ADSORPTIVE TREATMENT OF TEXTILE WASTEWATER BY ACTIVATED CARBON BASED ON PEANUT SHELL

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Submitted by

Rashmi Saluja
(Roll No.: 601111014)

UNDER THE GUIDANCE OF

Dr. V.K. Sangal
Assistant Professor
Department of Chemical Engineering
Thapar University, Patiala

Dr. J.P. Kushwaha
Assistant Professor
Department of Chemical Engineering
Thapar University, Patiala

DEPARTMENT OF CHEMICAL ENGINEERING
THAPAR UNIVERSITY
PATIALA-147004, PUNJAB, INDIA
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CERTIFICATE

This is to certify that the dissertation entitled, “Adsorptive Treatment of Textile Wastewater by Activated Carbon Based on Peanut Shell” is an authentic record of my own work carried out as requirements for the award of degree of Master of Technology in Chemical Engineering from Thapar University, Patiala, under the supervision of Dr. V.K. Sangal, Assistant Professor, Department of Chemical Engineering and Dr. J.P. Kushwaha, Assistant Professor, Department of Chemical Engineering during July, 2012 to June, 2013.

Date: 24/06/13

Rashmi

Rashmi Saluja
(601111014)

It is certified that the above statement made by student is correct to the best of our knowledge and belief.

Dr. V.K. Sangal
Assistant Professor
Chemical Engineering Department

Dr. J.P. Kushwaha
Assistant Professor
Chemical Engineering Department

Countersigned by:

09.07.13

Dr. Rajeev Mehta
Head, Chemical Engineering Department
Thapar University, Patiala

Dr. S.K. Mohpatra
Dean, Academic Affairs
Thapar University, Patiala

ABSTRACT

Approximately 125–150 L of water per kg of textile product produced is consumed in textile industries. Also, during the textile processing, varieties of dyes and chemicals are used, which make textile wastewaters very environmental challenging not only in terms of liquid waste, but also in its chemical composition.

In the present study, Activated carbon were prepared from peanut shell and its suitability for the adsorptive removal of Reactive Black 15 (RB-15) dye from aqueous solution have been explored. For this, Dosage study was carried out by varying the adsorbent dosages in the range of 2-30 g/l the natural pH and 300 K. The adsorption of RB-15 dye was studied over a initial pH range of 3–9 at 300K with optimum adsorbent dosage of 20 g/l. The pH of the adsorbate solutions was adjusted using N/10 aqueous solution of either HCl or NaOH.

To explore the effect of time on the adsorption process, kinetic study were performed at various C_0 values (50-300 mg/l) at optimum dosage of adsorbent (m_{ad}**)** and optimum pH (**pH_{opt}**), and experimental data were tested for their validation with pseudo-first-order and pseudo-second-order model.

Equilibrium adsorption isotherm equations are essential criterion for the design of adsorption systems. Therefore, it is important to establish the most suitable correlation for the equilibrium adsorption. Isothermal experiments were performed at 293, 313 K with C_0 values of 25, 50, 100, 150, 200, 250, 300 and 350 mg/l at **pH_{opt}** and **m_{ad}** of adsorbent .Isotherms such as Freundlich, Langmuir, Redlich-Peterson (R-P) and Tempkin were used to represent the adsorption equilibrium data.

It was found that pseudo-second-order kinetic model best fitted the experimental kinetic data, whereas, isothermal study showed that the process is endothermic in nature, and Temkin isotherm best fitted the experimental equilibrium data.

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q_t	The amount of the adsorbate adsorbed on the adsorbent in time t.
q_e	The amount of the adsorbate adsorbed on the adsorbent under equilibrium condition
q_m	Adsorption capacity
k_F	Pseudo-first order rate constant
t	Time
k_s	Pseudo-second order rate constant
h	Initial sorption rate
K_F	Freundlich constant
C_e	Equilibrium liquid phase concentration
K_L	Langmuir adsorption constant
K_R	R–P isotherm constant
a_R	R–P isotherm constant
β	Exponent to R-P isotherm
n	Heterogeneity factor
C_0	Initial rb-15 dye concentration
pH_{opt}	Optimum pH
$m_{\mathbf{ad}}$	Optimum dosage of adsorbent
C_t	Dye concentration at time *t*
V	Volume of the solution
q_{texp}	Experimental values of the amount of the adsorbate adsorbed on the adsorbent in time t.
$q_{t\,cal}$	Calculated values of the amount of the adsorbate adsorbed on the adsorbent in time t.

CHAPTER- 1

INTRODUCTION

Growth and development of any country very much depends on industrialization. Development has improved life style and living standard of peoples, and this improvement is at the cost of very high increase in use of natural resources and increase in industrial production.

The textile industry uses vegetable fibers such as cotton, animal fibers, silk, and synthetic materials such as nylon, polyester, and acrylics. The textile industries consume high energy, water, and chemical. About 60% of the energy is used by dyeing and finishing operations. Being very water intensive, textile industries produce large amount of wastewater. Therefore, Environmental problems associated with the textile industry are typically those associated with water pollution.

1.1. PROPERTY, USES AND TOXICITY OF REACTIVE DYE

A dye, which is capable of reacting chemically with a substrate to form a covalent dye substrate linkage, is known as reactive dye.

Reactive dyes first appeared commercially in 1956, after their invention in 1954 by Rattee and Stephens at the Imperial Chemical Industries Dyestuffs Division site in Blackley, Manchester, United Kingdom.

Here the dye contains a reactive group and this reactive group makes covalent bond with the fibre polymer and act as an integral part of fibre. This covalent bond is formed between the dye molecules and the terminal –OH (hydroxyl) group of cellulose fibres on between the dye molecules and the terminal $-NH_2$ (amino) group of poly-amide or wool fibres.

$$\text{D-SO}_2\text{-CH}_2\text{-CH}_2\text{-OSO}_3\text{Na} + \text{OH-C} \Rightarrow \text{D-SO}_2\text{-CH}_2\text{-CH}_2\text{-O-cell} + \text{NaHSO}_3$$

$$\text{D-SO}_2\text{-CH}_2\text{-CH}_2\text{-OSO}_3\text{Na} + \text{NH}_2\text{- W} \Rightarrow \text{D-SO}_2\text{-CH}_2\text{-CH}_2\text{-NH-Wool} + \text{NaHSO}_3$$

Where, D (dye part), W (wool polymer) and C (cellulosic polymer).

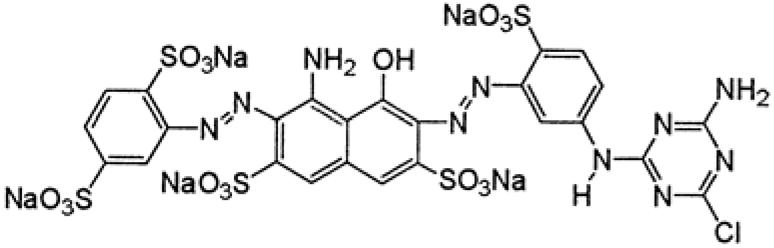

Fig 1.1. Reactive Black 15

The concentration of reactive dyes used in textile industries varies from 10 to 10000 mg/L, depending on the dye quality and process. During the process nearly 30% of reactive dye is wasted, and discharged into wastewater stream.

Reactive dyes have following Properties:

1. Reactive dyes are cationic dyes, which are used for dyeing cellulose, protein and polyamide fibers.
2. During dyeing the reactive group of this dye forms covalent bond with fibre polymer and becomes an integral parts of the fibre.
3. Reactive dyes are soluble in water.
4. They have very good light fastness with rating about 6. The dyes have very stable electron arrangement.
5. Reactive dye gives brighter shades and has moderate rubbing fastness.

Reactive dye powders are very light and fly easily, forming invisible dust clouds around weighing and mixing areas and this dusts may remain suspended in the workplace atmosphere for 15 minutes or more. These are carcinogenic in nature, skin allergic and non-biodegradable (Gregory et al, 1986).

1.2. WASTEWATER CHARACTERSTICS AND DISCHARGE STANDARD

Approximately 125–150 L of water per kg of textile product produced is consumed in textile industries (Korbahti et al., 2008). Also, during the textile processing, varieties of dyes and chemicals are used, which make textile wastewaters very environmental challenging not only in terms of liquid waste, but also in its chemical composition (Venceslau et al.,1994).

Dyes used contribute to overall toxicity at all process. Dye bath effluent carries high level of biochemical oxygen demand (BOD)/ chemical oxygen demand (COD), colour, toxicity, surfactants, fibers, turbidity and heavy metals. Therefore, these wastewaters bear high suspended solids, COD, colour, and high pH (Dae-Hee et al.,1999; Venceslau et al.,1999). Typical characteristics of textile effluent are given in Table 1.1.

These wastewaters may also carry oils and grease, waxes and heavy metals such as chromium, copper, zinc and mercury (EPA, 1974). Heavy metals enter from dyeing operation. Copper is toxic to aquatic plants at concentrations below 1.0 mg/l while concentrations near this level can be toxic to aquatic life (Sawyer et al.,1978).

Table 1.1 Typical characteristics of textile effluent

Parameters	Values
pH	6.0-10.0
Temperature	35-45˚C
Biochemical Oygen Demand (mg/l)	100-4,000
Chemical Oxygen Demand (mg/l)	250-10,000
Total Suspended Solids (mg/l)	100-5000
Total Dissolved Solids (mg/l)	1,800-6,000
Chlorides (mg/l)	1,000-6,000
Total Alkanity (mg/l)	500-800
Sodium (mg/l)	600-2,175
Total Kjeldahl Nitrogen (mg/l)	70-80

Central pollution control board, CPCB (Wastewater discharge regulatory body in India) has set Minimal National Standards (MINAS), for the discharge of pollutants from various industries. MINAS for some dye utilizing industries are tabulated in Table 1.2, 1.3 and 1.4.

Table 1.2 MINAS for cotton textile industries (composite and processing)

Parameter	**Concentration not to exceed, milligram per liter (except for pH and bioassay)**
pH	5.5. to 9.0
Suspended solids	100
BOD, 3 days at 27^{o}C	150
Oil and grease	10
Bio-assay test	90% survival of fish of after 96 hours in 100% effluent
Total chromium (as Cr)	2
Sulphide (as S)	2
Phenolic compounds (as C6H5OH)	5

Source: http://www.cpcb.nic.in/standard41.htm

Table 1.3 MINAS for man-made fiber industry

Process	**Parameter**	**Concentration not to exceed, mg/l (except for pH)**
Synthetic	Suspended Solids	100
	BOD, 3 days at 27 ^{o}C	30
	pH	5.5 to 9.0
Semi-synthetic	pH	5.5-9.0
	Suspended Solids	100
	BOD, 3 days at 27 ^{o}C	30
	Zinc (as Zn)	5

Source: http://www.cpcb.nic.in/standard41.htm

Table 1.4 MINAS for dye and dye intermediate industry

Parameter	Concentration not to exceed milligrams per liter (except for pH, temperature and bio-assay)
pH	6.0 – 9.0
Colour Hazen Unit	400.0
Suspended Solids	100.0
BOD (3 days at 27 ^{o}C)	100.0
Oil and Grease	10.0
Phenolics as C6H5OH	1.0
Cadmium as Cd	0.2
Copper as Cu	2.0
Manganese as Mn	2.0
Lead as Pb	0.1
Mercury as Hg	0.01
Nickel as Ni	2.0
Zinc as Zn	5.0
Total Chromium	2.0
Bio-assay test	90% survival in 96 hours.

