Feasibility study of Malachite Green dye removal from aqueous solution using Groundnut cake Activated carbon

Thesis Submitted

by

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CERTIFICATE

This is to certify that the thesis entitled **“Feasibility study of Malachite Green dye removal from aqueous solution using Groundnut cake activated carbon”** submitted to the National Institute of Technology, Rourkela by **ATUL KUMAR SESODIA**, Roll No. **213CH1126** in partial fulfillment of the requirements for the award of the degree of **Master of Technology** in **Chemical Engineering**, is a bona fide record of research work carried out by him under my supervision and guidance. The thesis, which is based on candidate’s own work, has not been submitted elsewhere for any degree/diploma.

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ABSTRACT

The preparation of activated carbon by the activation of groundnut cake from orthophosphoric acid and its ability to remove the Malachite Green (MG) dye from the aqueous solution in batch process were presented in this study. The effect of adsorbent dose, initial pH of the dye solution, temperature and initial dye concentration on the removal of MG were explored. The activated carbon was characterised by the Field emission scanning electron microscopy (FESEM) and Fourier transform infra-red (FTIR) spectroscopy. Result shows that the adsorption was more effective in the acidic medium and increase with contact time and initial dye concentration but decreases with temperature. The adsorption capacity of the prepared groundnut cake activated carbon was 6.45 mg/g. The kinetic study of adsorption was better described by Pseudo-2nd order kinetic model and Freundlich isotherm describes the MG adsorption equilibrium data better than Langmuir isotherm. Thermodynamic parameters such as change in Gibbs free energy, enthalpy and entropy also determined.

Key words: Malachite Green, activated carbon, groundnut cake, adsorption, kinetics.

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NOMENCLATURE:

A = % ash content in the sample

I = Intrapartical diffusion constant (mg/g)

M = % moisture content in the sample

R = Universal gas constant (8.314 J/mol K)

T = Absolute temperature (K)

V = Volume of the solution taken in flask (l)

W = Amount of adsorbent (g)

C_0 = Initial dye concentration (mg/l)

C_e = Final dye concentration (mg/l)

K_1 = Pseudo-first-order rate constant (min^{-1})

K_2 = Pseudo-second order rate constant (g/mg min)

K_f = Freundlich constant ($\text{mg}^{1-1/n}\, \text{l}^{1/n}\, /\text{g}^1$)

K_{id} = Inter particle diffusion rate ($\text{mg/g min}^{1/2}$)

V_m = % volatile matter in the sample

W_1 = Weight of the empty crucible (g)

W_2 = Weight of the crucible with sample before put in to the furnace (g)

W_3 = Weight of the crucible with sample after taking out from furnace (g)

b = Langmuir constant (l/mg)

t = Time (min.)

q_t = Amount of solute adsorbed per unit weight of adsorbent at any time t (mg/g)

q_e = Amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg/g)

q_m = Monolayer adsorption capacity of the adsorbent (mg/g)

Greek letters:

ΔG^0 = Change in Gibbs free energy (kJ/mol)

ΔH^0 = Change in enthalpy (kJ/mol)

ΔS^0 = Change in entropy (J/mol K)

α = Initial adsorption rate (mg/g. min)

β = desorption constant (g/mg)

Chapter 1

1. INTRODUCTION

Water pollution is a major global problem of present time. One of the main constituent of the water pollution is the effluent from various industries which contain various pollutants typically dyes. The residual dyes present in effluent originated from different sources such as Paper and pulp industry, Kraft bleaching industry, dye and dye intermediate industry etc. It also contains a wide range of organic pollutants which are contaminating the water resources. The textile industry is one of the largest polluters of water (of dye pollutant) in the world.

The presence of dye or their degraded products even in very low concentration in water can cause serious human health disorder like hemorrhage, ulceration of skin and can cause severe damage to kidneys, liver, brain reproductive system and central nervous system. Among 40,000 dyes listed in EDTA (Ecological and Toxicological Association of dye stuff) prescribed LD_{50} value grater then 200 mg/kg. The rate of toxicity was much higher for diazo and basic dye (Garg et al. 2004). Hence it is necessary to find economical and efficient methods for successively remove them.

Large quantity of dyes (originated from textile and paper and pulp industry, dye manufacturing industry) makes it difficult to treat the contaminated water because the color tends to persist even after the conventional removal process. There are several techniques for removal of dyes and decolorization, (1) Physical methods, such as adsorption on peat, activated carbon, fly ash, wood, silica and other process like ion-exchange, membrane filtration, coagulation and reverse osmosis; (2) Chemical methods, involves oxidation using oxidizing agents like Fenton’s reagent , ozone, sodium hypochlorite etc. Others include photochemical methods and electrochemical degradation; (3) Biological methods, using fungi and bacteria as the dye degrading agent. Some of these techniques are effective to remove the dye from solution. However these processes have limitations such as more uses of chemical, accumulation of concentrated used sludge that has disposal problem, lack of effective color reduction and expensive.

Malachite Green dye is particularly used in various industries such as textile, paper and acrylic etc. It is highly unsafe if present in the effluent stream without proper treatment. Techniques employed for removal of MG dye include photo-catalytic degradation, photo-degradation, adsorption and bioremediation (Anbia et al., 2011; Mall et al., 2005). Although removal of dyes from aqueous solution through adsorption by activated carbon is quite effective as compare to other techniques, but commercial application of activated carbons is still restricted due to its regeneration and fabrication costs.

Adsorption is the accumulation of adsorbate on to the surface of solids adsorbent. Adsorption is a process where particles from solution are bound to the surface of adsorbent by physical or chemical forces. This technique is better than other color removal methods in term of low introductory expense, straightforwardness of configuration, simplicity of operation, and non-toxicity of the used adsorbent contrasted with other waste water treatment techniques. The availability cost, effectiveness and adsorption capacity are the main criteria for the activated carbon to utilize them as adsorbent to remove the dyes from waste water. Activated carbon is used as an absorbent in many industries for removal of dyes from wastewater. Activated carbon has good adsorption capacity because of its micro-porous, pores structure with high surface area and it also shows the stability in acidic and basic medium. However in present time because of high cost of commercial grade activated carbon, activated carbon is preparing from cheaper precursors, such as hen feather (Mittal, 2006) and rise husk (Sharma et al. 2009). Various research studies had shown that many lesser price precursors are used as an adsorbent for dye removal from aqueous solutions by adsorption. However, very few low price activated carbons can be well used to remove dye from the waste water.

Nowadays, there is a more interest in finding less expensive and effective alternatives to the existing commercial activated carbon. Exploring cheap and effective activated carbon may contribute to environment sustainability and give benefits for future industrial application. Objective of the present study is to use groundnut cake for preparation of activated carbon. It also includes study of the capacity of activated carbon for removal of MG from aqueous solution as there is limited research had done on application of the groundnut cake as a precursor for activated carbon. Effect of contact time, initial dye solution concentration, temperature, initial solution pH, activated carbon dose on the adsorption of the MG dye onto the prepared activated carbon were examined. The pseudo-1st order, pseudo-2nd order, Elovich equation, intra-particle diffusion models are used to correlate the adsorption kinetic data for adsorption of MG on the prepared activated carbon. Thermodynamic studies were also performed for removal of MG on the activated carbon.

Chapter 2

2. LITERATURE REVIEW

2.1. TEXTILE ORGANIC DYE

A dye is a colored substance that has an affinity toward the substrate to which it is being applied. Dye can be prepared by two types either by natural process and other by synthetic process. The natural dyes were used in textile industries until 1866, and these dyes are based on the extracts from the vegetables and animals. It is known that indigo dye was extracted from the indigo plant since 3000 BC in India.

The synthetic dye was firstly discovered in 1856, beginning with mauveine dye (aniline), brilliant fuchsia color syntheses by W.H. Perkin (UK), and some other azo dyes were also syntheses by diazotization reaction of various compounds in 1958. These dyes are aromatic in nature and produced by chemical synthesis, having aromatic rings in their structure that contain de-located electrons and different functional groups for different dyes. Their color is due to the chromogen (contain aromatic structure mainly of benzene, naphthalene) –chromophore (contain double conjugated links with dislocated electrons) structure which are acceptor of electrons, and the dyeing capacity is due to auxochrome groups which are donor of electrons.

Dye is applied in an aqueous solution that needs a mordant component to increase the easiness and fastness of the dye to color the substrate. A dye loses its color when some its chemical properties changes. Dyes contain auxochromes which are called color helpers. Carboxylic acid, sulfonic acid, amino groups are some common of the auxochromes. These auxochromes changes the solubility of the dye in aqueous solution. Due to presence of these chemicals in the dye it is of more concern to remove the dye from the effluent of the industries.

The World Bank date shows that almost 15-20% of global industrial water pollution is due to the treatment and dyeing of textiles. Nearly 10-15% of dyes are released through effluent during dyeing process which makes the effluent highly colored.

Figure 2-1: Waste water effulent from the taxtile industry

India is the world's second largest exporter of dyestuffs, after China. In India, textile industries are the largest consumer of dyes, at nearly 80% of the total dye production taking in every type of dye and pigment produced, and this amount is close to 80000 tons per year. The table shows the color limits of the effluent from various industries set by the United States Public Health Association (UPSHA) and Bureau of Indian Standards (BIS).

Table 2-1: Color concentration limits and quantum of water generated from industry (Anjaneyulu et al., 2005)

Industry	Quantum of water generated standards (m^3/Ton)	Color concentration (hazen units)	Color limits (Hazen units)	
			USPHA	BIS
Textile	120 m^3/ton_{fiber}	1100-1300	0-25	0-20
Pulp & Paper		100-600	0-10	5-101
Large	175 m^3/ton_{paper}			
Small	150 m^3/ton_{paper}			
Tannery	28 $m^3/ton_{raw\ hide}$	400-500	10-50	0-25
Kraft mill	40 m^3/ ton	2100-2300	10-40	0-20
Sugar	0.4 m^3/ton_{cane}	150-200	5-10	0-20

2.2. ADSORPTION

Adsorption occurs when a solute accumulates on the surface adsorbent to form a molecular film of adsorbate. Adsorption process is widely used industrial applications process as in water purification and synthetic resins. There are two types of adsorption process,

1. **Physisorption** or physical adsorption: The process in which adsorbate adsorbed on the surface of adsorbent through weak Van der Waals intermolecular forces.
2. **Chemisorption** or chemical adsorption is the adsorption in which a molecule adsorbed on surface through the formation of a chemical bond. In chemisorption molecule adheres on the surface more strongly than physisorption.

Adsorption of synthetic dyes on efficient and inexpensive solid adsorbent (activated carbon) has been considered a simple and economical technique for removal of dye from wastewater, producing clear water which making it an effective alternative for the water treatment, especially when the adsorbent is less expensive. Adsorption is better than other techniques for wastewater treatment in terms of flexibility and simplicity of design, initial cost, ease of operation, sensitivity to toxic pollutants and nontoxic adsorbent after adsorption.

