the mechanism of adsorption is a hybrid and does not follow ideal monolayer adsorption. Where, β is a constant parameter and is normally less than unity. This equation reduces to a linear isotherm at low surface coverage, to the freundlich isotherm at high adsorbate concentration and to the Langmuir isotherm when β=1. However, the equation cannot be linearised for easy estimation of the isotherm parameter K_R, a_R and β. The linearization of the expression gives the following relation:

its limiting behaviour is summarised here. where β=1

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \quad \textbf{(17)}$$

It becomes a Langmuir equation. Where β=0 i.e. the Henry's Law equation

$$q_e = \frac{K_R C_e}{1 + a_R C_e} \quad \textbf{(18)}$$

This equation can be converted to a linear form by taking logarithms:

$$\ln\left(K_R \frac{C_e}{q_e} - 1 \right) = \beta \ln(C_e) + \ln(a_R) \quad \textbf{(19)}$$

$$\text{Or } \frac{C_e}{q_e} = \frac{1}{K_R} + \frac{a_R}{K_R} C_e^{\beta} \quad \textbf{(20)}$$

Plotting C_e/q_e against C_e^{β}

Three isotherm constants, *A, B,* and K_R *(*isotherm constants) are shown in Table 8 below. These can be evaluated from the linear plot represented by using a trial and error procedure. Computer operation was developed to determine the isotherm parameters by optimization routine to maximize the coefficient of determination R^2.The quality of the fit of the experimental data with the isotherm equation is assessed on the magnitude of the correlation coefficient for the regression. In other words, the isotherm giving the correlation coefficient closest to unity provides the best fit.

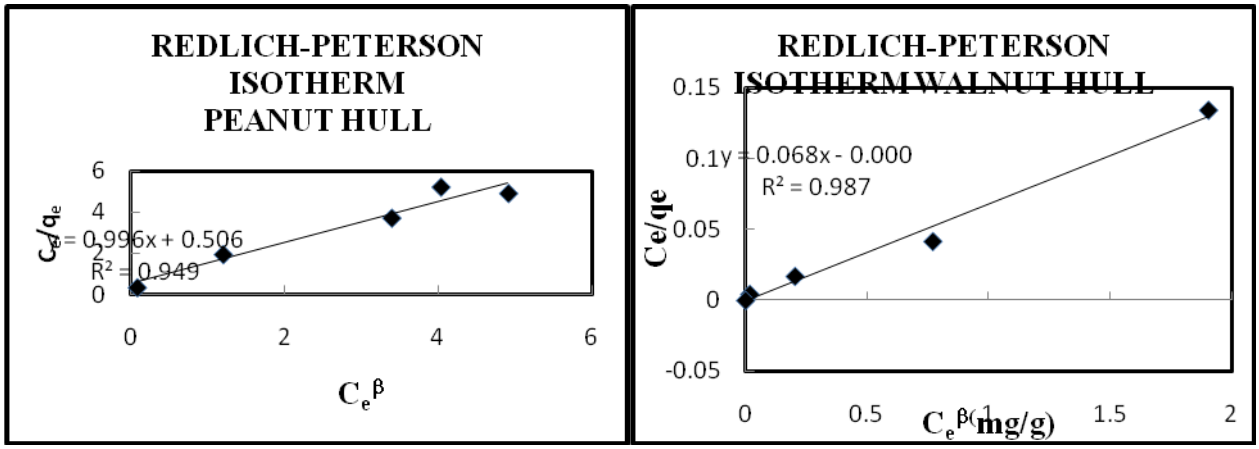


Figure 24:The Redlich-Peterson Isotherm

Table 8:: Parameters of Redlich-Peterson Isotherm

Adsorbent	$slope = \frac{a_R}{K_R}$	$\text{int}\, ercept = \frac{1}{K_R}$	a_R	K_R	β	R^2
Peanut Hull	0.996	0.506	1.968	1.976	0.55	0.949
Walnut Hull	0.068	0.00	0.00	0.00	0.99	0.987

7.3 Temkin Isotherm

The Temkin isotherm equation (shown in Figure 25) assumes that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy (Temkin, 1940). The Temkin isotherm is represented by the following equation: The Temkin isotherm is represented by the following equation:

$$q_e = \frac{RT}{b}\ln(K_T C_e) \quad \textbf{(21)}$$

Equation can be expressed in its linear form as:

$$q_e = B_T \ln K_T + B_T \ln C_e \quad \textbf{(22)}$$

;Where, T is the absolute temperature (K),

R is the universal gas constant (8.314J/mol.K),

K_T is the equilibrium binding constant (L/mg),

b_T is the variation of adsorption energy (kJ/mol).