Source: http://www.cpcb.nic.in/standard24.htm, EPA Notification GSR 742(E) dt. 30th Aug., 1990

1.3. VARIOUS METHODS FOR THE REMOVAL OF DYE CONTAINING WASTEWATER

Few decades earlier, the dye selection, application and uses were not given a major consideration with respect to their environmental impact. Even the chemical composition of half of the dyes used in the industry was estimated to be unknown. With the growing concern on health mainly aesthetic grounds, it was more from 80s that people started paying much attention to the dye waste too. Since initially there was no discharge limit, so the treatment of waste water started with some physical treatments such as sedimentations and equalization to maintain the pH, Total Dissolve Solids (TDS), and total suspended solids (TSS). Later some secondary treatments such as activated sludge, biological process were used to treat the dye waste water. After sometimes, physico-chemical treatment such as adsorption, ion-exchange, Advanced oxidation and membrane separations were introduced for the treatment of textile waste water. A selection of treatment process based on the effectiveness of the process for the removal of targeted contaminants, Reliability, Adaptability/Flexibility, Energy requirements, construction cost and total costs. Table 1.5 shows the comparative study of the different process for textile waste water treatment process.

In addition, the adsorption process has been widely used for colour removal. Adsorption is one of the process, which besides among widely used for the dye removal and also has wide applicability in waste water treatment (Bansal et al., 2005)

The history on carbon adsorption in the purification of water dates back to ancient times. Adsorption on porous carbons was used as early as 1500 B.C for medical purposes. However in scientific records, the phenomenon of adsorption was observed by C.W. Sheele in 1773 for gases exposed to carbon. This was followed by observations made by Lowitz in 1785 of the reversible removal of colour and odour producing compounds from water by wood charcoal. Larvitz in 1792 and kehl in 1793 observed similar phenomenon with vegetable oil and animal charcoal respectively. Activated carbon which are widely used as a adsorbents, not only remove different types of dyes but also organic and inorganic pollutants such as metal ions (Carrott et al., 2005), phenols (Caturla et al., 1988) and chlorinated hydrocarbons and many other chemicals. Studies have been shown that Commercially available activated carbons good materials for the removal of different types of dyes but there use is sometimes restricted due to the higher cost also, the activated carbon after their use become exhausted and no longer capable of further adsorbing the dyes. Once Activated carbon has been exhausted. It has to be regenerated for further use in purifying water and any regeneration process adds cost as well as the adsorption capacity of regenerated activated is lower in comparison to the original one. This has resulted in attempts to prepare low cost adsorbents which may replace activated carbons in pollution control through adsorption process. Table1.6 shows adsorption capacity of various biosorbents.

Table 1.5 Comparative study of the different process for textile waste water treatment process.

Process	Definition	Advantages	Drawbacks
Sedimentation	Sedimentation is the gravitational accumulation of solids at the bottom of a fluid (air or water)	Cost effectiveness & low energy consumption	More time required to complete the process. No clear solution
Activated sludge Process	In Activated sludge process, atmospheric air or pure oxygen is bubbled through primary wastewater combined with organism in aeration tank to develop a biological floc which reduces the organic content of the waste water	Low installation cost Low Land requirement Good quality effluent	Operating cost is high It is a rigid process. Sensitive to certain process
Biological Waste Water treatment	Biological Wastewater Treatment consists of ensuring contact between the water to be treated and bacteria, which feed on the organic materials in the wastewater, thereby reducing its Biological Oxygen Demand (BOD) content.	Elimination of secondary clarifier Rapid strat up	Total cost is high
Ion exchange	Ion exchange is a reversible chemical reaction where an ion from solution from solution is exchanged for a similarity charged ion attached to an immobile solid particle.	Can be used with fluctuating flow rates Makes effluent contaminates impossible	Pretreatment is required Sensitive to other ions present
Membrane Separation	A membrane is a selective barrier that permits the separation of certain species in a fluid by combination of sieving and diffusion mechanisms. Membranes can separate particles and molecules and over a wide particle size range and molecular weights.	Energy saving Environmental Friendly Clean Technology	Low selectivity Fouling
Advanced Oxidation	Advanced Oxidation Processes (AOP) refers to a set of chemical treatment procedures enhanced by Ultra sound and UV activation, designed to remove organic and inorganic materials in waste water.	Potential to reduce toxicity and possibly complete mineralization of organic treated. Reaction does not produce chemical sludge.	Expensive Demand large amount of peroxide.

Adsorption	Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate).	Greater Flexibility. Superior removal of organic waste constituents. Potential for significant heavy metal removal.	Required Prediction. Knowledge of the process.

Source: (Weber et al., 1974.)

1.4. PEANUT SHELLS AS AN ADSORBENT

Adsorption on to activated carbon prepared from Peanut shell is one of the most attractive methods for removal of dye and organic matter in aqueous solution. Adsorption capacity of the activated carbon depends on characteristics of activated carbon's like surface area, pore size distributions, surface chemistry (surface functional groups), and ash content. Adsorption capacity also depends on adsorbate characteristics like molecular weight, and functional groups and also affected by the solution pH.

Peanut shell activated carbon has large surface area vary between 1000-1200 m^2/g (Malik et al., 2006).

Peanut shell extensively used as adsorbent for the removal of non- biodegradable dyes from aqueous solution. The adsorption capacity of peanut shell is much higher than the other agro- based adsorbents (Abbas et al., 2012). The metal ions($Cd^{2+,}$ Cu^{2+}, Pb^{2+}, Ni^{2+}) also removed by the peanut shell Activated carbon (Wilson et al., 2006; Idris et al., 2012).

Table1.6 Adsorption capacity of various Adsorbent

Adsorbent	**Adsorbent Capacity(mg/g)**
Peanut Shell activated Carbon	164.9
Tannery Sludge	55.87
Rice Husk	50
Charcoal	22
Orange peel	18.6
Peat	12.7
Bagasse	5.78

Source: (Gupta et al., 2009)

1.5. OBJECTIVES

1. Characterization of the activated carbon based on Peanut Shell.
2. To study the effect of initial pH, adsorbent dose, contact time, initial concentration and temperature on the removal of reactive dye from the aqueous solution.
3. To perform the equilibrium adsorption and the kinetics of adsorption of reactive dye onto peanut shell based activated carbon, and to analyze the experimental data using various kinetic and isotherm models.

CHAPTER- 2

LITERATURE REVIEW

In this chapter, various adsorption studies of Reactive Dye on varieties of adsorbents, available in open literature, have been discussed.

Ahmed et al. (2012) investigated the four adsorbents; Orange peel, Sodium hydroxide treated orange peel, Cetyltrimethylammonium bromide Modified orange peel and Cetyltrimethylammonium bromide modified Sodium hydroxide treated orange peel and their sorption capacity towards reactive blue 19 (RB19). The adsorption of the dye was assessed with these adsorbents at different pH levels, temperatures and contact time is considered for determining the order and rate constants for adsorption process. The adsorption of reactive blue19 was reported to the pseudo-first-order kinetics. The adsorption data were analyzed by Freundlich, Langmuir, Elovich and Tempkin models. The adsorption of RB-19 was highly affected by temperature, it increases from 303 to 313 K and further increase of the temperature from 313 to 333 K may be sufficient to weaken the binding energy between the sorbent sites and sorbate molecules, and desorption started.

Gaikwad et al. (2010) investigated that the Sugar cane bagasse ash, an agricultural byproduct, acts as an effective adsorbent for the removal of dye (Orange-II) from aqueous phase. Adsorbents are very efficient in decolorized diluted solution. The effects of bed depth on breakthrough curve, effects of flow rate on breakthrough curve were investigated with the help of Thomas,Yoon-Nelson model .The removal of dyes at different flow rate (contact time),bed height by Sugarcane Bagasse Ash as an adsorbent has been studied. It is found that percent adsorption of dyes increases by decreasing flow rate from 2 lit/hr to 1 lit/hr, by increasing bed height from 15cm to 45cm.

Geetha et al. (2011) reported that reactive dye with most stable molecular structures is difficult to degrade. An attempt was made to remove colors using natural adsorbents like, Garlic husk, Chewing tobacco and Egg shell. The natural adsorbents were first treated with acid, washed with water and finally dried and used as adsorbents. The dye removal efficiency was at the maximum level. The effect of initial concentration, pH, adsorbent dose, time and kinetics were studied. The effect of contact time (24 to 48 hr) with 1.0 g adsorbent dose in 50 mL of 10 ppm dye solutions was investigated and the result shows, as dose of adsorbent increased, the adsorption increases and as concentration increases the adsorption decreases. The adsorption increases with time. The isotherm Freundlich and Langmuir were applied, which showed the favorable model.

Geethakarthi et al. (2011) investigated the adsorption of two reactive dyes, Reactive Red 31 and Reactive Red 2 onto tannery sludge developed activated carbon depending on parameters such as initial dye concentration, pH, agitation speed, adsorbent dosage and temperature by employing batch experiment. The activated carbon of particle size 600 µm was selected for adsorption. The Pseudo second order adsorption mechanism was predominant for the adsorption of the reactive dyes. The adsorption data correlated well with Langmuir model compared to the Freundlich isotherm model. The maximum adsorption capacity found in the range of 23.15-39.37 mg/g and 47.62-55.87 mg/g for reactive dyes reactive red 31 and reactive red 2, respectively.

Girgis (2011) investigate the six carbon precursor seed hulls (or coats) of peanut, soybean, cottonseed, lupine, broad beans, and sunflower seeds, were subjected to various treatments in order to get adsorbing carbons for the removal of methylene Blue. All the adsorbents are pretreated by simple pyrolysis at 500^0C yields low adsorbing carbons of meso-/macroporous character, steam activation of these chars at 850^0C which enhances porosity, in micropores, to a limited extent and chemical activation with H_3PO_4 at 500^0C , producing high adsorbing carbons with evenly distributed porosity within micro-mesopore ranges. It was found that phosphoric acid activation of the studied precursors enhanced the yield, surface area and pore volume; 32- 46%, 437–1022 m^2/g and 0.444–0.809, respectively, as compared to other treatments. Characterization of porosity was determined by N_2/77 K adsorption isotherms. Peanut shells proved the best feasible raw material under all treatment processes.