Activated carbon is most reliable and effective physicochemical treatment for removal of dyes. Activated carbons of commercial grade are very expensive. This produces the need to find effective activated carbons at low cost which can be applied to polluted water treatment. Many researches are going worldwide to find a low cost activated carbon for the dye polluted wastewater treatment. A wide variety of low cost activated carbon such as bagasse pith, clay minerals, wood, neem saw dust, maize cob, orange peel was used as viable replacement for commercial grade activated carbon for the removal of dyes from colored wastewater. The adsorption capacities of the low cost activated carbons are not high, thus the search for new adsorbents are still going on. Commercial grade activated carbons can be applied to different types of pollutants in wastewater. If low cost non-conventional precursors are used to prepare activated carbons for particular pollutants, then they can be economical for treatment of wastewater.

2.3. ADSORBATE

In the present study the adsorbate use is Malachite Green Oxalate dye, which is also known as Basic Green 4(malachite green does not contain the mineral named Malachite, name of the dye comes from similarity of color). The IUPAC name of the dye with molecular formula $C_{25}H_{54}N_4O_{12}$ is [4-[[4-(dimethylamino)phenyl]-phenylmethylidene]cyclohexa-2,5-dien-1-ylidene]-dimethylazanium;2-hydroxy-2-oxoacetate. MG is a triarylmethane dye.

Malachite green is obtained by condensation of benzaldehyde with dimethyl aniline in sulfuric acid to give colorless leuco malachite green (LMG) according to the reaction,

$$C_6H_5CHO+2C_6H_5N(CH_3)_2 \longrightarrow C_6H_5CH(C_6H_4N(CH_3)_2)_2 + H_2O$$

and then oxidation of the leuco compound in the presence of HCOOH solution with lead dioxide or manganese dioxide as catalyst,

$$C_6H_5CH(C_6H_4N(CH_3)_2)_2 + HCOOH + \tfrac{1}{2} O_2 \longrightarrow [C_6H_5C(C_6H_4N(CH_3)_2)_2]COOH + H_2O$$

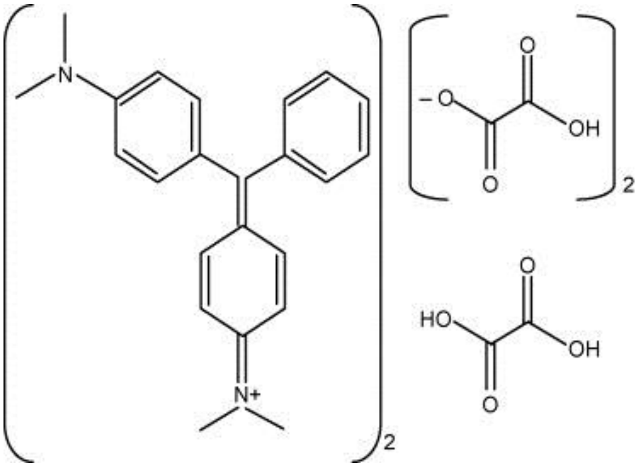


Figure 2-2: Malachite Green oxalate dye structure.

Malachite Green dye is widely used by several industries including textile, food, paper and acrylic and among others. Malachite green is contains very toxic properties which affects the cells of mammals and also is a major cause of creating tumor in liver.

MG is environmentally steady and toxic to many of terrestrial and aquatic animals. MG dye causes serious health hazards and water pollution problem. Both experimental and clinical observations shows so far reveal that MG is a multi-organ toxin. Study indicates that toxicity of MG increases with increase in concentration and with rise in temperature. The effects of MG dye on the intestine of fish included necrosis, increase in goblet cell population, cytolysis and degeneration of epithelial cell lining (Srivastava et al.2004). Histopathology has find that MG causes serious effects in kidney, liver, intestine, gill and gonads. It causes damages mitochondria and also causes nuclear alterations and focal necrosis in liver (Gerundo et al., 1991). MG is also used to treat and prevent parasitic and fungal infections in which process it is reduced to leuco malachite green which accumulates in the tissues of exposed fish.

There are several studies are done for finding the non- conventional, low cost activated carbon for removal of MG from the aqueous solution:

Iqbal et al., (2007) study the adsorption of alizarine red-S, malachite green, methyl blue, methylene blue, bromophenol blue, Eriochrome black-T, phenol red and methyl violet from the aqueous solution by the activated charcoal (commercially supplied) under different experimental conditions. They found that as we increase temperature and pH the adsorption of the Malachite Green was decrease also the adsorption is spontaneous and exothermic according to the thermodynamic study. It was found that optimum time for reaching the adsorption equilibrium on the activated charcoal for all dye was 30 minutes and the optimum amount of adsorbent was 0.01g/25ml of the dye solutions. It was observed that methylene blue had the highest affinity toward activated charcol as compared to other dyes. Maximum adsorption capacity of the activated charcoal for the MG is found to be 0.179 mg/g.

Zhang et al., (2008) used carbon prepared from the Arundo donax root for the adsorption of the MG. During the study they find that adsorption of MG on activated carbon is best describe by the Langmuir isotherm and pseudo-2nd order equation and the time need for reached equilibrium for adsorption is found to be 180 min with the optimum adsorption dose for the experiment is 0.6 g/100 ml of the MG dye solution. The surface area of the carbon is reported to be 158 m^2/g.it is also found the at the pH 9 the color of the MG solution start reducing, due to some change in the structure of MG. Thermodynamic study of the experiment shows spontaneous and endothermic nature of adsorption since ΔG value was negative and ΔH value was positive. It was reported that maximum adsorption capacity of the carbon for the adsorption of the MG is 8.70 mg/g under the optimum condition.

Tahir et al., (2006) studied bentonite clay for removal MG from aqueous solutions under different process conditions such as different initial dye concentrations, adsorbent dose, pH, temperature and shaking time. The surface area of the bentonite clay is found to be 46.61m^2/g. Kinetic data indicates that adsorption of MG on the bentonite clay was controlled by intra-particle diffusion process and the sorption being was of pseudo-1storder, the adsorption is found to be maximum at 9 pH as the dye solution has more positive ions on dissolution in the distil water. The optimum adsorbent dose is found to be0.05g/100ml for the MG dye solution. The maximum capacity of adsorption of the bentonite clay for the MG dye was found to be 7.72 mg/g.

Khattri et al., (2009) used the MG dye as adsorbate and the Neem sawdust (Azadirachta indica) as an adsorbent for the adsorption study under various experimental conditions. The neem sawdust was activated by dilute hydrochloric acid. It was found that as we increase the initial concentration of dye the adsorption capacity of adsorbent is increase but the percent of the dye removal from the solution was reduce. It was also observed that adsorption capacity of the adsorbent increase but percent removal od dye decrease as we decrease the size of adsorbent. There was almost no effect of the agitation speed of the shaker for the adsorption. As we increased the temperature the percent removal of dye decreases. A negative value of change in Gibbs free energy, enthalpy and entropy indicates the spontaneous, exothermic nature of adsorption of MG on the Neem sawdust and randomness of the system. The adsorption experiment was done with the use of 0.25g of adsorbent and 50ml of the dye solution, and it was found that adsorption process was better described by Langmuir adsorption isotherm at the pH of 7.2. As we increase the pH of solution, percent removal of dye increase and it was found that adsorption capacity of the Neem sawdust was 4.35 mg/g under the optimum condition.

Mall et al., (2005) used commercial grade activated carbon (ACC), bagasse fly ash(BFA), activated carbon of laboratory grade(ACL) as adsorbent for the study of adsorption of MG from aqueous solution. They used batch process for the study of adsorption and effect of various parameters on the adsorption of MG by activated carbon. From the study of the adsorption it was found that the optimum pH for adsorption of MG by all the three adsorbent was 7 the contact time needed for the reach the equilibrium was 4 hours. The optimum adsorbent dose for the adsorption was found to be 1, 20, and 4 g/l for BFA, ACC and ACL respectively. The equilibrium data study shows that, removal of MG by ACC and BFA was best shown by Freundlich isotherm but removal onto ACL is fitted onto Redlich-Peterson isotherm, but all the adsorbent shows pseudo-2nd order kinetics for removal of MG by adsorption under optimum parameters. From the economic point of view it was found that BFA is the great adsorbent for removal of MG by adsorption on the large scale as compared of other two. The maximum adsorption capacity for the adsorbent BFA, ACC, and ACL was found to be 170.33, 8.27, 42.18 mg/g respectively.

Hamdaoui et al., (2008) the dead leaves of plane tree (Platanus vulgaris) were investigated as a good bio sorbent for removing malachite green dye from waste water. In the present study malachite green dye uptake process on the plane tree leaves was controlled by pore diffusion. For plane tree activated carbon the contact time to reach equilibrium was about 300 min. during study It was found that kinetic data of the adsorption was best describe by the pseudo-2nd order modal, and the equilibrium isotherm was describe by Langmuir isotherm batter than that of Freundlich isotherm. $\Delta H°$ and $\Delta S°$ for the sorption process were calculated to be 5.7 kJ mol^{-1} and 104.5 J mol^{-1} K^{-1}, respectively which shows malachite green cations has good affinity towards dead leaves of plane tree and adsorption process was spontaneous and endothermic in nature. The adsorption capacity of the plane tree was found to be 16.8 mg/g at 50 mg/l dye concentration in solution and at 35 ^{0}C.

Mittal (2006) studied hen feather as an adsorbent to remove MG from wastewater. It was found that at different temperatures equilibrium was establish more rapidly (90 min) in lower concentration range of MG dye than at higher concentrations, where saturation takes place in 150 min. it was seen that the maximum percent removal of MG was at 7 pH which is around 87% with the amount of adsorbent of 0.1 g/25ml. Langmuir and Freundlich both models are applicable in the hen feather activated carbon at different temperatures. Study shows that as the temperature increase the adsorption increase and as the amount of adsorbent increase from 0.01g to 0.15g the adsorption increase but not much more at higher adsorbent dose (0.10-0.15g), thus the optimum adsorbent dose was found to be 0.01g. in this adsorption process inter-particle diffusion mechanism and external transport film diffusion mechanisms were rate controlling steps in lower and higher concentration ranges of the MG dye, respectively and the overall adsorption process was endothermic in nature.

In recent time many researchers worked on many cheap precursors to find low cost and effective activated carbon. Hen feather was used as precursor which was chemically activated by hydrogen peroxide for adsorbent (Mittal, 2006). Rise husk after carbonization (Sharma et al., 2009) and defective coffee press cake after microwave activation (France et al., 2010) was also used as adsorbent. Aljeboree et al., (2014) used sulphuric acid as activation agent for the adsorbent and citric acid and oxalic acid were used by Wang et al., (2014) while Li et al., (2013) studied the adsorbent after steam activation. Some of the precursor used only after some washing, drying and grinding (Annadurai et al., 2002; Uma et al., 2013).

Brunauer–Emmett–Teller (BET) was used for surface area and pore size of the activated carbon and Fourier transform infrared (FTIR) spectroscopy was used to analyses the chemical structure and bond present in the activated carbon. Field Emission Scanning Electron Microscopy (FESEM) analyses the surface morphology of the activated carbon. These methods are used to characterize the activated carbon for their different surface and structure characteristics. During the adsorption study effect of different parameters temperature, pH, initial dye concentration, contact time were studied. The rate of adsorption kinetics and form of the adsorption isotherm study were also done. In the present study Groundnut cake was used to prepare the activated carbon for removal of the MG from the aqueous solution.

Chapter 3

3. MATERIALS AND METHODS

3.1. MATERIALS

Instruments used in this study with their manufacturers, functions and the operating conditions are listed below,

Table 3-1: List of instruments used in this study with details.