B_T is Temkin constant related to the heat of adsorption (kJ/mol).

The Temkin adsorption isotherm model was chosen to evaluate the adsorption potentials of the adsorbent for adsorbates. Figure25 shows Temkin isotherm for peanut hull and walnut hull.

$$q_e = \frac{RT}{b}\ln(K_T C_e) \quad \textbf{(23)}$$

Equation can be expressed in its linear form as:

$$q_e = B_T \ln K_T + B_T \ln C_e$$

(24)

The Temkin adsorption isotherm model was chosen to evaluate the adsorption potentials of the adsorbent for adsorbates. Figure26 shows Temkin isotherm for peanut hull and walnut hull.

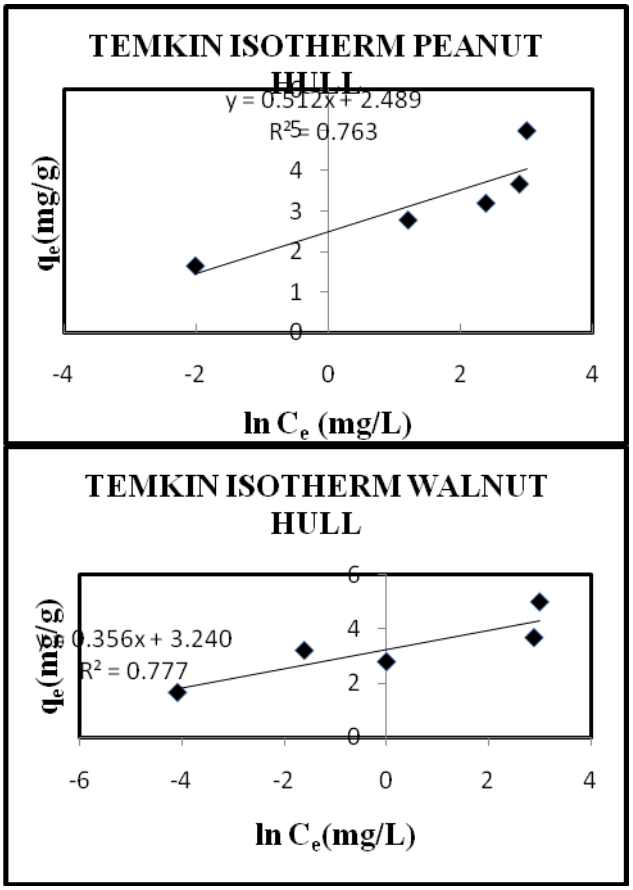


Figure 25: Temkin Isotherm

Table 9: Parameters of Temkin Isotherm

Adsorbent	$B_T = slope = \frac{RT}{b_T}$	$b_T = \frac{RT}{slope}$	$Intercept = \frac{RT\ln(K_T)}{b_T}$	R^2
Peanut Hull	0.512	5085.180	2.489	0.579
Walnut Hull	2.665877	947.4571	15.47	0.663

7.5 The Dubinin-Radushkevich Isotherm

This isotherm is generally expressed as follows given by Dubinin in the year1960:

$$q_e = q_t \exp\left\{ - B_D \left[RT \ln\left(1 + \frac{1}{C_e} \right) \right]^2 \right\} \quad \textbf{(25)}$$