Kassim et al. (2012) investigated the feasibility of using an agricultural waste, mangrove bark for removal of Reactive Black 5 dye from aqueous solutions under different process conditions. Adsorbent was prepared by pre-treating the mangrove bark with formaldehyde. Various factors such as pH, contact time, initial dyes concentrations, and amount of adsorbent were taken into account. The rate of dye removal from the aqueous solutions is sensitive to the pH and initial concentration of dye in solution phase, for this purpose pH was observe up to the 10 value. The result revealed that a very rapid adsorption at first 10 minutes, and there after it proceeds at slower increase and finally attains saturation at certain contact time for different initial concentrations with the experimental conditions like Initial pH of solution = 2.0, adsorbent dosage = 0.80 g, agitation speed = 100 rpm. The removal efficiencies were more than 90 % at optimum condition (up to 500 mg/L initial dye concentrations). It was found that the adsorption process by mangrove bark adsorbent could be well described by the Langmuir isotherm.

Khatod Indira (2013) studied the behavior of two adsorbent, neem leaf and orange peel powder for the adsorption of dye mixer of methylene blue in aqueous phase. The purpose of study was design of adsorption columns for dye removal. Adsorption studies are carried out by observing the effect of experimental parameters amount of adsorbents, dye concentration and contact time. Spectrophotometric technique was used for the measurement of concentration of dye before and after adsorption. First order kinetics was predominant. The observe data was fitted on Langmuir adsorption equations. The maximum and minimum adsorption values were obtained at concentrations of 2.5×10^{-5}mg/L and 1×10^{-5} mg/L, respectively. A maximum removal of 90-95% was obtained for an adsorbent dose of 0.3 gm. at 2.5×10-5 mg/L between 15-20 min.

Kumar et al. (2012) studied the continuous removal of methylene blue from aqueous solution using a fixed packed bed of groundnut shell powder. Bed service depth model and Thomas model were employed to study the adsorption kinetics and to predict break through curves for the system. Thomas model could satisfactorily predict the adsorption break through curve with high R^2 value. Percentage removal of dye depends on bed height. It increases with increases in bed height. Upto 80% color removal was possible with the fixed bed. It was found that adsorption potential of GNSP was in the range of 0.238 to 0.272 kg/kg of adsorbent.

Parvathi et al. (2010) studied the adsorption capacity of the activated carbon produced from agricultural waste, Tapioca Peel was used for the adsorption of reactive dye (Megenta MB)from its aqueous solutions. For the preparation of activated carbon Tapioca peel was rinsed in the cold water two or three times and then it was dried under the direct sun light for about 48h in order to dry it completely without leaving any moisture content present in it and this purified Tapioca peel was further used for chemical activation. Adsorption studies were performed by varying parameters such as dye concentration, pH of the dye solution and contact time. The equilibrium adsorption data obtained were used to calculate the Freundlich and Langmuir isotherm parameters. Higher adsorption percentages were observed at lower concentrations of Megenta MB. Optimum pH value for dye adsorption was determined as 7. Maximum dye was removed within 120 min after the beginning for every experiment.

Rattan et al. (2010) studied the batch experiments on the removal of two different dyes Reactive Yellow 15 (RY15) and Reactive Black 5 (RB5) from textile wastewater onto Activated Carbon prepared from Walnut shell separately. The experiments depend on pH, adsorbent dose and kinetics. The adsorbent mass(g) with removal were analyzed which shows that the removal of both the dyes were increase up to 1 g and then it remain almost constant with the most favorable condition of acidic pH is1.The data fitted well with the Temkin and D-R isotherms for RY15 and RB5, respectively. Pseudo first-order and pseudo second-order kinetic models were attempted and Pseudo-second order is the best agreement with the absorption of both these dyes. The findings show that the surface area (BET) is 248.99 m^2/g with a total pore volume of 0.153 cm^3/g.

Suteu et al. (2010) investigate the potential of corn cob, a natural low-cost lignocellulosic material, for the removal of reactive dye Orange 16 from an aqueous solution. Sorption isotherms were determined at 3 temperatures (5, 18 and 45 °C), in solutions with initial dye concentrations in the 37.05-370.5 mg/Lrange. The sorption equilibrium process was described well by the Langmuir isotherm model. According to the Langmuir isotherm, the maximum sorption capacity was estimated 25.25 mg g-1 (18 °C). The values of the thermodynamic parameters confirm the adsorption of reactive dye onto corncob was an entropy-driven, exothermic sorption process as well as the mechanism of adsorption was combination of electrostatic interactions and physical sorption. The kinetic studies show a good agreement of the experimental data with the pseudo-second order model.

Suteu et al. (2011) studied the sunflower seed shells adsorbents capacity for the removal of Orange 16 reactive dye from aqueous environments as a function of pH, sorbent dose, dye concentration, temperature and contact time. The removal of dye highly affected by the adsorbent dose, temperature variation and the dye concentration. When the adsorbent dose is 2 to 20 g/L increased the percentage of dye removal from 53.53 to 87.07 % in five hours. The Langmuir adsorption isotherms were used to describe the equilibrium adsorption data. Thermodynamic parameters indicated that the sorption of reactive dye onto sunflower seed shells was a spontaneous, endothermic and entropy-driven process. The kinetic data were evaluated by pseudo-second order. The absorption capacity of sunflower seed shells was higher than similar type adsorbents.

Wong et al. (2009) studied the absorption capacity of modified sugar cane bagasse for the removal of both Basic Blue3 & Reactive orange16 dye from aqueous solution either in single or binary dye system. Batch experiment was carried out by adjusting the pH from 2-10, varying the agitation speed from 50 to 250 rpm and temperature from 20 to 80^0 C with the initial dye concentration 100 mg/L. The contact time intervals ranging from 5 to 8 hr. The absorption isotherm model was obtained by varying the dye concentration from 50 to 150 mg/L for both single and binary system. The result indicates the optimum pH is in the range of 6–8. The kinetics of dye sorption processes fit a pseudo-second order kinetic model. The adsorption isotherm fitted well into both the Langmuir and Freundlich equations. The sorption of Basic Blue3 was favorable with increasing temperature, while the sorption of Reactive orange16 was favorable at lower temperatures. The optimum adsorbent dosage for the dye sorption was 0.10 g in 20 ml of 100mg/L dye solution. Table 2.1 shows the comparative assessment of various adsorption studies with Reactive Dye.

TABLE 2.1 VARIOUS ADSORPTION STUDIES OF REACTIVE DYE

Adsorbate	**Adsorbent**	**Isotherm**	**Model**	**Results/Conclusion**	**Reference**
Reactive Red 31 & Reactive Red 2	Tannery sludge developed activated carbon	Langmuir model	Pseudo second order	Tannery sludge showed higher adsorbent capacity for Reactive Red 2	(Geethakarthi et al., 2011)
Reactive Dye Methylene Blue	peanut, soybean, cottonseed, lupine, broad beans, and sunflower seeds	N2/77 K Isotherm model	---	Peanut shells proved the best feasible raw material under all treatment processes, whereas lupine seeds and sunflower seed hulls show relatively the least affected	(Girgis et al., 2011)
Reactive Green Dye	Peanut shell & Commercial activated Carbon	Frendulich isotherm	Pseudo second order	The results of comparative adsorption capacity of both carbons indicate that groundnut shell can be used as a low-cost alternative to commercial powdered activated carbon in aqueous solution for dye removal.	(Malik et al.,2006)
Reactive Blue 19 Dye	Modified Orange peel,	Freundlich, Langmuir, Elovich and Tempkin	pseudo-first-order	The adsorption of RB-19 was highly affected by temperature.	(Ahmad et al.,2012)
Reactive Blue Dye	Sugar cane bagasse ash	Thomas,Yoon-Nelson	-	adsorption of dyes increases by decreasing flow rate	(Gaikwad et al., 2010)
Reactive Orange Dye	Garlic husk, Chewing tobacco and Egg shell	Freundlich and Langmuir	pseudo-first-order	As dose of adsorbent increased, the adsorption increases and as concentration increases the adsorption decreases. The adsorption increases	(Geetha et al., 2011)

				with time.	
Reactive Black 5 Dye	Mangrove bark	Langmuir isotherm	pseudo-first-order	The removal efficiencies were more than 90 % at optimum condition (up to 500 mg/L initial dye concentrations*)*.	(Kassim et al., 2012)
Reactive Blue Dye	Neem leaf and orange peel powder	Langmuir adsorption	pseudo-first-order	A maximum removal of 90-95% was obtained for an adsorbent dose of 0.3 gm. at 2.5×10-5 mg/L between 15-20 min	(Khatod Indira 2013)
Reactive Methylene Blue	groundnut shell powder	Bed service depth model and Thomas model	Pseudo second order	Upto 80% color removal was possible with the fixed bed	(Kumar et al.,2012)
Megenta MB cold brand Reactive Dye	Tapioca Peel	Freundlich and Langmuir isotherm	pseudo-first-order	maximum dye was removed within 120 min at Optimum pH	(Parvathi et al.,2010)
Reactive Yellow 15 & Reactive Black 5	Walnut shell	Temkin and D-R isotherms	pseudo-first-order	The removal of both the dyes were increase up to 1 g and then it remain almost constant with the most favorable condition of acidic pH is1	(Rattan et al., 2010)
Reactive Orange 16	Corn cob	Langmuir isotherm model.	pseudo-second order	The maximum sorption capacity was estimated 25.25 mg g-1 (18 °C). The values of the thermodynamic parameters confirm the adsorption of reactive dye onto corncob was an entropy-driven, exothermic sorption process.	(Suteu et al.,2010)
Reactive	Sunflower	The Langmuir	pseudo-	When the adsorbent	(Suteu et

Orange 16	seed shells	adsorption isotherms	second order	dose is 2 to 20 g/L increased the percentage of dye removal from 53.53 to 87.07 % in five hours	al.,2011)
Reactive Orange 16	Sugar cane bagasse	Langmuir and Freundlich	pseudo-second order	The sorption of Basic Blue3 was favorable with increasing temperature, while the sorption of Reactive orange16 was favorable at lower temperatures.	(Wong et al., 2009)

CHAPTER- 3

THEORY

3.1 GENERAL

Adsorption is a process, in which molecules from gas/liquid phase interact with and attach to solid surfaces, and the degree of interaction depends on the nature of adsorbate and the adsorbent.Molecules can attach to surfaces with physical adsorption (physisorption) and/or chemical adsorption (chemisorption).

1. **Physisorption:** If the adsorbate molecules are attracted by weak Van der Waals forces towards the adsorbent, the adsorption is known as physical adsorption or physisorption.
2. **Chemisorption:** If the adsorbate molecules are bound to the adsorbent by chemical bonding, the adsorption is known as chemisorption. Chemical adsorption occurs usually at higher temperatures than those at which physical adsorption occurs; furthermore, chemical adsorption is ordinarily a slower process than physical adsorption and, like most chemical reactions, frequently involves an energy of activation.