Instrument	Manufacture	Function	Operation conditions
Analytical balance	Sartorius (BS223S)	Weight measurement	100mg - 20g
pH meter	Systronics (361)	pH measurement	pH 1 to 14
Incubator shaker	REICO	Shaking of conical flasks	Speed: 100 rpm.
			Temperature: 20°C-40°C.
Field Emission Scanning Electron microscopy	FEI Nova NanoSEM 230 FESEM	To study the surface structure and chemical composition	Magnification: up to 10000X
			Resolution : 1µm
UV-spectrophotometer	Labindia	To determine the absorbance	Wavelength-615nm
(BET) Surface Area analyzer	Quantachrome Instruments	To determine the pore size and surface area of the sample.	Degassing of N_2 gas at 70^0C
Fourier Transform Infrared spectroscopy (FTIR)	Perkin-Elmer	To predict the organic compounds present in the samples	Resolution of 400 cm-1
			Range 400-4000 cm-1
			Temp-500 ^{O}C
Hot Air Oven	WEIBER	For drying of samples	Done at 60°C
Muffle Furnace	WEIBER, ADCO	For proximate analysis Preparing carbon	As per standards

3.1.1. Chemicals and glassware

All the reagents used during the adsorption study were of analytical grade and all the solutions were prepared using distilled-water. Glassware used for the experiments such as volumetric flasks, weighing cylinder, pipette etc. are procured from Borosil Company and Tarson Product Private Limited. All the glassware were rinsed thoroughly with tap water, subsequently with distilled water and dried in hot air oven to remove any trace of moisture present. Other chemicals used in the experiments were Potassium Iodide (Merck specialties Pvt. Ltd.), Iodine resublimed (Himedia Laboratories pvt. Ltd.), Sodium Thiosulphate (Loba Chemie pvy. Ltd.), Orthophosphoric acid (Fisher Scientific).

3.2. METHODS

3.2.1. Preparation of adsorbent

Groundnut cake was obtained from the local market and was subjected to pretreatment to prepare the adsorbent. Initially the groundnut cake was dried to remove traces of oil in it, and then the cake was ground into powder form after which it was washed to remove any adhering impurities in it and then dried at 90 ^{0}C for 24 hours. The dried grounded groundnut cake was then impregnated chemically using 10% orthophosphoric acid for a period of 5-6 hours. The impregnated cake was then dried in the hot air oven for 4 days at the temperature of 60^{0}C. The dried impregnated cake was then again grounded to fine particle size in the grinder. A sample of this groundnut cake was then pyrolysis at a temperature of 300^{0}C in a Tubular furnace using N_2 gas at a flow rate 10 cm^3/min. The yield of the activated carbon was about 70.27%. After pyrolysis the activated carbon was again grind to the fine powder and then washed several times with distilled water to remove ash content from the carbon. It was subsequently dried in the hot air oven at 45^{0}C. Some samples of the activated groundnut cake was also pyrolysis at different temperature 400^{0}C and 500 ^{0}C to observe the change in surface area and the adsorption capacity of the activated carbon.

3.2.2. Adsorbate

The dye used as adsorbate in present study was malachite green (MG) oxalate dye ($C_{23}H_{25}N_2.C_2HO_4$ .1/2$C_2H_2O_4$, MW: 463.50 and $ʎ_{max}$ = 615nm). MG dye stock solution was prepared in distilled water (100 mg/L) and the working solutions were prepared by diluting the stock solution with distilled water for adsorption study.

3.3. BATCH EXPERIMENTAL PROCEDURE

The adsorption of MG dye was studied using the groundnut cake activated carbon in the batch operation for contact time of 150 minutes. First we took 100 ml of dye solution was taken in the 250 ml conical flask, by diluting the stock solution of the dye. Then a known amount of the activated carbon was added into the conical flask. The conical flask was kept in to the shaker at 100 rpm. Each sample of liquid (1ml) was pipetted out at regular time interval of time for 150 minute contact time. Collected liquid sample was subjected to centrifuge till clear liquid was separated from activated carbon. Using UV-Spectrophotometer at $ʎ_{max}$ 615 the absorbance of clear liquid sample was estimated. To obtain the dye concentration the calibration curve was plotted and the absorbance of the unknown dye solution obtained from spectroscopic analysis was used to estimate the dye concentration.

3.4. METHODS FOR CHARACTERIZATION OF SAMPLE

3.4.1. Proximate analysis

The proximate analysis of a substance determined distribution of products when a sample is subjected to high temperature under specified conditions. Proximate analysis separates the products into its four contents: (1) moisture, (2) fixed carbon, (3) volatile matter and (4) ash. It is the most often analysis used for characterizing a material.

Volatile matter:

Volatile content of the sample indicate the combustible matter of the sample when subjected to high temperature. 1g sample was weighed and taken in a closed lid crucible. The crucible was heated to 925 ^{0}C for 7.5 min in a muffle furnace. After heating the crucible was taken out and cooled in a desicator and then weighed,

$$V_m = \frac{(W_2 - W_3)}{W_2 - W_1} * 100 \qquad \text{……… (3.1)}$$

Ash content:

Presence of ash indicates the density and combustible material present in the sample. 1g sample was weighed and taken into an open crucible. Crucible with sample was heated to 750 ^{0}C for 1.5 hr. After heating, crucible was taken out and cooled in a desicator and then weighed.

$$\mathrm{A} = \frac{(W_3 - W_1)}{W_2 - W_1} * 100 \qquad \text{……… (3.2)}$$

Moisture content:

Moisture content indicates the quantity of water contained in a sample. 1g of sample was weighed and taken in a petri dish. Sample was spread uniformly on the petri dish. Petri dish was then heated at 105 ^{0}C for 1.5 hr in a hot air oven. After heating the petri dish was taken out and cooled in desicator and then weighed,

$$\mathrm{M} = \frac{(W_2 - W_3)}{W_2 - W_1} * 100 \qquad \text{……… (3.3)}$$

Fixed carbon:

Fixed carbon indicates solid combustible residue that remains after volatile matter is removed. The fixed-carbon content of sample was determined from moisture, volatile matter, and ash contents of the sample.

$$\% \text{ Fixed carbon} = 100 - (V_m + A + M) \qquad \text{……… (3.4)}$$

3.4.2. Thermo-Gravimetric Analysis

Pyrolysis is the heating of a substance in the absence of air at a specific temperature. To understand the change in mass of the groundnut cake with temperature and time, thermo-gravimetric analysis was performed. In Thermo gravimetric analysis (TGA) weight of sample is measured as a function of temperature or time when sample was heated in a controlled atmosphere. A little amount of groundnut cake was taken and heated up to a final temperature of 800 ^{0}C. TGA was performed in controlled atmospheres at a heating rate of 25 ^{0}C/Min. Weight lose curve was plotted against temperature which provides the temperature range in which thermal degradation of groundnut cake was takes place.

3.4.3. Solubility

The solubility of activated carbon indicates its dissolving nature in different solutions. Solubility of the activated carbon is tested because of its end use. The activated carbon is to be used in the dye absorbance in the waste water which may be acidic or alkali in nature.

The solubility of the activated carbon is tested in water, acidic medium (solution of HCl) and in the basic medium (NaOH).

3.4.4. Iodine value test

The adsorption of aqueous I_2 is gives an indication about adsorption sits present in the sample. The iodine value, the amount of aqueous iodine adsorbed per gram of activated carbon at equilibrium with 0.1N Iodine solution, was measured according to the procedure set by the American Society for Testing and Materials (ASTM 2006). Iodine Number is the most acceptable fundamental test used to characterize activated carbon. Iodine value gives the measure of unsaturation level (higher Iodine number indicates more adsorption sits present on the activated carbon) of the sample.

- 0.1N Iodine solution
- 0.05N Sodium Thiosulphate solution
- 1% Starch solution
- Activated carbon

Procedure of the iodine value test:

1. *Standardization of Iodine solution,*

- 10ml of 0.1N Iodine solution was taken in conical flask.
- 2 drops of Starch indicator was added to the flask.
- Pale yellow color of Iodine Solution turned Blue.
- The solution was titrated with 0.05N Sodium Thiosulphate solution till it becomes Colorless.
- Burette reading was noted as blank reading (B).

2. *To test iodine value of activated carbon,*

- 0.2 g of Activated carbon was weighed.
- Weighed activated carbon was taken into completely dry conical flask.
- 40ml of 0.1N Iodine solution was then added the flask.
- The flask was shaken for 4 minutes and then solution was filtered.
- The filtrate collected in a completely dry flask and then 10ml of the filtrate was titrated with 0.05N Sodium thiosulphate solution using starch as indicator until colorless solution appear.
- Burette reading noted as activated carbon reading (A).

Now Iodine value can be calculated using the equation below,

$$\text{Iodine value} = \text{C x Conversion factor (mg/g)}$$

Where,

$$\text{Conversion factor} = \frac{(253.81) * \text{normality of iodine solution} * 40}{\text{Wt. of carbon} * \text{B}}$$

$$\text{C} = \text{B} - \text{A}$$

3.4.5. Brunauer-Emmett-Teller (BET) analysis

The effectiveness of an adsorbent is given by its surface properties such as large surface area, and higher porosity and uniform pore size. Activated carbon is often characterized by its extremely large surface area as an adsorbent. The surface area and pore volume of the sample was determined by BET analysis. The specific surface area of the activated carbon was calculated by monolayer physical adsorption of a gas (nitrogen) on the surface of the activated carbon. Physical adsorption occurs when adsorbate molecule adsorbed on the adsorbent surface by weak Van-der walls forces. The determination of surface area of groundnut cake activated carbon was carried out at the temperature 77.37 K of liquid nitrogen.

3.4.6. FESEM/EDX analysis

Field Emission scanning electron Microscopy (FESEM) provides information about the surface morphology of sample. In FESEM emitted electrons from an electron gun strike the surface of sample and generate other low energy secondary electrons. Intensity of the generated secondary electrons from surface of the sample was changed by the surface topography of the sample. An image based on the intensity of secondary electron was constructed as a function of the arrangement of the scanning primary electron beam. The preparation of the sample is done by coating it with gold to avoid ionization of the sample.

Energy Dispersive X-ray (EDX) analysis is used to know the chemical composition of sample. The intensity of secondary electrons generated by electron strike is correlated with atomic number of the element which gives different components present in the sampling volume. Hence, quantitative elemental information of the sample can be known.

3.4.7. FTIR analysis

FT-IR stands for Fourier Transform Infrared, used to know the chemical structure of the sample. In FTIR spectroscopy, Infrared radiation is passed through the sample, from which some of the radiation is absorbed within the sample and some radiation is passed transmitted by the sample. The resulting spectrum from absorbance and transmitting of infrared by sample was represents the molecule absorption and transmission, which creating a molecular identification image of the sample. Every molecule and molecular bonds formed a different infrared spectrum at the radiation receiver. Therefore, FTIR spectroscopy give result to identify the (qualitative analysis) of different kind of bonds and structure of the sample. In the present study FTIR of groundnut cake, activated carbon before adsorption and activated carbon after adsorption was done.