Radushkevich in the year 1949 and Dubinin in the year 1965 have reported that the characteristic sorption curve is related to the porous structure of the sorbent and can be well applied to the data of intermediate concentration range. As reported by Dada et al., (2012), this isotherm model is generally applied to explain adsorption on heterogeneous surfaces and their Gaussian energy distribution. It is also a temperature dependent model i.e the plot between $\ln(q_e)$ vs ε^2 gives a characteristic curve

$$q_e = q_t (\exp)(-K_{ad}\varepsilon^2) \quad \textbf{(26)}$$

or $$\ln q_e = \ln(q_t) - (K_{ad}\varepsilon^2) \quad \textbf{(27)}$$

Where q_e = amount of adsorbate in the adsorbent at equilibrium (mg/g);

q_t = theoretical isotherm saturation capacity (mg/g);

K_{ad} = Dubinin–Radushkevich isotherm constant (mol^2/kJ^2)

ε^2 =Dubinin–Radushkevich isotherm constant, where; $\varepsilon = RT \ln\left(1 + \frac{1}{C_e} \right)$

S. G. Chen and R. T. Yang (1994) describes that this model helps distinguish between physical and chemical adsorption of with its mean free energy, E per molecule of adsorbate (for removing

a molecule from its location in the sorption space to the infinity) can be determined by the relationship $E = \frac{1}{\sqrt{2B_D}}$ **(28)**

The constant, B_D Is related to the mean free energy of sorption per mole of the sorbate as it is transferred to the surface of the solid from infinite distance in the solution and this Energy can be computed using the following relationship as described by Itodo et al.,2010. Dubinin-Isotherm for peanut hull and walnut hull is shown in Figure 26.

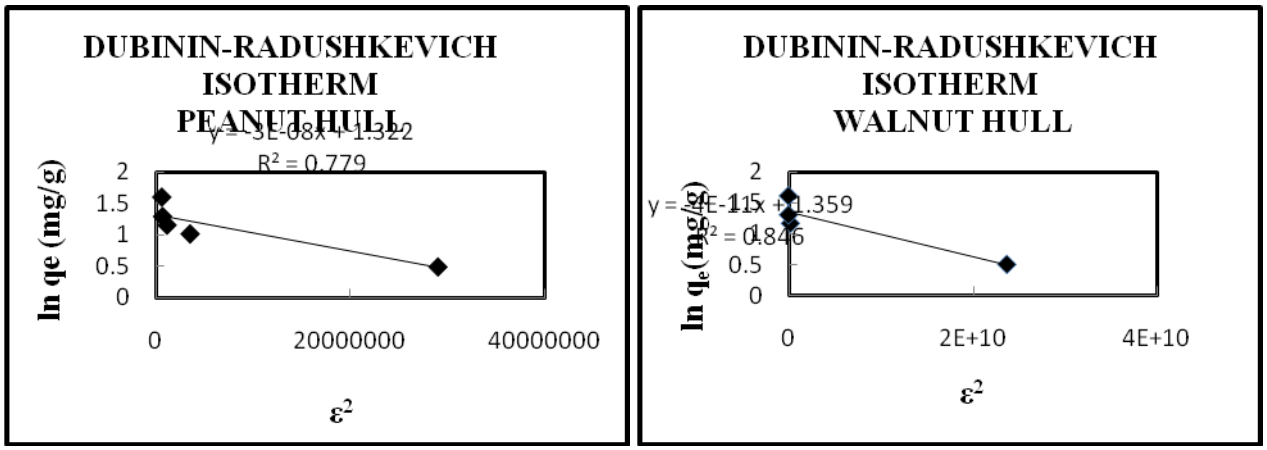


Figure 146: The Dubinin-Radushkevich Isotherm

Table 10: Parameters of Dubinin-Radushkevich Isotherm

Adsorbent	$-B_D = \frac{slope}{R^2T^2}$	q_t=exp(intercept)	$E = \frac{1}{\sqrt{2B_D}}$	R^2
Peanut Hull	4.43×10^{-15}	1.322	16920.209	0.779
Walnut Hull	6.296×10^{-18}	1.359	281797.63	0.846

CHAPTER-8

CONCLUSION

The following conclusions have been derived from the experimental analysis carried out so far.