3.2. ADSORPTION PROCESS

The adsorption rate is predicted by the rate of transfer of the adsorbate from the bulk to the surface of adsorbate. The movement of adsorbate components from the solution into the pores of the adsorbent is controlled either by one or more of the following steps:

- Film or external diffusion
- Pore diffusion
- Surface diffusion and adsorption on the pore surface.

Slowest step involved among these steps, will be the controlling step during the adsorption process. Therefore, it is necessary to find slowest step.

If the external diffusion is controlling, the system of adsorbate-adsorbent have poor mixing, dilute concentration of adsorbate, small particle sizes of adsorbent and higher affinity of adsorbate for adsorbent, whereas, for good mixing, large particle sizes of adsorbent, high concentration of adsorbate and low affinity of adsorbate for adsorbent systems, intraparticle diffusion controls the adsorption process. Table 3.1 shows the comparison of Physisorption & Chemisorption.

Table 3.1 Comparative table of physical adsorption and chemical adsorption

PROPERTY	**PHYSISORPTION**	**CHEMISORPTION**
Heat of adsorption	Low (< 2-3 times latent Heat of evaporation)	High (>2-3 times latent heat of evaporation)
Rate of adsorption	Rapid, non activated, Reversible	Activated, may be slow and irreversible
Rate of desorption	Activation energy for desorption equals heat of adsorption	Activation energy for desorption may be larger than heat of adsorption
Temperature range over which adsorption occurs	Close to condensation temperature of the adsorbate	Occurs at a wide range of temperatures and at temperatures much above the condensation temperature.
Electrical conductivity	Electrical conductivity of the catalyst not affected	May affect electrical conductivity of catalyst.

Adsorption occurs in three stages, when the concentration of adsorbate is increased. First, a single layer of molecules formed over the surface of adsorbate. This monolayer may be chemisorbed and is associated with a change in free energy that is a characteristic of the forces that hold it. Second and third layers form by physical adsorption. How many numbers of layers will be formed, this is decided by the size of the pores. Finally, for adsorption from the gas phase, capillary condensation may occur in which capillaries become filled with condensed adsorbate, when its partial pressure reaches a critical value relative to the size of the pore. The parameters that affect the adsorption process are initial pH (*pH)*, adsorbent dose (*m*), contact time (*t*) and temperature (*T)*.

3.3 ADSORPTION KINETICS

3.3.1 Pseudo-first-order Model

The adsorption of adsorbate onto adsorbent is considered as a reversible process, and equilibrium is established between the solution and the adsorbate.

Using first order kinetics, and assuming that there is no adsorbate initially present on the adsorbent, the uptake of the adsorbate by the adsorbent at any instant t is given as (Srivastava et al., 2006).

$$q_t = q_e \, [\, 1 - \exp(- k_f \, t \,)] \qquad (3.1)$$

Where, q_e is the amount of the adsorbate adsorbed on the adsorbent under equilibrium condition, k_f is the pseudo-first order rate constant, t is the time, q_t is the amount of the adsorbate adsorbed on the adsorbent in time t.

3.3.2 Pseudo-second-order Model

This is represented as (Ho and McKay, 1999):

$$q_t = \quad t \, K_s \, q_e^2 / 1^{+} \, t \, K_s \, q_e \qquad (3.2)$$

The initial sorption rate, h (mg/g min), at t –> 0 is defined as

$$h = K_s \, q_e \qquad (3.3)$$

3.4 Adsorption Isotherm

Equilibrium adsorption equations are required for the design of an adsorption system and t subsequent optimization (Sharma et al.,2010). Therefore, determination of most appropriate equilibrium isotherm is important to establish (Srivastava et al., 2007). Various isotherms like Freundlich, Langmuir, Redlich-Peterson isotherms are widely used. The

Freundlich isotherm is applicable for heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface, whereas in the Langmuir adsorption isotherm, the sorption takes place at specific homogeneous sites within the adsorbent. Table 3.2 shows the equation of isotherm models.

3.4.1 Langmuir's Isotherm

To describe the adsorption of adsorbate onto the surface of the adsorbent requires three assumptions (Yuh-Shan Ho.,2004)

(i) The surface of the adsorbent is in contact with a adsorbate, and is strongly attracted to the surface.

(ii) The surface of adsorbent has a large number of active sites, where the adsorbate molecules may be adsorbed.

(iii)The adsorption involves the attachment of only one layer of molecules to the surface, (monolayer adsorption).

3.4.2 Freundlich Isotherm

Freundlich (1906) give an empirical equation which representing the isothermal variation of Adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known as Freundlich Adsorption Isotherm or Freundlich Adsorption equation. (Hassan et al., 2008)

$$q_e = K_f \, C_e^{1/n} \tag{3.4}$$

K_f, and n are constants whose values depend upon adsorbent and gas at particular temperature.

3.4.3 Redlich-Peterson Isotherm

Jossens and co-workers modified the three parameter isotherm first proposed by Redlich and Peterson (1959) to incorporate features of both the Langmuir and Freundlich equations. It can be described as follows:

$$q_e = K_R \, C_e /(1 + a_R \, C_e^{\beta}) \tag{3.5}$$

At low concentrations the Redlich-Peterson isotherm approximates to Henry's lawand at high concentrations its behaviour approaches that of the Freundlich isotherm.

3.4.4 Tempkin Isotherm

The Temkin isotherm model assumes that the adsorption energy decreases linearly with the surface coverage due to adsorbent–adsorbate interactions. The linear form of Temkin isotherm model is given by the equation(Joseph et al., 2010)

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \tag{3.7}$$

Table 3.2 shows the empirical equation of various isotherm model.

Table 3.2 Isotherm equations for the adsorption process

ISOTHERM	EQUATION	REFERENCES
Freundlich	$q_e = K_f C_e^{1/n}$	(Freundlich, 1906)
Langmuir	$q_e = \frac{q_m k_L C_e}{1 + k_L C_e}$	(Langmuir, 1918)
Redlich-Peterson	$q_e = \frac{k_R C_e}{1 + a_R C_e^{\beta}}$	(Jossens et al, 1978)
Temkin Isotherm	$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$	(Joseph et al, 2010)

K_f : Freundlich constant (l/mg),
$1/n$: Heterogeneity factor,
K_L: Langmuir adsorption constant (l/mg),
q_m : adsorption capacity (mg/g).
K_R: *R–P isotherm constant (l/g)*
a_R: *R–P isotherm constant (l/mg),*
β: *Exponent* which lies between 0 and 1
C_e: Equilibrium liquid phase concentration (mg/l)

CHAPTER- 4

MATERIALS AND METHODS

4.1 GENERAL

In the present study, Activated carbon from peanut shell has been prepared for the adsorption of Reactive Black 15 (RB-15) dye from aqueous solution. Experimental details of the study have been presented in this chapter. These details include: preparation of adsorbent, batch study for adsorption.

4.2 ADSORBATE

Reactive Black 15 (RB-15) dye was dissolved in distilled water to make the dye solution of different concentrations. Initially 1g/l of stock solution was prepared which was further diluted to make the working solution of desired concentration as per the experiment requirement.

4.3 PREPARATION OF ADSORBENT

Peanut shell was collected from local market, and washed thoroughly with distilled water, dried, crushed and sieved upto 2 mm size. The sieved peanut shell material was kept in covered vessel in furnace at 400^0C for 30 min. The produced char was used for chemical activation by impregnation with Zinc Chloride ($ZnCl_2$) for 24 h at 7:4 ($ZnCl_2$: Char) (Malik et al.,2006; Malik et al.,2007) and added some water for proper mixing. After 24 h the mixture was filtered and char impregnated with $ZnCl_2$ was dried in hot air oven at 100 ± 5^0C. The impregnated char was again carbonized at 650 ^{0}C for 15 min in muffle furnace. Then after, the carbonized product was treated with HCl in same ratio for the removal of $ZnCl_2$. The carbonized product was washed thoroughly with hot distilled water for the removal of chlorides and acidity. It was finally dried at normal temperature. Fig 4.1 shows the flow diagram for the preparation of adsorbent from peanut shell.

4.4 Analytical Methods

The determination of the concentration of Reactive black dye (RB-15) was performed by finding out the absorbance using UV-VIS spectrophotometer. A dye solution of known concentration was taken. The maximum absorbance (λ_{max}) was determined. The λ_{max} for Reactive black (RB-15) were found to be 523 nm. Calibration curve was plotted between the absorbance and the concentration of RB-15 solution (Fig.4.2).