3.5. ADSORPTION STUDY

Study the effect of contact time:

To study the influence of contact time on the adsorption of MG dye, 100 ml of 50mg/l dye solution taken in a conical flask and 1.5g of activated carbon was added in the flask at solution pH. The flask was kept at 303 K in the shaker at 100rpm shaking speed. Then the sample was pipetted out at the interval of 1 min initially for starting 10 minute and then it was taken after 10 min for the next 60 minute and thereafter at 20 minute interval. The dye concentration in the remaining sample was analyzed for absorbance in the UV-spectrophotometer.

Study the effect of initial solution pH:

One of the important factors that affect the adsorbent capacity in wastewater treatment is pH of solution. To study the effect of pH on the adsorption of MG dye, 100 ml of 50mg/l dye solution taken in a conical flask and then different pH of the solution (2 to 8) were maintained in the different conical flasks, and 1.5g of activated carbon was added in every flask. Next the conical flask was kept at 303 K in the shaker at 100rpm. The sample was taken at the interval of every 40 minutes, and then the remaining dye concentration in the flask was calculated spectrophotometrically by absorbance.

Study the effect of adsorbent Dosage:

Effect of adsorbent Dosage on the adsorption of MG dye was studied by taking 100 ml of 50mg/l dye solution in a conical flask and then different amount of activated carbon

(0.5 to 2.0 g) were added in the different conical flask at 4 pH. After we keep the conical flask at 303 K in the shaker at 100rpm, the sample was collected at the interval of every 40 min to obtain the concentration of the remaining dye in the solution after adsorption.

Study the effect of Initial dye concentration:

To study the influence of the initial dye concentration on the adsorption, we take different concentration of dye (25, 50, 75, 100 mg/l), and then 1.5g of activated carbon added in every flask at 4 pH. After it we keep the conical flask at 303 K in the shaker at 100rpm. The sample was taken at the interval of every 40 minutes, and then we obtain the remaining dye concentration in the flask by absorbance.

Study the effect of temperature:

To study of the effect of temperature on the adsorption is done, 50mg/l of the dye solution in the conical flask and 1.5g. of activated carbon was added to it and the after which the flask was kept in the shaker at different temperature(20, 30 313 K), and at 100 rpm and at 4pH.

In all the study of different parameters, the absorbance capacity (q_e) of the activated carbon was calculated by the equation,

$$q_e = \frac{(C_0 - C_e) * V}{\mathrm{W}} \qquad \text{………. (3.5)}$$

and % removal was calculated by the equation,

$$q\ \% = \frac{(C_0 - C_e)}{C_0} * 100 \qquad \text{………. (3.6)}$$

3.6. ADSORPTION KINETIC STUDIES

Adsorption kinetics study is done for the understanding of the rate of adsorption, mechanism of adsorption, which are the two most important factors for the optimal design for the practical application. To analyses the adsorption kinetics of MG over activated carbon four models; Pseudo-1st, Pseudo-2nd order, Elovich equation, and intra-particle diffusion were tested.

Pseudo-1st equation:

In this equation it is assumed that the rate (dq_e/d_t) is proportional to the difference between the amount of adsorption at time t and the adsorption capacity of adsorbent ($q_e - q_t$). Let K_1 be the proportionality constant, then,

$$\frac{dq}{dt} = K_1(q_e - q) \qquad \text{………. (3.7)}$$

Linear form of above equation can be written as,

$$\ln \frac{(\, q_e - q)}{q_e} = -K_1 * t \qquad \text{………. (3.8)}$$

Pseudo-2nd order equation:

Pseudo-second order kinetics based on the equilibrium adsorption capacity is expressed as

$$\frac{dq}{dt} = K_2(\, q_e - q)^2 \qquad \text{………. (3.9)}$$

Linear form of the above equation can be get by integrating the equation,

$$\frac{t}{q_t} = \frac{1}{K_2 * {q_e}^2} + \frac{t}{q_e} \qquad \text{……. (3.10)}$$

The value of q_e and K_2 can be estimated from slope and intercept respectively from linear plot between t/q_t versus t.

Elovich equation:

The Elovich equation used for general application to chemisorption with a wide range of slow adsorption rate,

$$\frac{dq}{dt} = \alpha * e^{-\beta q} \qquad \text{……. (3.11)}$$

The linear form of the above equation is,

$$q = \frac{\ln(\alpha * \beta)}{\beta} + \frac{\ln t}{\beta} \qquad \ldots\ldots\ (3.12)$$

Where α and β can be determine by intercept and slope of the plot between q versus ln(t).

Intra-particle diffusion model:

The intra-particle diffusion model is based on the assumption that the adsorption uptake q_t varies proportionally with square root of contact time,

$$q_t = K_{id} * \sqrt{t} + I \qquad \ldots\ldots\ (3.13)$$

Where I is the intercept (mg/g) and k_{id} (mg/g.min$^{1/2}$) is inter particle diffusion rate constant and can be obtained from slope of the plot between q_t versus √t.

3.7. ADSORPTION EQUILIBRIUM STUDY

Adsorption is usually described by the isotherm, which give a relation between adsorbed amount of adsorbate and the concentration in bulk phase at constant temperature at equilibrium. Here Langmuir, Freundlich, models were applied to fit the equilibrium data.

Langmuir adsorption isotherm:

The Langmuir isotherm is based on the assumption that there was only one layer of molecules adsorbed on to the surface, i. e. monolayer adsorption of the adsorbate. The monolayer isotherm is represent by the equation,

$$q_e = \frac{q_m * b * C_e}{1 + \mathrm{b} * C_e} \qquad \ldots.\ (3.14)$$

On integrating the above equation we get the linear form of the above equation as,

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m * b} \qquad \ldots.\ (3.15)$$

The value of b and q_m can be obtained from the plot between C_e/q_e and C_e.

Freundlich isotherm:

Freundlich adsorption isotherm is based on the assumption that the distribution of the heat on the adsorbent surface is non-uniform, namely a heterogeneous adsorption. Freundlich model can be express as,

$$q_e = K_f * {C_e}^{1/n} \qquad \text{……. (3.16)}$$

Linear form of the above equation is written as,

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad \text{……. (3.17)}$$

The value of K_f and n can be determined from the plot between $\ln q_e$ versus $\ln C_e$.

3.8. THERMODYNAMIC STUDY

In the thermodynamic study, Gibb's free energy change (ΔG^0), change in enthalpy (ΔH^0), change in entropy (ΔS^0), was determined. Change in Gibbs free energy can be calculated by,

$$\Delta G^0 = -RT \ln K_0 \qquad \text{……. (3.18)}$$

K_0 can be determined from the intercept of plot between $\ln (q_e/C_e)$ versus Ce and extrapolating to $C_e = 0$. The value of ΔH^0 and ΔS^0 were determined from the plot between ΔG^0 versus T.

Chapter 4

4. RESULTS AND DISCUSSION

4.1. CHARACTERISTICS OF GROUNDNUT CAKE

Characterization of precursors is essential to know the ash and volatile content of the precursor. It indicates the available carbon in the form of fixed carbon to obtain the activated carbon.

4.1.1. Proximate analysis

Proximate analysis of the groundnut cake gives the following results,

Volatile matter:

$$V_m = \frac{(W_2 - W_3)}{W_2 - W_1} * 100$$

Where,

W_1 = 15.713 g, W_2 = 16.745 g, W_3 = 15.927 g,

Thus, $V_m = 78.57\%$.

Ash content:

$$\text{A} = \frac{(W_3 - W_1)}{W_2 - W_1} * 100$$

Where,

W_1 = 21.403 g, W_2 = 22.403 g, W_3 = 21.462 g,

Thus, $A = 5.90\%$.

Moisture content:

$$\text{M} = \frac{(W_2 - W_3)}{W_2 - W_1} * 100$$

Where,

W_1 = 32.557 g, W_2 = 33.557 g, W_3 = 33.430g, *Thus, M = 12.62%*

Fixed carbon:

$$\%\ \textit{fixed carbon} = 100 - (A + V_m + M)$$

$$= 2.91\%.$$

Table 4-1: Proximate analysis of groundnut cake

Content	Percentage (%)
Moisture content	12.62
Volatile matter	78.57
Ash content	5.90
Fixed Carbon	2.91

The above table indicates that the groundnut cake has high volatile and moisture content which lead to very low fixed carbon which is obtained by difference. Characterization report by Agrawalla, et al. indicates Volatile content (83%) which was very close to our reported values [Agrawalla et al. 2011].

4.2. CHARACTERISTICS OF ACTIVATED CARBON

4.2.1. BET analysis

In the BET analysis the surface area of three activated carbons was determined which pyrolysis at three different temperatures. The surface area of the all three activated carbon are listed below,

Table 4-2: Surface area of activated carbons

Temperature (K)	Surface area (m^2/g)
573	35.526
673	6.958
773	0.592

From the data listed in table 4, it is observed that as the temperature of the pyrolysis increase the surface area of the activated carbon decreased which occurs due to the collapse of the pore walls of activated groundnut cake at high temperature. Similar findings were also demonstrated by Della et al. during activation of rice husk ash-precursor by chemical method (Della et al., 2002). As the surface area of the activated carbon pyrolysis at 573 K was better thus activated carbon prepared at 573 K was used throughout the study.

4.2.2. Solubility

Activated carbon solubility was tested under three different conditions, in acid, in base and in water. After the solubility test it was observed that under all three conditions the activated carbon was insoluble in nature, which shows the capability of activated carbon as adsorbent for its end use application.

4.2.3. Iodine value test

Iodine value test give the information about adsorption sites available at the adsorbent for the adsorption. The higher the Iodine number the higher the adsorption capacity of the activated carbon for adsorption.

In the present work the iodine number of the groundnut cake activated carbon obtained was **706**. Ahmad et al. was reported that iodine value 473 for Pistacia Lentiscus leaves powder (Ahmad et al., 2012).

4.2.4. FTIR analysis

FTIR spectra of groundnut cake, activated carbon before and after adsorption are presented in figure 4-1. The bend spectrum around 3269 and 1635 cm^{-1} attribute to (O-H, stretch) alcohols and alkenes(C=C) respectively in the groundnut cake. The spectrum of 1438 and 2856 cm^{-1} show the molecular group of (C-H, deformation) alkanes and (O-H, stretch) carboxylic acid in the activated carbon before adsorption. Reduction in the C=C bond to the C-C and C-H confirm the activation of the groundnut cake.

The molecular group found in the activated carbon after adsorption consist spectrum band at 1772, 1559 and 1118 cm^{-1} which shows the molecular group of carboxylic acid(C=O), amines(NH_2) and amines(C-N). The presence of amine group in the activated carbon after adsorption IR spectra indicates the adsorption of the MG dye on the activated carbon.