- The low cost adsorbent i.e. Peanut Hull and Walnut Hull have been used successfully applied for the adsorptive removal of thionine dye from its aqueous solutions.
- The optimum adsorbent concentration and adsorbent dosage obtained from the experimental studies for thionine Dye is 10 mg/L and the adsorbent dosage of 6g/L for both the adsorbents
- λ_{max} for thionine dye solution was found to be 598 nm.
- Optimal pH value obtained is 8 for the peanut hull adsorbent system and it is 7 for the walnut hull adsorbent system.
- Optimal stirrer speed is 200 rpm for both the adsorbent systems
- Removal efficiency decreases with increasing the initial dye concentration.
- Removal efficiency increases with increasing the adsorption time.
- Adsorption process is exothermic and is favored at low temperatures.
- Experimental data matches well with the pseudo-second -order kinetics.

Experimental data matches well with the Langmuir isotherm than the Freundlich isotherm.

Most important observation in this work is that the Natural Walnut Hull is better than the Peanut Hull, but both can act as a very effective adsorbent for the removal of thionine dye. The removal efficiency increased with increasing the Peanut Hull concentration significantly and reached a value as high as 91.3% at lower concentrations (up to 10 mg/L) where as no significant change was observed at higher concentrations on the other hand the removal efficiency reached 100% in case of walnut hull.

Work done so far includes - studying the effect of various parameters on the removal of thionine dye. However, there is a lot of scope for further research in this area. Some of the objectives that can be studied in future are as follows.

1. Studying the performance of the Peanut Hull and Walnut Hull for the removal of other important dyes used in the industry.

2. Using the Peanut Hull and Walnut Hull for industrial wastewater treatment in continuous mode (fixed bed or fluidized bed studies).

3. Removal of heavy metals from water by adsorption with the natural Peanut Hull and Walnut Hull.

As the project has already been completed, the rest of this work is recommended as future work for the next batch of students

Cost-estimation of adsorbent used in the study

The Peanut Hull and walnut hull are the waste accumulates in the agro-industrial yards,it has no significant industrial and commercial uses, but becomes an issue and contributes to serious environmental problems. Hence, the utilization of such agriculture solid waste for wastewater treatment is most desirable. The cost of this waste as a dye sorbent is only associated with the transport and process expenses which are approximately US$ 50/ton whereas the average price of activated carbon used in South Asia is US$ 1000–1100/ton. Thus the proposed natural Peanut hull and walnut hull sorbent is more than 50 times cheaper than activated carbon. Although the adsorption capacity of natural adsorbents like peanut hull and walnut hull may be lower than commercial activated carbons, the adsorbent is renewable material, abundantly available and, therefore, low-cost adsorbent. The peanut hull and walnut hull can be an economical alternative for the commercially available activated carbon in removal of basic dye from aqueous solutions.

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NOMENCLATURE

- **C_0** initial dye concentration in aqueous solution (mg/dm^3)
- **C_e** equilibrium dye concentration in liquid phase (mg/dm^3)
- **D** adsorbent dosage (g/dm^3)
- **d_p** particle size (µm)
- **K_2** pseudo-second order rate constant (g mg^{-1} min^{-1})
- **K_F** Freundlich constant (mg g^{-1})(dm^3/ mg)
- **K_L** Langmuir adsorption constant (dm^3 mg-1)
- **1/n** Freundlich parameter
- **q_e** equilibrium dye concentration in solid phase (mg g^{-1})
- **q_m** maximum dye adsorbed per unit mass of adsorbent (mg g^{-1})
- **R** the gas universal constant (8.314 J/mol K)
- **R_L** Langmuir separation or equilibrium parameter (dimensionless)

- **RPM** speed of agitation, min^{-1}
- Babsolute temperature (K)
- **t** time (min)
- **G** free energy of adsorption (kJ mol-1)
- **H** change in enthalpy (kJ mol^{-1})
- **S** change in entropy (kJ mol^{-1} K^{-1})
- $\mathbf{K_{ad}}$ = Dubinin–Radushkevich isotherm constant (mol^2/kJ^2)
- ε^2 =Dubinin–Radushkevich isotherm constant,

- $\boldsymbol{R}$ is the universal gas constant (8.314J/mol.K),
- $\boldsymbol{K_T}$ is the equilibrium binding constant (L/mg),
- $\boldsymbol{b_T}$ is the variation of adsorption energy (kJ/mol).
- $\boldsymbol{B_T}$ is Temkin constant related to the heat of adsorption (kJ/mol).