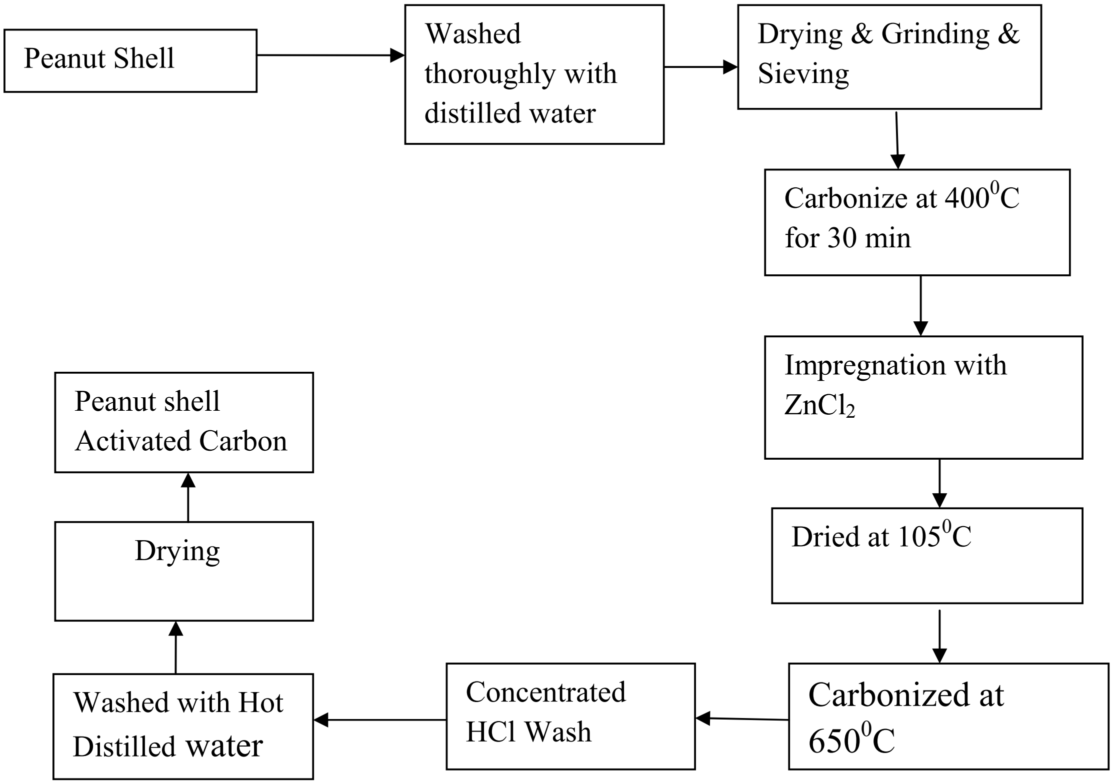

Fig 4.1 Flowchart for the preparation of Peanut Shell activated carbon

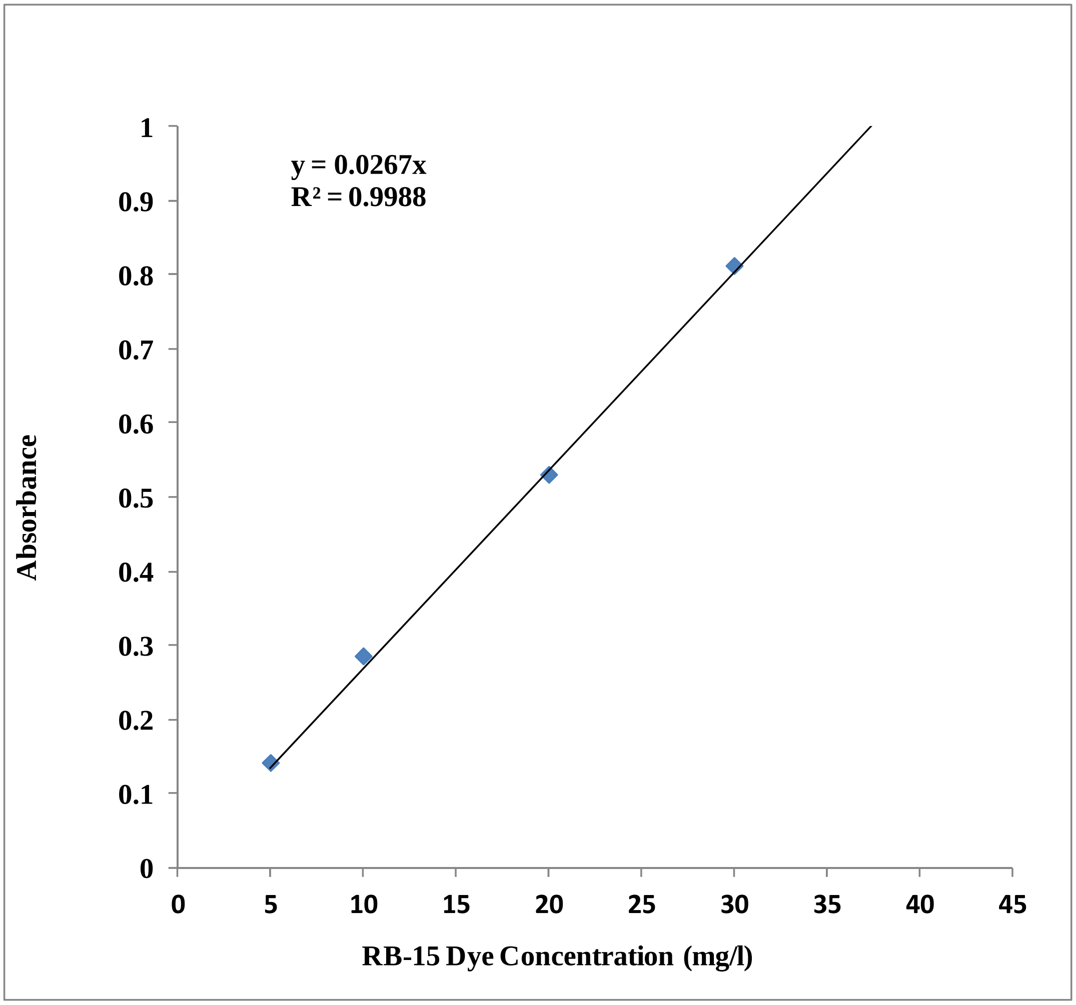

Fig 4.2 Calibration Curve for Reactive Black-15 Dye

4.4. Experimental Programme

For each experiment, 100 ml of RB-15 dye solution of desired concentration and pH was taken in 250 ml conical flasks, and a desired amount of the adsorbent was introduced in this. These prepared samples were placed in a incubator shaker at fixed temperature and at a constant speed of 150 rpm for different time intervals to attain the equilibrium. After the desired time samples were withdrawn from the incubator and the adsorbate and adsorbent was separated by filtration. Then after, the absorbance was measured with the help of UV-VIS spectrophotometer, and residual concentration was calculated from calibration plot.

The percentage removal of RB-15 was calculated using the following relationship

$$\text{Percent TA removal} = \frac{(C_0 - C_e)100}{C_0} \tag{4.1}$$

Where, C_o is initial RB-15 concentration (mg/l) and C_e is the equilibrium RB-15 concentration (mg/l).

Dosage study was carried out by varying the adsorbent dosages (*m*) in the range of 2-30 g/l the natural pH and 300 K.

The adsorption of RB-15 dye was studied over a initial pH range of 3–9 at 300K with optimum adsorbent dosage of 20 g/l. The pH of the adsorbate solutions was adjusted using N/10 aqueous solution of either HCl or NaOH.

4.4.1. Kinetics of adsorption: Kinetic parameters of pseudo-first-order and pseudo-second-order model were calculated at various C_0 values (50-300 mg/l) at optimum dosage of adsorbent (***m_{ad}***) and optimum pH (***pH_{opt}***). For this the solution was kept in incubator shaker at predefined temperature and a constant speed of 150 rpm. The amount of adsorbate adsorbed, q_t (mg/g), at any time *t* was calculated as:

$$q_t = \frac{(C_0 - C_t)}{m_{ad}} V \tag{4.2}$$

Where, C_t is the RB-15 concentration (mg/l) at time *t*, *V* is the volume of the solution (litre).

An error function, Marquardt’s percent standard deviation (MPSD) (Marquardt, 1963) was used to find out the most suitable kinetic model to represent the experimental data. This error functions is given as:

$$MPSD = 100\sqrt{\frac{1}{n_m - n_p}\sum_{i=1}^{n}\left(\frac{q_{t,i,\exp} - q_{t,i,cal}}{q_{t,i,\exp}}\right)^2} \tag{4.3}$$

In this equation, the subscript ‘exp’ and ‘cal’ represent the experimental and calculated values, n_m is the number of measurements, and n_p is the number of parameters in the model.

4.4.2. Isothermal study: Equilibrium adsorption isotherm equations are essential criterion for the design of adsorption systems. Therefore, it is important to establish the most suitable correlation for the equilibrium adsorption. Isothermal experiments were performed at 293, 313 K with C_0 values of 25, 50, 100, 150, 200, 250, 300 and 350 mg/l at $\boldsymbol{pH_{opt}}$ and $\boldsymbol{m_{ad}}$ of adsorbent .Isotherms such as Freundlich, Langmuir, Redlich-Peterson (R-P) and Tempkin were used to represent the adsorption equilibrium data.

The adsorbent separated from the RB-15 solution after 6 h and analysed for equilibrium RB-15 concentration (C_e). The equilibrium adsorption uptake, q_e (mg/g), were calculated using the following relationship:

$$q_e = \frac{(C_0 - C_e)}{w} V \tag{4.4}$$

The Chi-square error analysis function was used to find out best fit isotherm model. It is given as:

$$CHI^2 = \sum_{i=1}^{n} \frac{(q_{e,i,\exp} - q_{e,i,cal})^2}{q_{e,i,\exp}} \tag{4.5}$$

CHAPTER- 5

RESULTS AND DISCUSSION

5.1. GENERAL

In this chapter, adsorptive removal of RB-15 dye from its aqueous solution in batches on to activated carbon prepared from peanut shell is reported, and results obtained during the removal and their interpretations have been discussed in detail.

5.2 EFFECT OF ADSORBENT DOSAGE (m_{ad})

The significance of m_{ad} on the adsorption of RB-15 dye by peanut shell based activated carbon was studied at C_o = 200 mg/l, pH =6.29 and T=300 K. (Fig. 5.1) an increase in adsorbent dosage (m_{ad}) resulted in an increase in dye removal and it becomes nearly constant with further increases in adsorbent dosage. Maximum removal of RB-15 dye was found at m_{ad}=20 g/l giving 89.13% removal. Therefore m_{ad}= 20 g/l was taken as optimum dosage of adsorbent for further study.

Increase in the removal of RB-15 dye with the increase in m_{ad} is basically due to availability of higher surface area and the more active adsorption sites. For $m_{ad} \geq 20$ g/l there is nearly constant removal is observed. Therefore, this may be interpreted that the removal efficiency of prepared activated carbon depends more upon the concentration of the RB-15 dye in the aqueous solution and less depends upon the m_{ad}.

5.3 EFFECT OF INITIAL pH (*pHi*)

Fig. 5.2 shows the effect of *pHi* on the Reactive Black 15 dye removal from aqueous solution by peanut shell activated carbon. Maximum percentage removal 82% and 84%were obtained at *pHi* =3 and 4, respectively. Therefore the optimum initial pH (pH_{opt}) = 4 was chosen for further studies. The Reactive dye removal first decreases to a minimum value of 50.69% and then becomes nearly constant.

Fig 5.3a and Fig 5.3b shows FTIR spectra of unloaded and loaded (with RB-15 dye) activated carbon prepared from peanut shell. It can be seen that there is large difference in peaks intensities, showing adsorption of RB-15 dye.