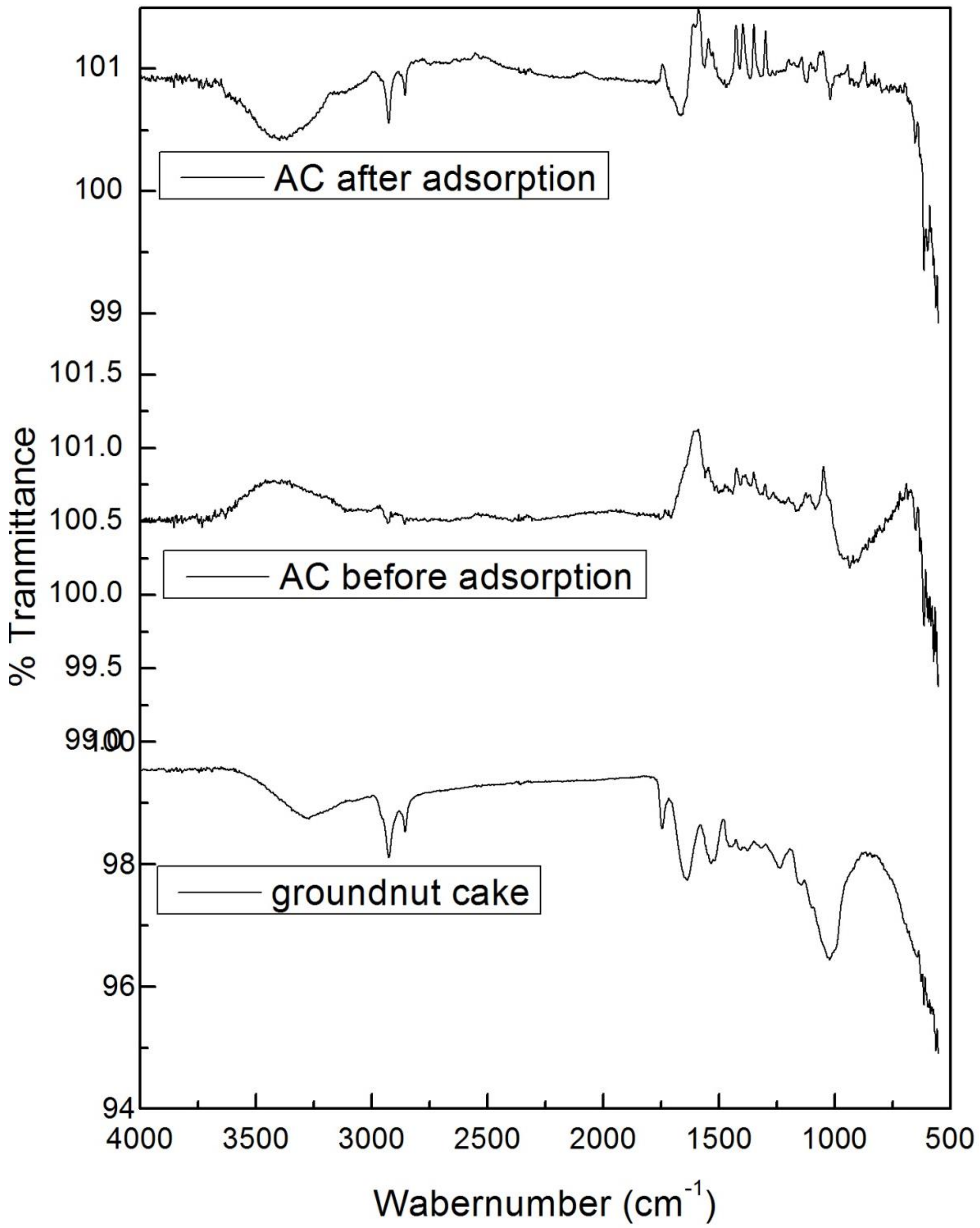


Figure 4-1: FT-IR spectra of groundnut cake, activated carbon before adsorption, activated carbon after adsorption

4.2.5. FESEM/EDX analysis

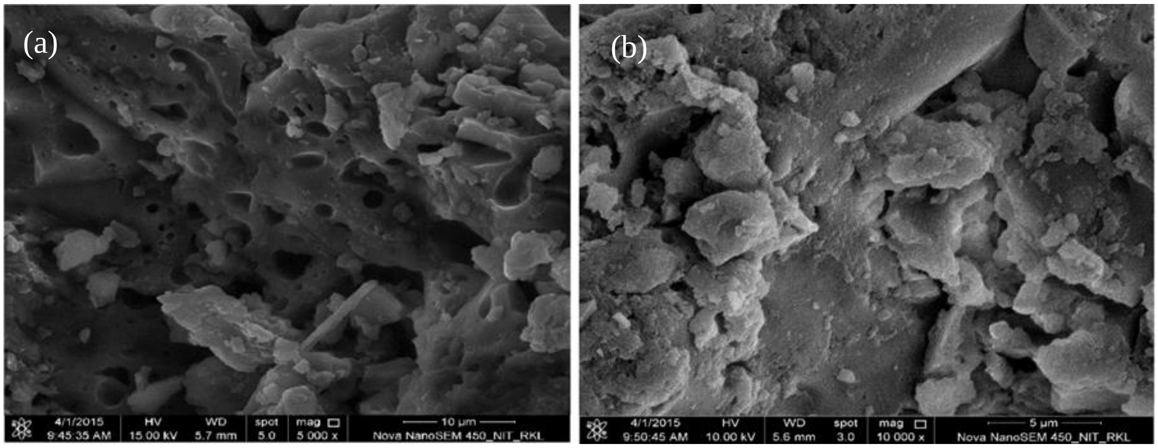


Figure 4-2: FESEM images of (a) activated carbon before adsorption, (b) activated carbon after adsorption

FESEM is the tool for surface characterization of the sample. Fig. 4 shows images of activated carbon before and after adsorption. It is seen that there is a good chances of adsorption of the MG dye on the activated carbon as there are many pores available on the surface of the activated carbon (fig. 4-2(a)), while fig. 4-2(b) shows the activated carbon after adsorption, in which it was clearly seen that there are a layer of the MG dye and pores on the surface of groundnut cake activated carbon was filled. The dye molecule seems to form a void free film on the surface of the activated carbon which shows a good adsorption of the dye on the adsorbent (Aljeboree 2014).

Table 4-3: Elemental analysis of activated carbon

Element	%Value (before adsorption)	%Value (after adsorption)
C	48.14	77.47
P	26.45	12.69
O	25.40	9.84

The elemental data listed in above table shows that the amount of carbon increases after adsorption while the activation agent (P through soaking by orthophosphoric acid) used in the activation of the groundnut cake and the oxygen was reduced after adsorption due to the reaction that occurs between the dye and the elements present on the surface of the activated carbon.

4.3. ADSORPTION STUDIES

4.3.1. Effect of adsorbent dose

Use of optimum dose of the activated carbon in the adsorption is a crucial factor for the cost effective industrial application of the process. To know the effect of adsorbent dose, batch experiments were conducted with 100 ml of 50 mg/l MG solution at 100 rpm and at 303 K. It was seen from the fig. 4-3 (appendix A-1) that as we increase the adsorbent doses from 5 g/l to 20 g/l the percent removal of the MG dye increased from 79.51 to 99.43 % but the adsorption capacity decreased from 7.91 to 2.47 mg/g. The percent removal of MG dye increased because of increase in the amount of activated carbon as the adsorption sites increase. A similar result was previously obtained for the removal of MG dye by bagasse activated carbon and fly ash (Mall et al., 2005).

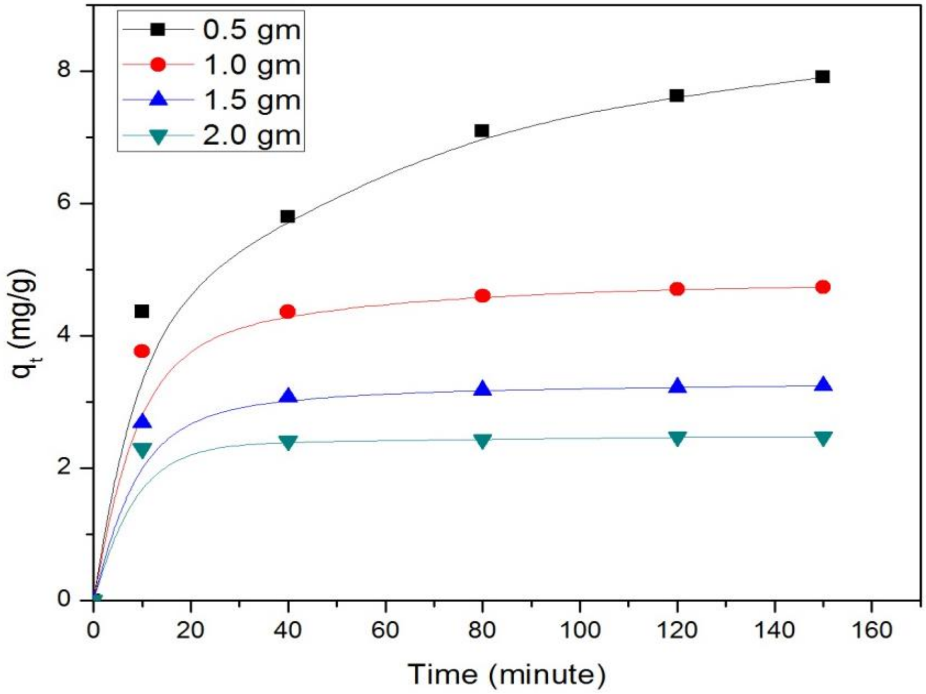


Figure 4-3: Effect of adsorbent dose on adsorbent’s adsorption capacity

As the adsorption sites increased some sites of the activated carbon remained unsaturated due to which the adsorption capacity was decreased. It is also seen that as we increase the activated carbon dose the contact time necessary to reach the equilibrium was reduced from 150 min to 50 min, which was also due to the higher adsorbent sites for the adsorption.

4.3.2. Effect of initial dye concentration

To know the effect of the initial dye concentration on the adsorption batch experiment was done at constant temperature of 303 K and 1.5g/100ml of MG dye solution in which the dye concentration was varied 25, 50, 75 and 100 mg/l at constant shaking speed of 100rpm.

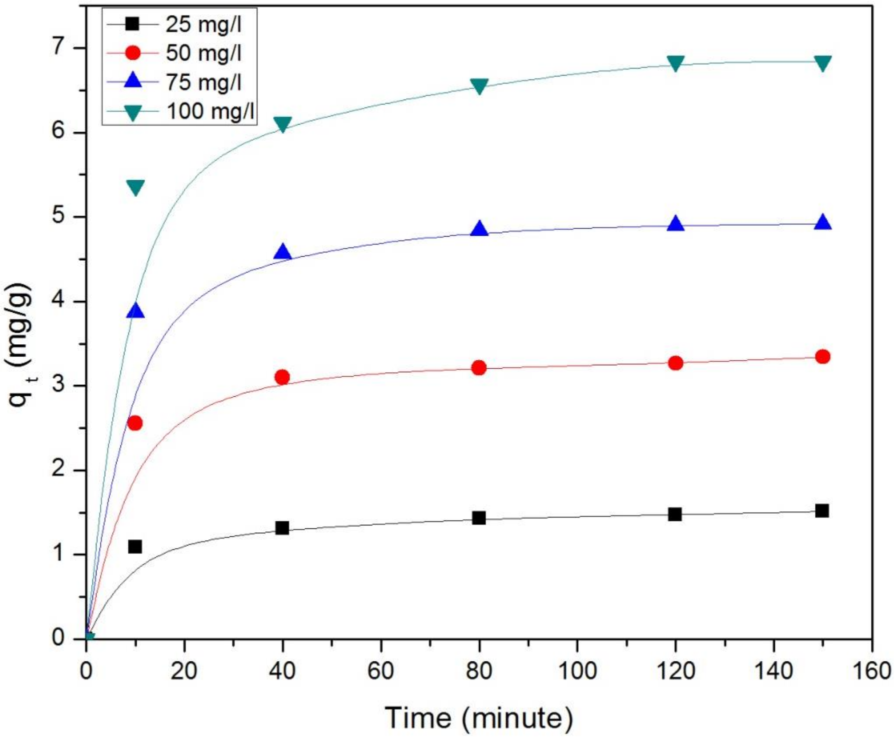


Figure 4-4: Effect of initial dye concentration on adsorbent's adsorption capacity

It can be seen from the fig. 4-4 (appendix A-2) that as the dye concentration increased adsorption capacity of the groundnut cake activated carbon increased from 1.51 to 6.84 mg/g. It is because more dye will be adsorbed on the adsorption sites of the activated carbon as the dye concentration increased. It was also seen that percentage removal of dye increase from 95.13 to 97.22 % as the dye concentration increases from 25 to 75 mg/l but at 100 mg/l it decreases to 95.88 %. Decrease in percentage dye removal happened because as we increase the dye concentration the more dye will adsorb on the activated carbon but at higher dye concentration after some time the adsorption sites of the activated carbon become saturated so the dye removal will decrease. It is observed from the plot that the time needed to reach the equilibrium adsorption is less than that of higher dye concentration. As the initial dye concentration increase, concentration gradient increases which increase the driving force to reach the equilibrium. The initial rate of adsorption of MG dye on the activated carbon is higher for higher dye concentration due to low resistant to the dye uptake on the adsorption sites (Hamdaoui, 2008).

4.3.3. Effect of the temperature

The effect of temperature was studied at the temperature 20, 30, 313 K, at the 4pH, with 50 mg/l of dye concentration and at 100 rpm and with activated carbon dose of 1.5 g /100 ml of dye solution.

It is observed from the fig. 4-5 (appendix A-3) that as the temperature rise the adsorption capacity of the activated carbon decreases from 3.50 to 3.28 mg/g. this may be caused because of increase in the solubility of the dye in the solution at higher temperature which can cause less interaction between dye and the adsorbent. The change in adsorption capacity of groundnut cake activated carbon can be described by change in chemical potential i.e. solubility of the MG dye which increases with temperature. It was also noticed that on increase of temperature form 293 K to 303 K the percent removal of the dye increases from 96.06% to 99.76%. But as we further increase the temperature from 303 K to 313 K the percent removal of the MG dye from solution was slightly decreased from 99.76% to 99.00% due to exothermic nature of the adsorption process (Wang et al., 2014).

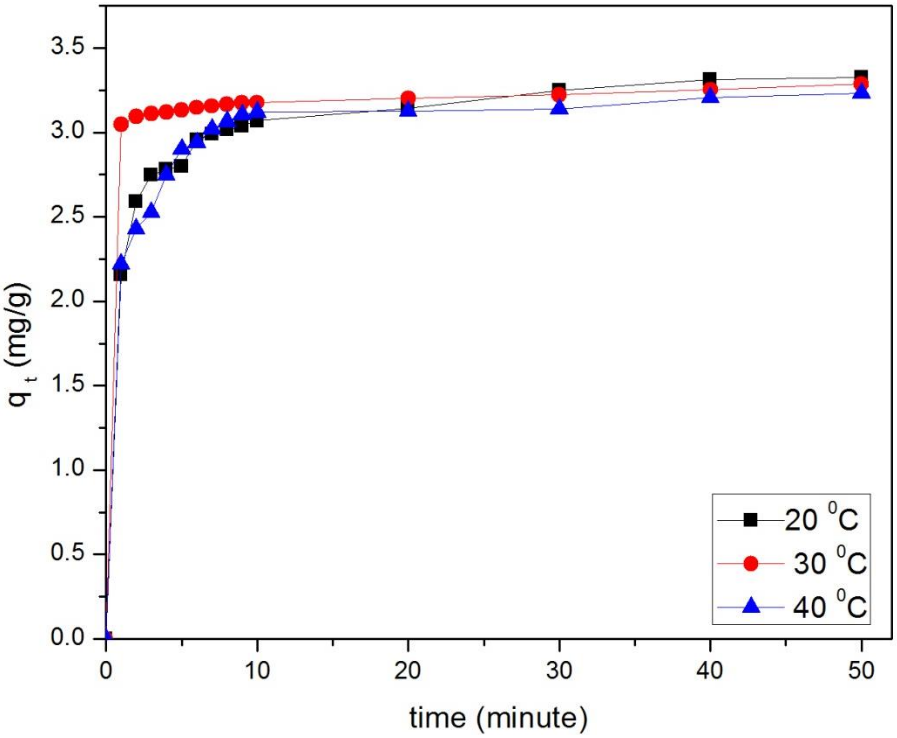


Figure 4-5: Effect of temperature on adsorbent's adsorption capacity

4.3.4. Effect of initial solution pH

The pH of the dye solution has significant effect on the dye adsorption. Solution pH alters the charge on surface of adsorbent as well as the extent of ionization of aqueous adsorbate species in the solution and consequently the rate of adsorption.

The change in the pH affected the adsorption capacity due to the presence of functional group at the adsorbent and adsorbate surface. It was observed from the fig. 4-6 (appendix A- 4) that as we increased the pH of the dye solution from 2 to 8 the adsorbent capacity of the activated carbon was affected significantly. As we increased the pH from 2 to 4 the adsorption capacity increased from 2.57 to 3.46 mg/g, but again as we further increased the pH of the solution from 4 to 8 it was found that the adsorption capacity reduced from 3.46 to 1.98 respectively. This was attributed to the fact that as the pH of the solution increase the negatively charge ion of the solution neutralized the positive charge of the surface of the activated carbon that caused the reduction of the adsorbent capacity of the activated carbon (Ahmad, 2010). It was also observed that there was negligible effect on the percent removal of the dye.

The zeta potential of the activated carbon was 6.47 but after the adsorption the zeta potential were reduced to 0.17, which confirms that the activated carbon has the great capability of removing the MG dye from the solution.

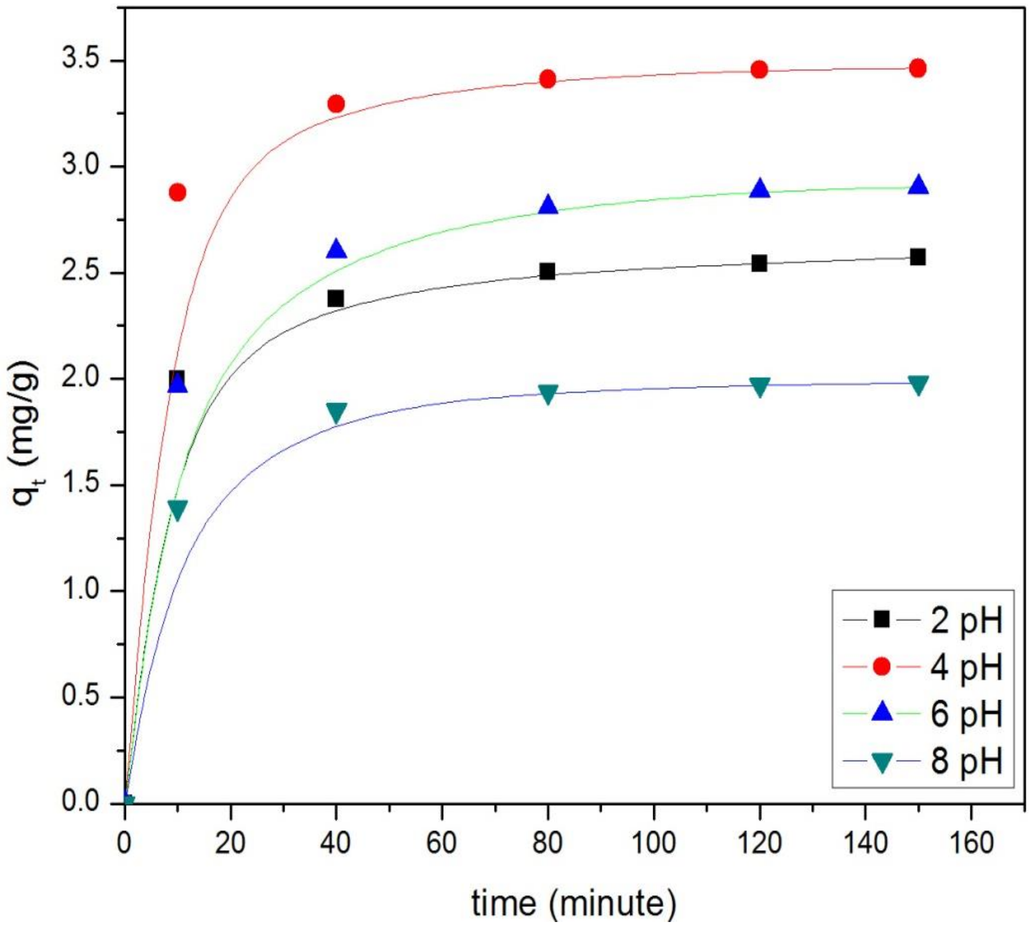


Figure 4-6: Effect of initial solution pH on adsorbent's adsorption capacity

4.4. ADSORPTION KINETIC STUDIES

In the present study kinetics of the adsorption of MG on the activated carbon was tested at three different temperatures, as 20, 30 and 313 K. Following table shows the parameter of the four different kinetics models as,

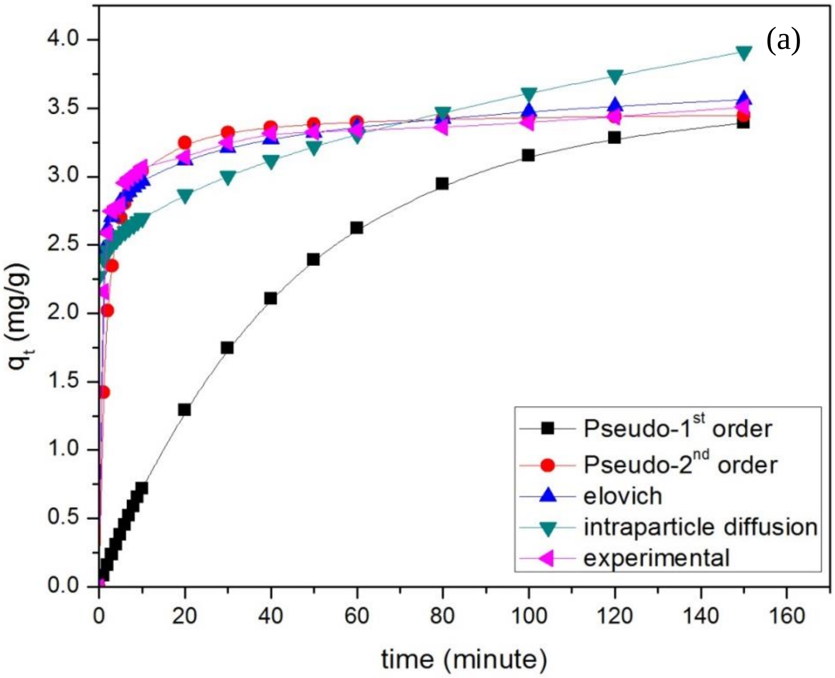
Table 4-4: Parameters of different kinetic models at different temperatures