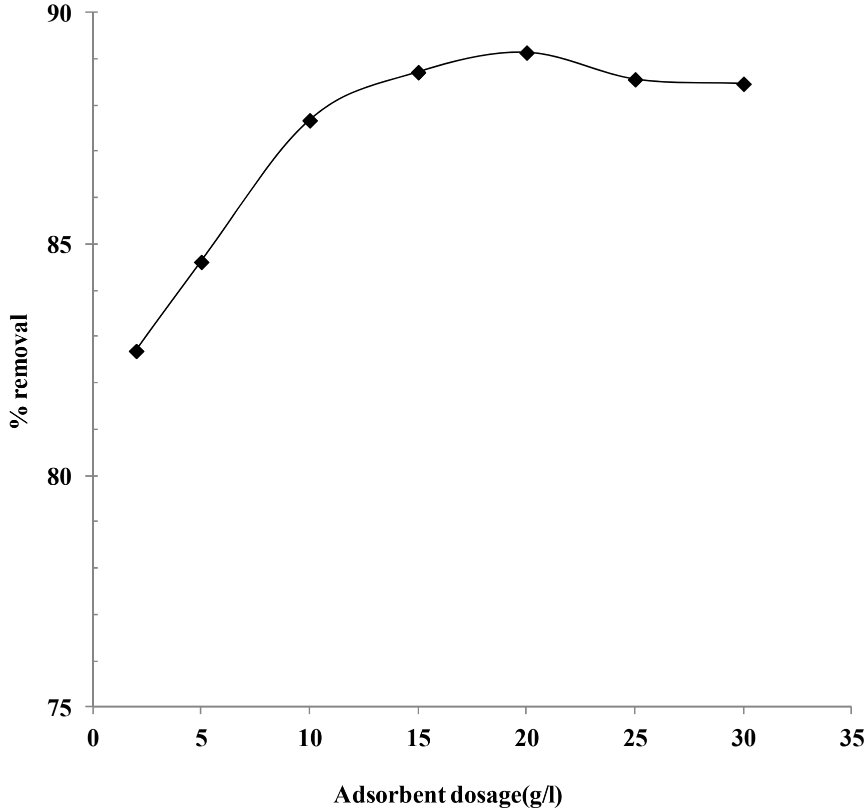

Fig 5.1 Effect of adsorbent Dosage on the RB-15 dye Removal By Peanut Shell adsorbent (T=300K, t=5 hr, C_0 = 200mg/l, pH =6.29)

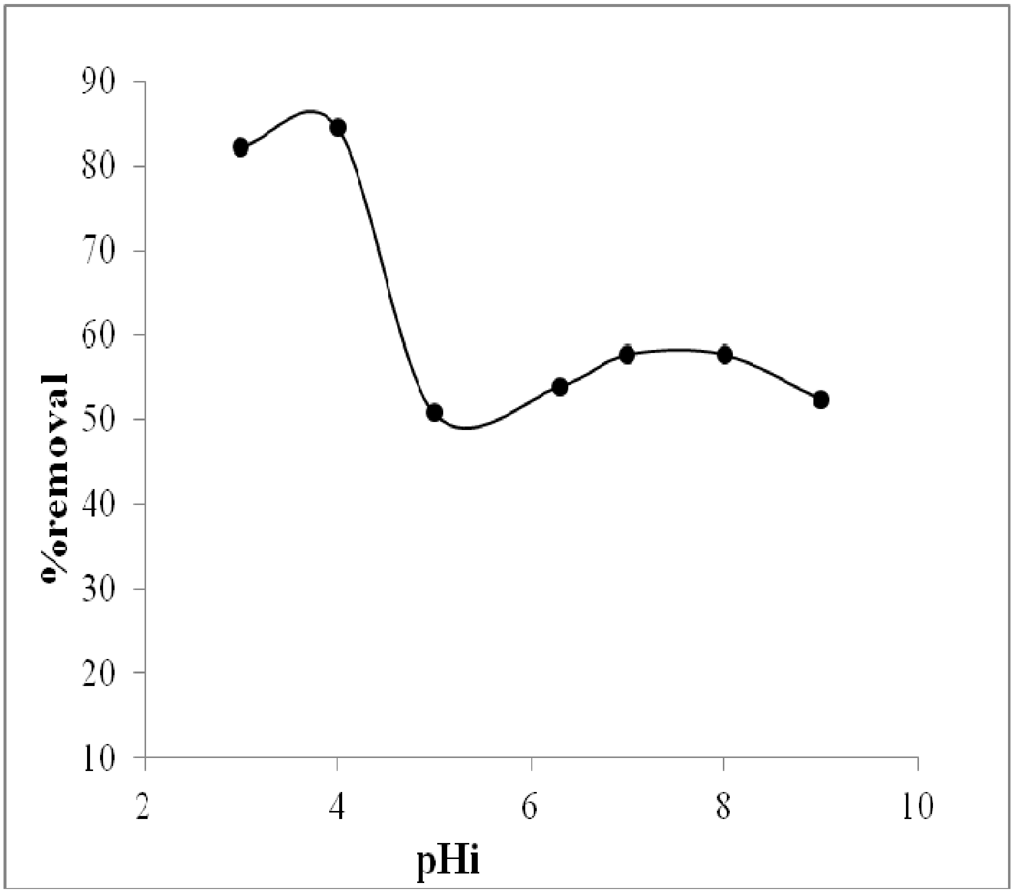

Fig 5.2 Effect of initial pH (pH_i)

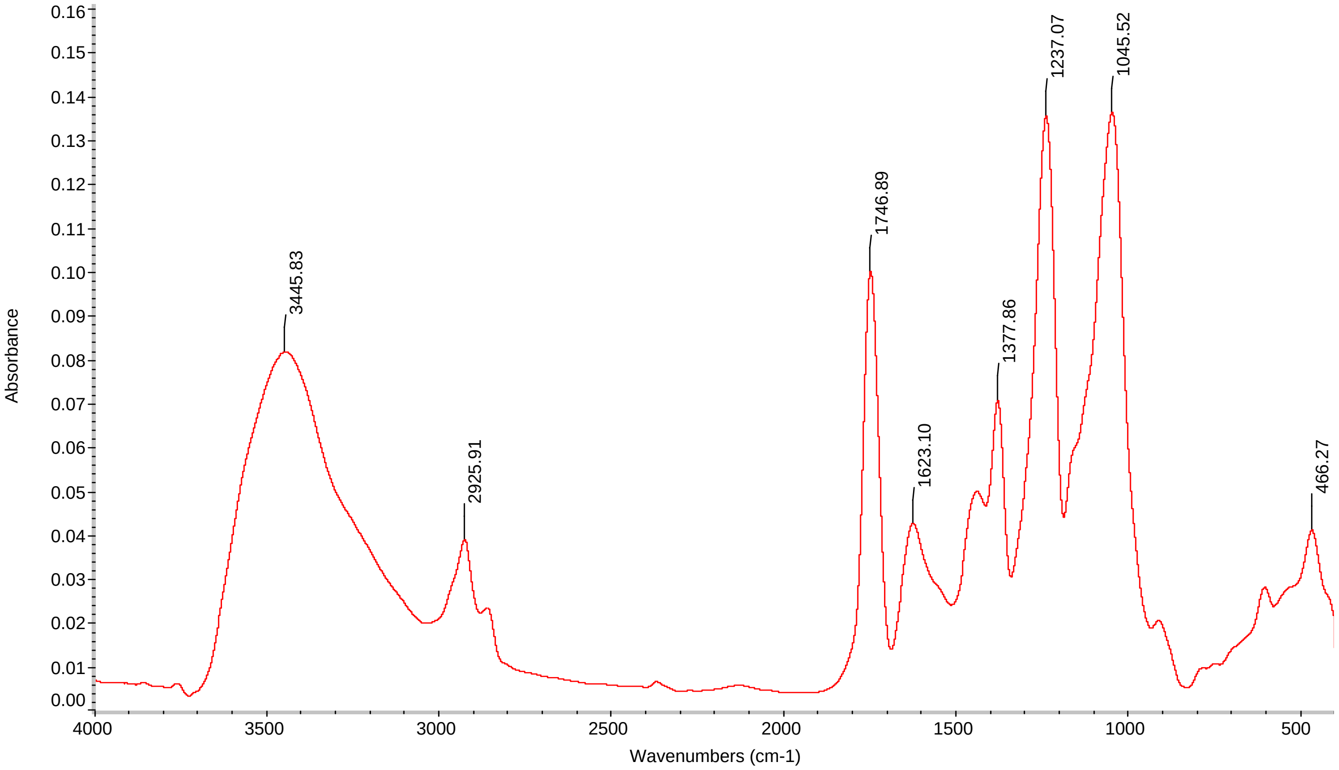

Fig. 5.3a FTIR Spectra of unloaded activated carbon prepared from peanut shell

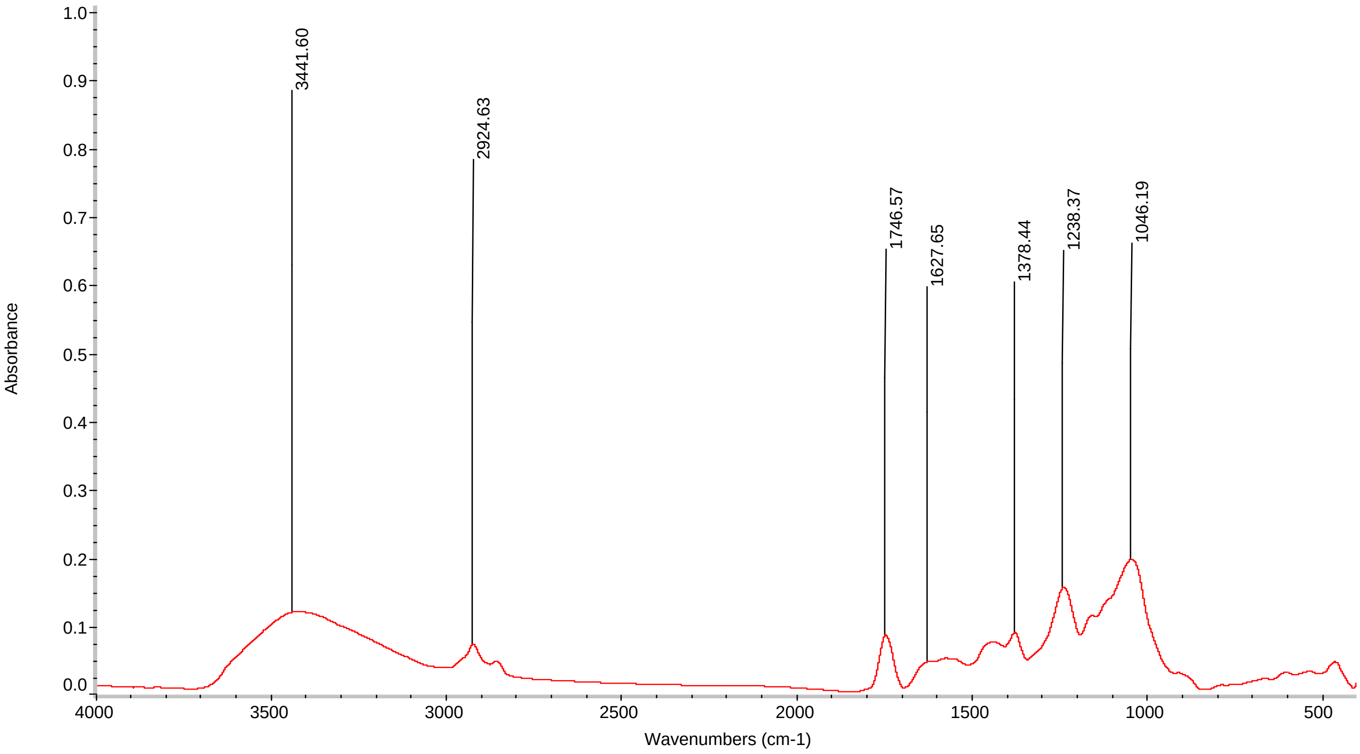

Fig. 5.3b FTIR Spectra of loaded activated carbon prepared from peanut shell with RB-15 dye

5.4 EFFECT OF TIME

To study the effect of contact time on removal of RB-15 dye from its aqueous solution having C_0 (50-300 mg/l) at pH_{opt} = 4.0, were kept in contact with the Peanut shell adsorbent (m_{ad} =20 g/l) for 6 h. Fig. 5.3 shows the effect of contact time on RB-15 removal by Peanut shell adsorbent. It can be seen that RB-15 adsorption is very fast during first 75 min of adsorption process. After 4 h, adsorption on adsorbent reached nearly equilibrium.