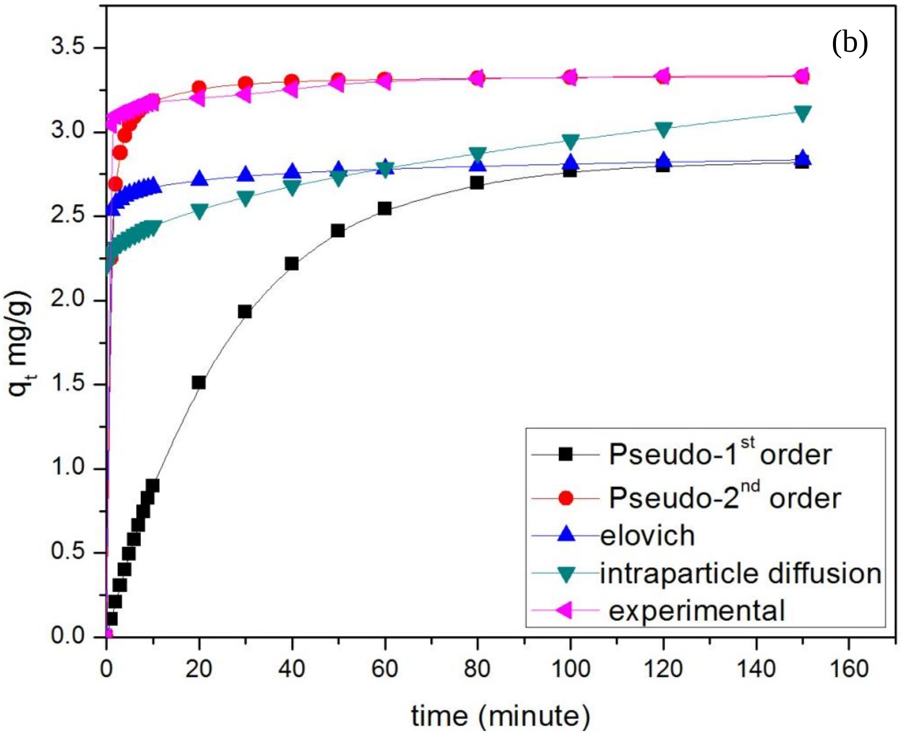
Kinetic model	**Constants**	**Value (**at different temperatures**)**		
		293 K	303 K	313 K
Pseudo -1st order	K_1	0.0229	0.0384	0.0394
	R^2	0.8745	0.9809	0.9251
Pseudo- 2nd order	q_e	3.482	3.34	3.295
	K_2	0.198	0.621	0.379
	R^2	0.9995	0.9999	0.9999
Elovich modal	α	16193.75	1.44*10^7	122488.13
	β	4.5516	16.694	5.367
	R^2	0.9208	0.9875	0.9891
Intra-particle diffusion	K_{id}	0.1343	0.0745	0.1178
	I	2.2678	2.2077	2.2911
	R^2	0.7319	0.9288	0.8575

From the above table all the experimental data shows that the adsorption of MG can be described better by the Pseudo-2nd order kinetic model in term of higher correlation coefficient $R^2 > 0.9995$.

Fig.4-7 (appendix A-5, 6, 8) represents the various adsorption kinetics models along with the experimental value of adsorption capacity of activated carbon. Fig. 4-7 indicate that the adsorption was rapid in initial stage of the adsorption due to more available activate site on the surface of groundnut cake activated carbon. The adsorption capacity of the activated carbon (q_e) was calculated from Pseudo-2nd order kinetics (3.329mg/g) and the value obtained from experiment (3.335mg/g) at 303 K.

By comparing these four kinetic models, it is observed that Pseudo-2nd order kinetic model described the adsorption kinetic more accurately then other three. Besides, the correlation coefficient was very high for the same under all experimental conditions (Wang et al., 2014).





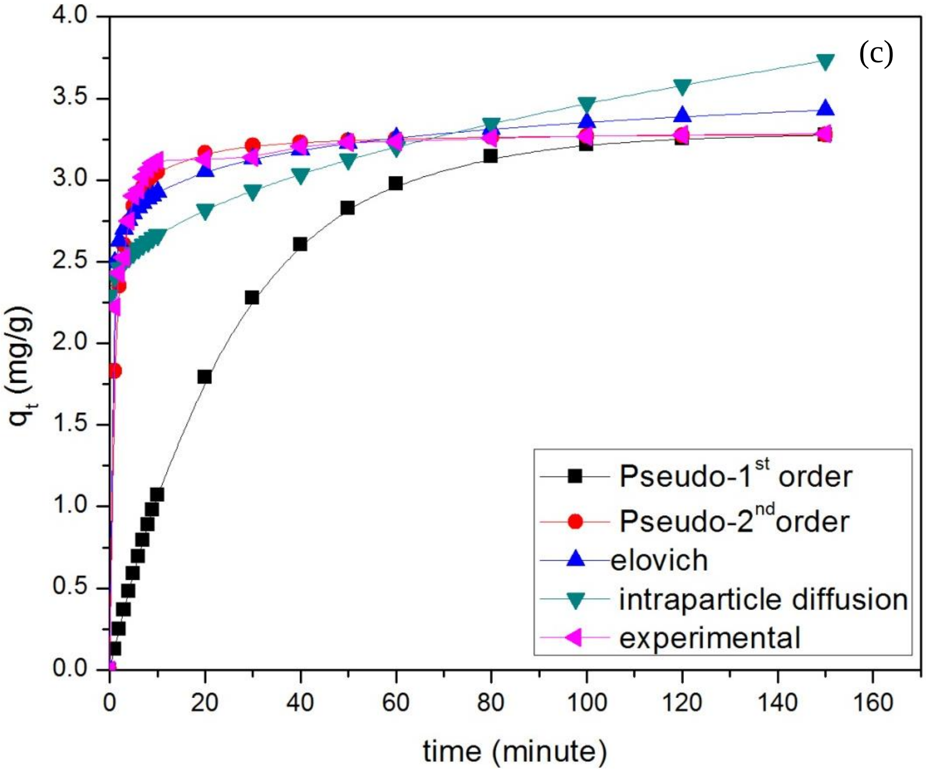


Figure 4-7: Adsorption rate curves at, (a) 293 K, (b) 303 K, (c) 313 K

4.5. ADSORPTION EQUILIBRIUM STUDIES

The coefficient of determination and other parameter of the Langmuir and Freundlich isotherm are listed below,

Table 4-5: Adsorption isotherm parameter at different temperatures

Isotherm models	**Constants**	**Value** (at different temperatures)		
		293 K	303 K	313 K
Langmuir	q_m	14.430	6.024	34.129
	K_L	0.0305	0.2954	0.043
	R^2	0.7299	0.7643	0.8208
Freundlich	K_f	0.3464	1.2130	1.5062
	1/n	1.2766	1.1782	1.2713
	R^2	0.9228	0.9838	0.9037

From the data listed in the table 7, it was observed that Freundlich adsorption model was found to fit the experimental data with high correlation coefficient (0.9838) as compared to the Langmuir adsorption isotherm (0.7643) at the same temperature. The value of 1/n above unity indicates the cooperative adsorption of MG on the activated carbon. Freundlich isotherm gives the maximum adsorption capacity at equilibrium (7.65 mg/g).

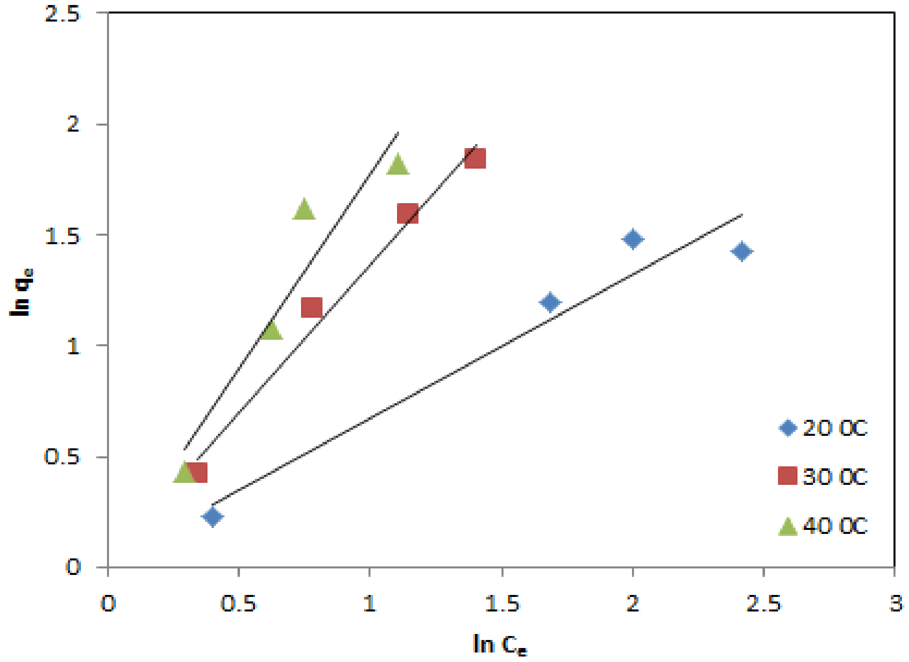


Figure 4-8: Freundlich isotherm plots for the adsorption of MG on Activated carbon at different temperatures.

From fig. 4-8 (appendix A-8) it is observed that Freundlich isotherm gives theoretically linear plots with high correlation coefficient (R^2) which shows the applicability of Freundlich isotherm for the adsorption of MG on the groundnut cake activated carbon under all three temperatures. Hence Freundlich isotherm was best describing the adsorption behavior at equilibrium than Langmuir isotherm.

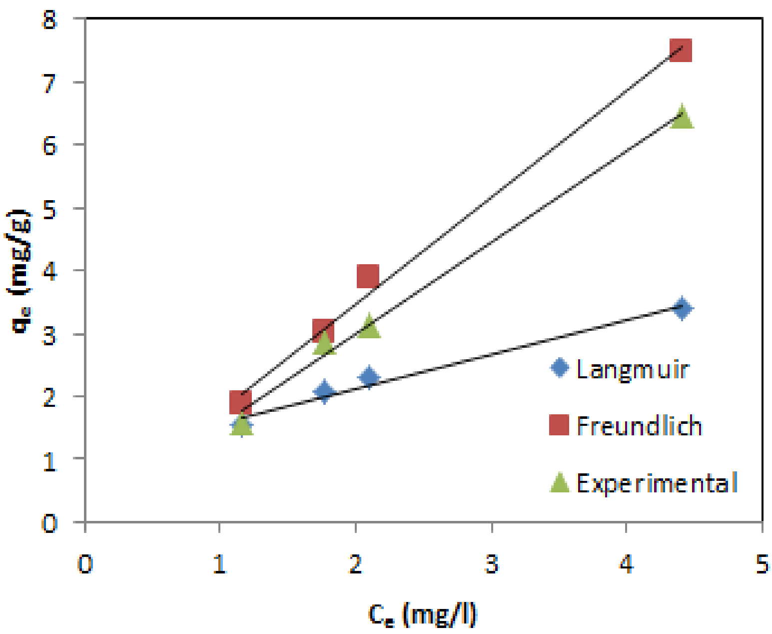


Figure 4-9: Adsorption isotherms at 303 K

From fig. 4-9 (appendix A-9) it is observe that from the two models (Freundlich and Langmuir) it the Freundlich adsorption isotherm is most adopted fitting adsorption isotherm and Freundlich isotherm gives the maximum adsorption capacity at the equilibrium.