From this fast adsorption of RB-15 and reaching at equilibrium in a short period of 4 h indicates the high efficiency of the peanut shell adsorbent for removal of RB-15 dye. After 6 h, no considerable removal was observed. 6 h contact time can be assumed to be equilibrium time for the adsorption of reactive black onto peanut shell adsorbent.

5.5 ADSORPTION KINETICS

Pseudo-first-order and pseudo-second-order kinetic models were used in this study to verify their validity with the experimental kinetic adsorption data. Model parameters, correlation coefficients and MPSD error values for best fit Pseudo-first-order and pseudo-second-order kinetic models are given in Table 5.1. The validity of pseudo second-order model along with experimental kinetic data is shown in Fig. 5.3 by solid line.

It may be seen in Table 5.1 that the value of q_e and k_s increases with increase in the C_o. Therefore, it may be interpreted that the adsorption of RB-15 on to prepared activated carbon is limited by concentration of RB-15 in the solution. Basically, the adsorption rate is dependent on the C_0 of RB-15and affinity to the adsorbent, diffusion coefficient, the pore size distribution of the adsorbent, and the extent of mixing (Zogorski et al., 1976). All these factors provide the necessary driving force to the adsorbate to be adsorbed on to surface of adsorbent. The increase in C_o value increases the driving force, and hence, the rate of adsorption increases with the increase in C_0.

MPSD error and R^2 values (Table 5.1) concludes that pseudo-second-order kinetic model best fit the experimental kinetic data, and the fitting of pseudo second-order model along with experimental kinetic data is shown in Fig. 5.3 by solid line.

Table 5.1. Kinetic parameters for the RB-15 removal (t = 6 h, C_0=50-300 mg/l, m_{ad}=20 g/l).

Pseudo-first-order model					
C_0 **(mg/l)**	$q_{e,exp}$ **(mg/g)**	$q_{e,calc}$ **(mg/g)**	k_f **(min^{-1})**	R^2	**MPSD**
300	11.538	9.815	10.000	0.95	25.87
100	4.538	4.115	0.028	0.98	21.09
50	2.370	3.159	0.003	0.96	30.63

Pseudo-second-order model					
C_o **(mg/l)**	$q_{e,calc}$ **(mg/g)**	k_s **(g/mg min)**	h **(mg/g min)**	R^2	**MPSD**
300	11.074	0.009	1.159	0.98	8.39
100	4.295	0.009	0.183	1.00	9.62
50	1.896	0.001	0.011	0.96	33.70

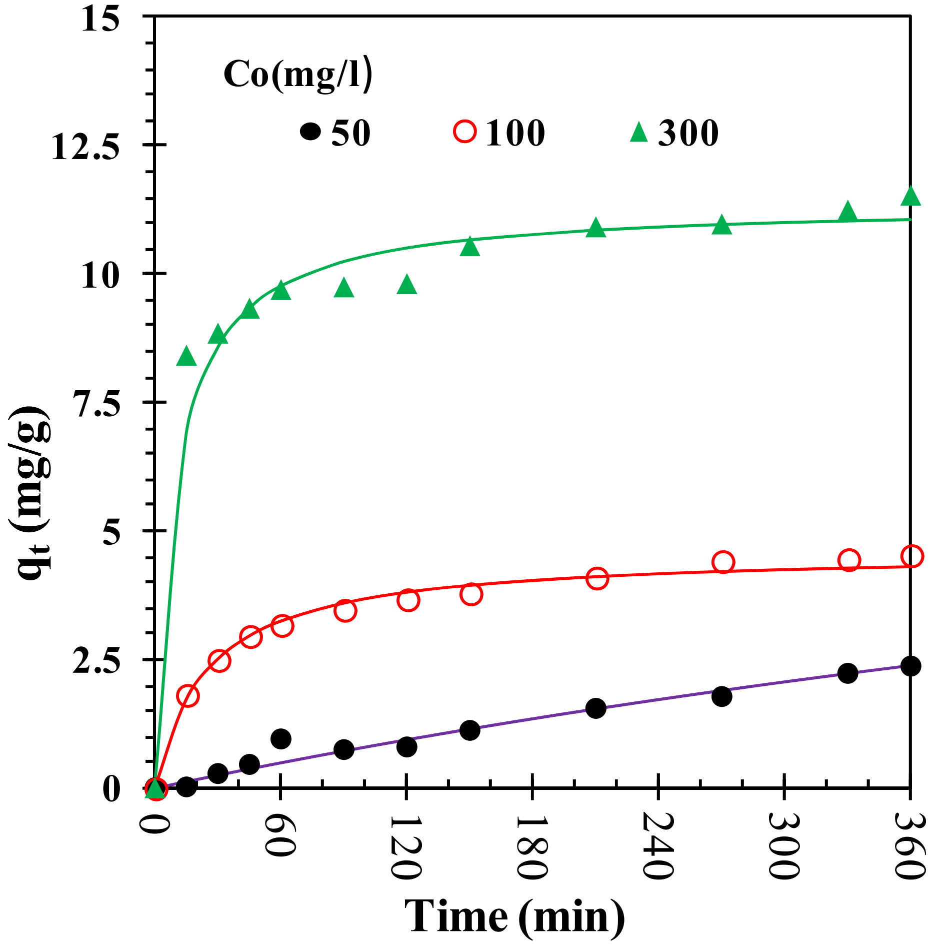

Fig 5.4 Effect of contact time on the RB-15 Dye removal by Peanut Shell Adsorbent. Experimental data points given by the symbols and the solid lines predicted by the pseudo second- order model. T **= 303 K,** m_{ad} **= 20 g/l**

5.6 ADSORPTION ISOTHERM

5.6.1 Temperature Effect on Adsorption

Temperature has a significant effect on the adsorption capacity of the adsorbents. To study the effect of temperature on dye adsorption onto peanut shell adsorbent was studied at two different temperatures 293 and 313 K, and it was found that adsorption of RB-15 on to prepared activated carbon increases with increase in temperature. Therefore, Adsorption of RB-15 dye on to prepared activated carbon is endothermic in nature.

Generally, adsorption is not an endothermic, but it is an exothermic process. However, if diffusion process (intraparticle transport-pore diffusion) control the adsorption process, the adsorption capacity is increased by the increase in temperature. This is basically due to the fact that the diffusion is an endothermic process (Srivastava et al., 2007).

5.6.2 Isotherm Modelling

For isotherms modeling, various isotherms like Freundlich, Langmuir, R-P isotherms and Temkin have been tested for their validity with the experimental equilibrium adsorption data. Table 5.2 shows the values of various isotherm parameters, R^2 and CHI^2 for the fitting to the experimental data. It may be seen in Table 5.2 that the R^2 and CHI^2 values for Langmuir, R-Pand and Temkin isotherms are nearly same. Therefore, any of the Langmuir, R-P and Temkin isotherms may be used to represent the experimental equilibrium adsorption data for RB-15 adsorption on peanut shell based activated carbon. However, among these isotherms, temkin isotherm is best fitting the data. The validation of various isotherms studied with experimental data points is shown in Fig. 5.4 by solid lines.

K_F value indicates the adsorption capacity. K_F value increases with increase in temperature, showing adsorption capacity is increasing. This also confirms the endothermic nature of adsorption of RB-15 on peanut shell adsorbent. Aslo, high q_m value indicates a higher affinity. q_m was found to increased with increase in temperature (Table 5.2) showing higher affinity to adsorbent at higher temperature.

Table 5.2 Parameters of isotherm Models (t = 5h, C_0=50-300 mg/l, m=20 g/l)

Freundlich $q_e = K_F C_e^{1/n}$

T (K)	K_F ((mg/g)/(l/mg)$^{1/n}$)	$1/n$	R^2	CHI2
293	0.156	0.827	0.94	2.937
313	0.206	0.828	0.95	2.874

Langmuir $q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$

T (K)	K_L (l/mg)	q_m (mg/g)	R^2	CHI2
293	0.00473	22.788	0.96	2.349
313	0.00568	25.788	0.95	2.568

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

T (K)	K_T (l/mg)	B_T (kJ/mol)	R^2	CHI2
303	0.09	3.53	0.99	0.60
313	3.83	0.12	0.97	1.02

Redlich-Peterson $q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}}$

T (K)	K_R (l/g)	a_R (l/mg)$^{1/\beta}$	β	R^2	CHI2
293	0.108	0.005	1	0.96	2.349
313	0.14	0.003	1.1	0.95	2.550

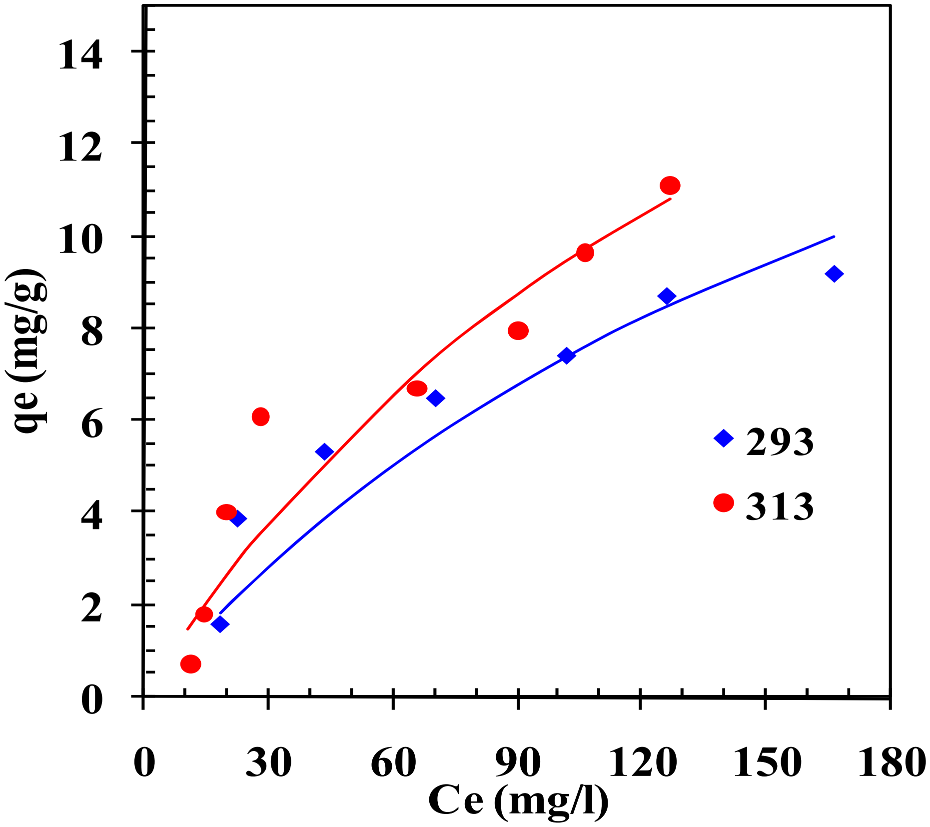

Fig 5.5a Equilibrium adsorption isotherms at different temperature (293 – 313K) for the RB-15 dye removal by peanut shell Activated carbon. Lines show the Langmuir isotherm model. *t* = 6 h, C_o =25-350 mg/l, m_{ad} = 20 g/l.

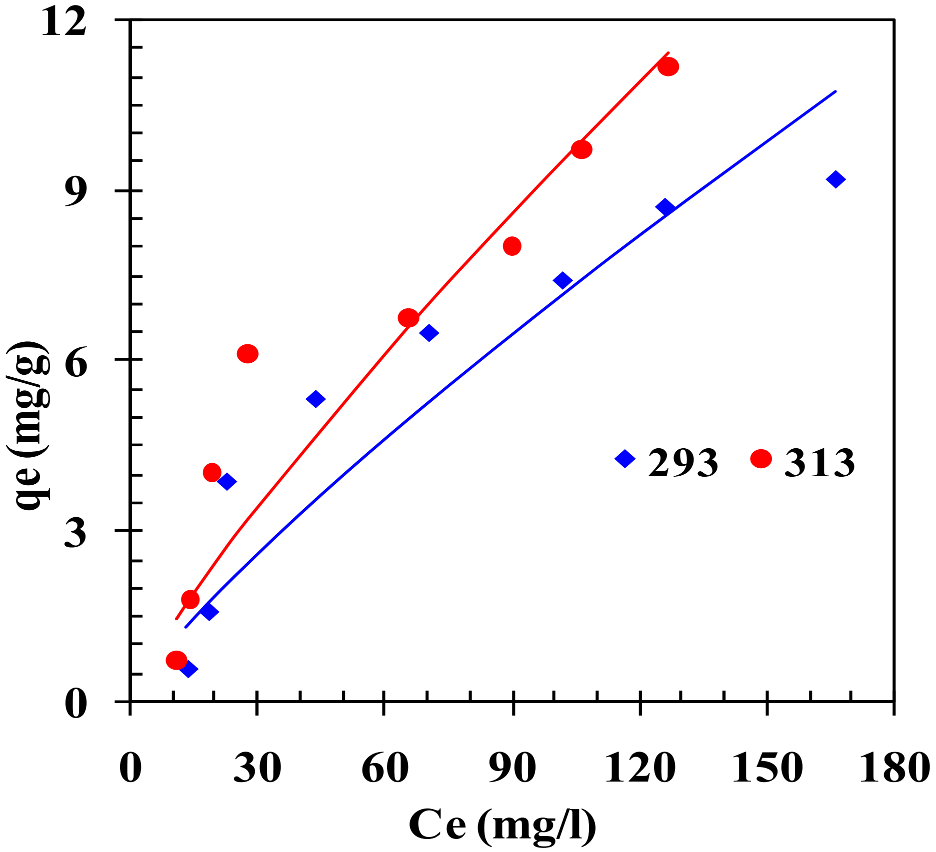

Fig 5.5b Equilibrium adsorption isotherms at different temperature(293 – 313K) for the RB-15 dye removal by peanut shell Activated carbon. Lines shows the Freundlich isotherm model. *t* = 6 h, C_o =25-350 mg/l, m_{ad} = 20 g/l.

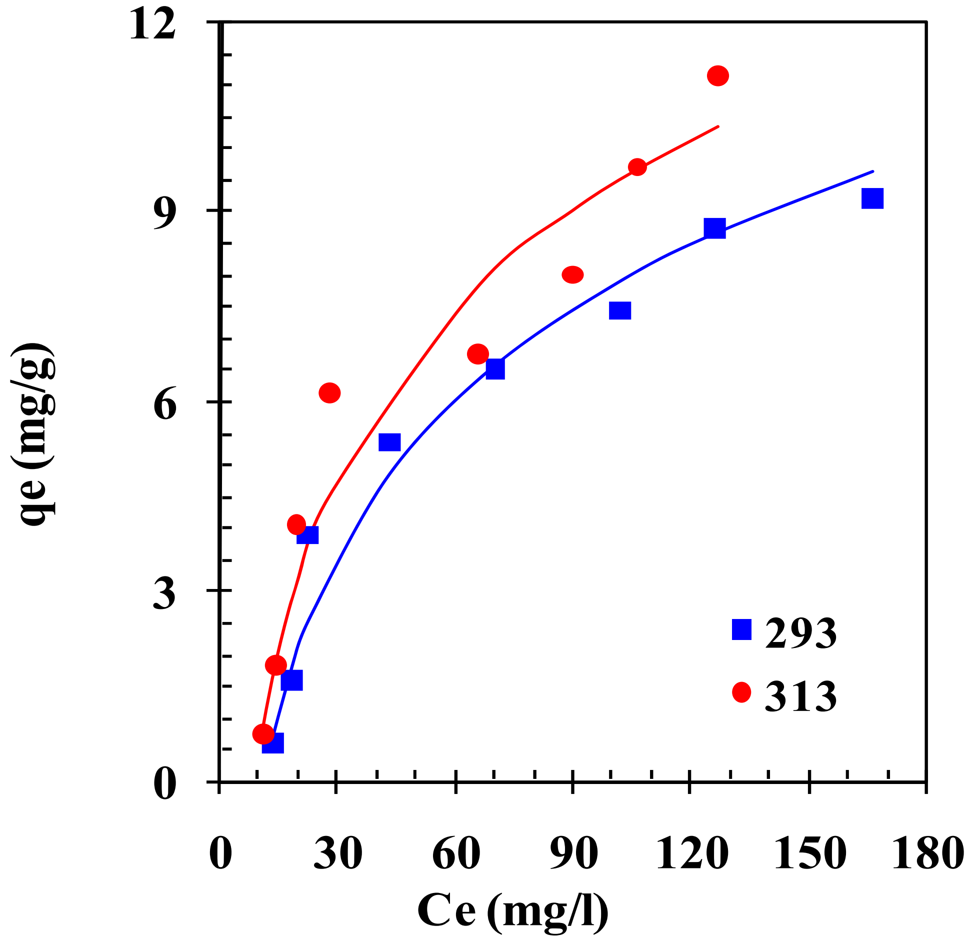

Fig 5.5c Equilibrium adsorption isotherms at different temperature (293 –313K) for the RB-15 dye removal by peanut shell Activated carbon. Lines show the R-P isotherm model *t* = 5 h, *C_o* =25-350 mg/l, *m_{ad}* = 20 g/l.

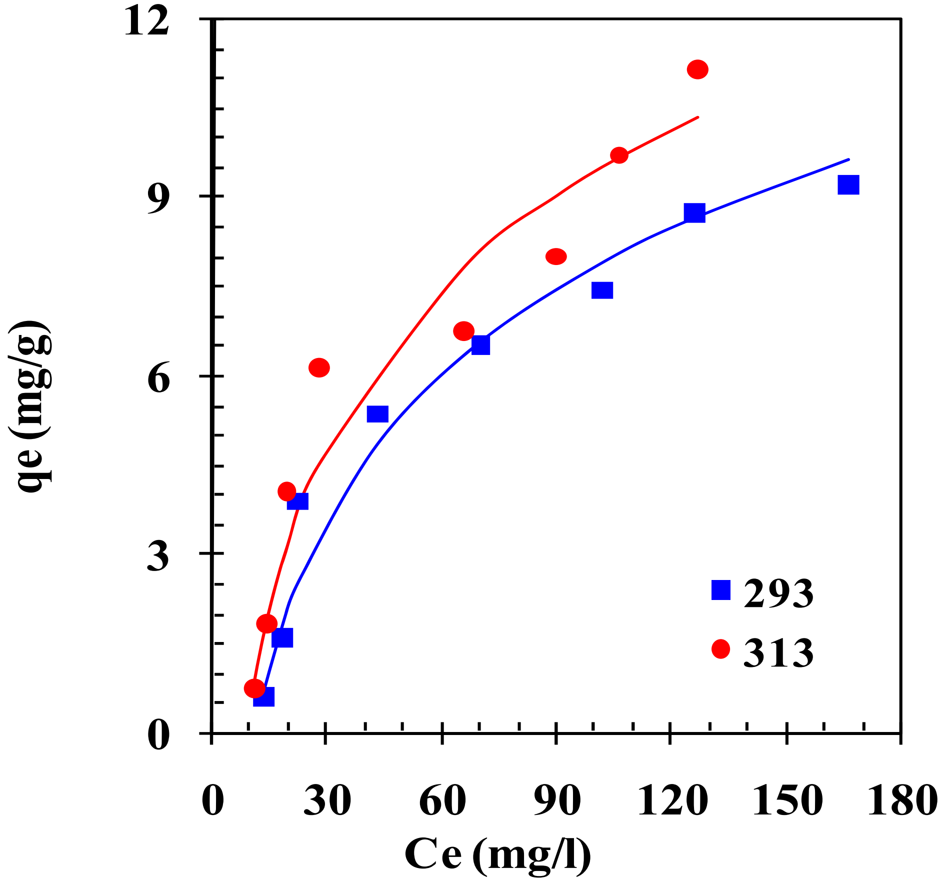

Fig 5.5d Equilibrium adsorption isotherms at different temperature (293 – 313K) for the RB-15 dye removal by peanut shell Activated carbon. Lines show the Tempkin isotherm model, *t* = 5 h, C_o =25-350 mg/l, m_{ad} = 20 g/l.

CHAPTER- 6

CONCLUSIONS

On the basis of the experimenRB-15 dyel results and discussion presented for the adsorptive removal of RB-15 dye on to activated carbon prepared from peanut shell, following conclusions can be drawn:

- Optimum conditions for the adsorptive removal of RB-15 dye by activated carbon prepared from peanut shell were found to be: initial pH ≈ 4.0, adsorbent dose of 20 g/l and contact time ≈6 h.
- Pseudo-second order kinetic model was found to best fit the kinetic data.
- It was found that q_e values increases with increase in C_o. Therefore, the uptake of RB-15 dye is limited by the C_o.
- Adsorption process was found to be endothermic in nature and Temkin isotherm model was found to best fit the equilibrium experimental data.
- K_F value indicates the adsorption capacity. K_F value increases with increase in temperature, showing adsorption capacity is increasing. This also confirms the endothermic nature of adsorption of RB-15 on peanut shell adsorbent.
- High q_m value indicates a higher affinity. q_m was also found to increased with increase in temperature showing higher affinity to adsorbent at higher temperature.

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