Table 4-6: Comparison of adsorption capacity of groundnut cake activated carbon for removal of MG dye with other low-cost adsorbents

Adsorbent	**Maximum adsorption capacity, q_{max} (mg/g)**	**Reference**
Arundo donax root carbon	8.96	Zhang et al., (2008)
Bentonite	7.72	Tahir et al., (2006)
Tamarind fruit shell	1.951	Saha et al., (2010)
Activated charcoal	0.179	Iqbal etal., (2007)
Sugarcane dust	4.88	Khattri et al., (1999)
Cellulose	2.422	Sekhar et al., (2009)
Groundnut cake activated carbon	6.45	Present study

Table 8 shows the maximum MG adsorption capacities of various adsorbents including groundnut cake activated carbon. The comparison shows that groundnut cake activated carbon has good adsorption capacity of MG as compare to other low cost reported adsorbents, reflecting a promising future for groundnut cake activated carbon as an alternative for many other adsorbents for MG removal from aqueous solutions.

4.5.1. Separation factor

In order to find out whether the adsorption of MG on the activated carbon is "favorable" or "unfavorable," a dimensionless constant called separation factor (R_L) has been calculated by,

$$R_L = \frac{1}{1 + K_f \, * \, C_1}$$

The value of R_L indicate that the adsorption is irreversible equilibrium (R_L = 0), favorable equilibrium (0< R_L < 1), linear case (R_L =1) and unfavorable (R_L >1).

The result for the different Freundlich constant was listed below,

Table 4-7: Separation factor for different Freundlich constant

Freundlich constant ($K_{1)}$	separation factor (R_L)
1.043	0.0545
1.699	0.0162
1.54	0.0131

From the calculated data listed in the above table it can be seen that the adsorption of MG on the groundnut cake activated carbon was "favorable equilibrium" (Wang et al., 2014).

4.6. THERMODYNAMICS STUDY

Different parameter of the thermodynamic study of this work is listed below,

Table 4-8: Thermodynamic function for MG adsorbed on groundnut cake activated carbon.

Temperature (K)	ΔG^0 (J/mol)	ΔH^0 (J/mol)	ΔS^0 (J/K mol)
293	-2.0174	-0.10051	17.228
303	-3.63007		
313	-4.02753		

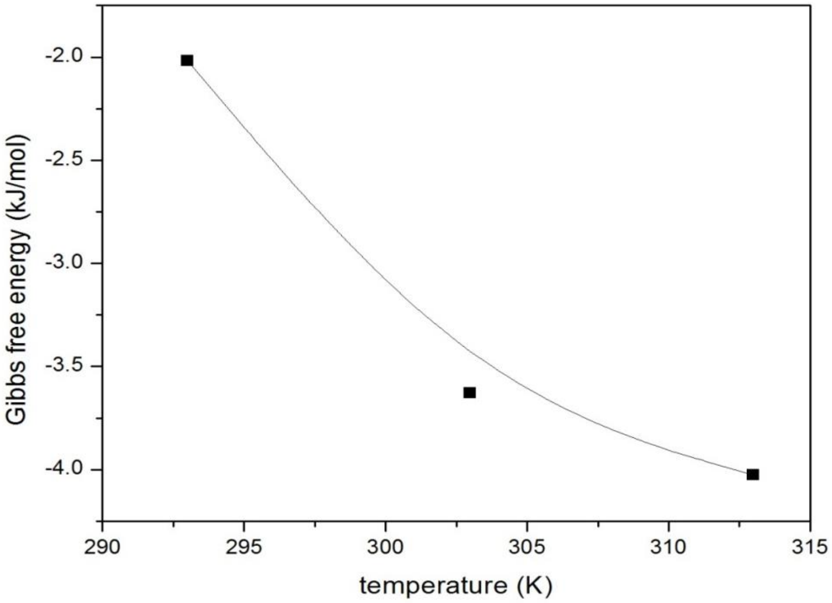


Figure 4-10: Change in Gibbs free energy in adsorption at different temperature.

The negative value of the ΔG^0 confirmed spontaneous nature of the adsorption process with high percentages of adsorption of MG on the activated carbon, and decreasing value of ΔG^0 with increase in temperature shows that the adsorption becomes less favorable at higher temperature. The negative value of the ΔH^0 indicates exothermic nature of adsorption process. Also the positive value of ΔS^0 shows increase in the highly randomness of the dye molecule at the solid/liquid interface and an affinity of the dye toward adsorbent (Hamdaoui at el., 2008).

Chapter 5

5. CONCLUSION

Groundnut cake was successfully used as a cheap precursor for removal of Malachite Green dye from aqueous solution. Following conclusions are made by the present study of removal of MG dye by groundnut cake activated carbon from aqueous solution.

- The shifting of peaks in FTIR spectrum and images from FESEM confirms the adsorption of MG dye on groundnut cake activated carbon.
- Groundnut cake has surface are of 34 m^2/g, 2.91% fixed carbon and Iodine no. as 706.
- Adsorption of MG increase with initial dye concentration, contact time and adsorbent dose but decrease with increase in temperature and initial solution pH.
- The optimum conditions for adsorption was found to be 50 mg/l (initial dye concentration), 1.5 g/100ml (activated carbon dose), 4pH, 303 K and 100 rpm shaking speed.
- At this optimum condition experimental values were validated with Frendulich isotherm models which were fitted well to the experimental data ($R^2 = 0.9838$).
- The kinetic of the adsorption process agreed well to the Pseudo-2nd order model.
- The adsorption of MG on activated carbon was exothermic and spontaneous in nature.

The adsorption capacity of the groundnut cake activated carbon is within the range of the adsorption capacity of the other adsorbent. Thus the present study shows that groundnut cake activated carbon can be used as an inexpensive and efficient adsorbent for removal of MG dye from aqueous solution.

Chapter 6

6. REFERENCES

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Appendix

A. Appendix

Table A-1: Adsorbent capacity for different amount of adsorbent dose

Time	q_t (mg/g)			
	0.5 (g)	1.0 (g)	1.5 (g)	2.0(g)
0	0	0	0	0
10	4.362	3.763	2.684	2.289
40	5.801	4.362	3.075	2.402
80	7.095	4.601	3.178	2.429
120	7.622	4.707	3.219	2.469
150	7.910	4.737	3.244	2.472

Table A-2: Adsorbent capacity for different initial dye concentration

Time	q_t (mg/g)			
	25 (mg/l)	50 (mg/l)	75 (mg/l)	100 (mg/l)
0	0	0	0	0
10	1.086	2.556	3.867	5.369
40	1.306	3.100	4.570	6.120
80	1.426	3.211	4.836	6.568
120	1.473	3.266	4.900	6.835
150	1.512	3.341	4.917	6.842

Table A-3: Adsorbent capacity at different temperatures

Time	q_t (mg/g)		
	293 K	303 K	313 K
0	0	0	0
1	2.157	3.047	2.221
2	2.588	3.095	2.429
3	2.748	3.111	2.525
4	2.780	3.121	2.748
5	2.796	3.133	2.901
6	2.956	3.147	2.940
7	2.988	3.156	3.018
8	3.013	3.165	3.064
9	3.036	3.174	3.105
10	3.068	3.177	3.119
20	3.142	3.202	3.127
30	3.247	3.222	3.138
40	3.314	3.253	3.206
50	3.324	3.286	3.231
60	3.340	3.300	3.236
80	3.361	3.319	3.256
100	3.395	3.324	3.269
120	3.438	3.332	3.276

Table A-4: Adsorbent capacity at different initial solution pH

Time	q_t (mg/g)			
	2 pH	4 pH	6 pH	8 pH
0	0	0	0	0
10	1.997	2.876	1.965	1.390
40	2.374	3.294	2.600	1.849
80	2.500	3.410	2.806	1.930
120	2.5429	3.454	2.885	1.971
150	2.572	3.462	2.903	1.980

Table A-5: Adsorbent capacity by different adsorption kinetic model at 293 K

time	q_t (mg/g)				
	Pseudo-1st order	Pseudo-2nd order	Elovich model	Intra-particle diffusion model	Experimental
0	0	0	0	0	0
1	0.079	1.421	2.462	2.402	2.157
2	0.1570	2.010	2.614	2.457	2.588
3	0.232	2.347	2.703	2.500	2.748
4	0.307	2.555	2.766	2.536	2.780
5	0.37	2.699	2.815	2.568	2.796
6	0.450	2.800	2.850	2.5962	2.956
7	0.510	2.884	2.889	2.620	2.988
8	0.587	2.947	2.919	2.6478	3.013
9	0.653	2.998	2.9451	2.000	3.036
10	0.717	3.041	2.968	2.692	3.068
20	1.289	3.240	3.120	2.868	3.142
30	1.743	3.321	3.209	3.003	3.247
40	2.104	3.360	3.272	3.117	3.314
50	2.391	3.383	3.320	3.217	3.324
60	2.620	3.399	3.360	3.308	3.340
80	2.946	3.420	3.420	3.469	3.361
100	3.152	3.432	3.474	3.611	3.395
120	3.283	3.440	3.514	3.739	3.438
150	3.394	3.448	3.562	3.912	3.508

Table A-6: Adsorbent capacity by different adsorption kinetic model at 303 K

Time	q_t (mg/g)				
	Pseudo-1st order	Pseudo-2nd order	Elovich model	Intra-particle diffusion model	Experimental
0	0	0	0	0	0
1	0.126	1.829	2.495	2.408	2.221
2	0.243	2.352	2.624	2.457	2.429
3	0.365	2.600	2.700	2.495	2.525
4	0.478	2.745	2.753	2.526	2.748
5	0.587	2.840	2.795	2.554	2.901
6	0.691	2.906	2.829	2.579	2.940
7	0.791	2.956	2.856	2.604	3.018
8	0.887	2.990	2.88	2.624	3.064
9	0.981	3.025	2.905	2.644	3.102
10	1.069	3.050	2.924	2.663	3.119
20	1.790	3.167	3.053	2.817	3.127
30	2.276	3.209	3.129	2.936	3.138
40	2.604	3.230	3.182	3.036	3.206
50	2.825	3.240	3.224	3.123	3.231
60	2.974	3.251	3.258	3.203	3.236
80	3.142	3.262	3.312	3.344	3.256
100	3.219	3.268	3.353	3.469	3.269
120	3.253	3.272	3.387	3.581	3.276
150	3.270	3.277	3.429	3.733	3.283

Table A-7: %removal of dye at different initial pH of dye solution

Time (minute)	% Removal of dye			
	2 pH	4 pH	6 pH	8 pH
0	0	0	0	0
10	75.988	82.004	66.666	69.323
40	90.325	93.905	88.201	92.217
80	95.129	97.239	95.181	96.648
120	96.731	98.483	97.878	98.280
150	97.857	98.705	98.460	98.747

Table A-8: Adsorbent capacity by different adsorption kinetic model at 313 K

Time	q_t (mg/g)				
	Pseudo-1st order	Pseudo-2nd order	Elovich model	Intra-particle diffusion model	Experimental
0	0	0	0	0	0
1	0.106	1.801	2.535	2.282	2.221
2	0.208	2.202	2.57	2.313	2.429
3	0.306	2.370	2.601	2.336	2.525
4	0.400	2.478	2.618	2.356	2.748
5	0.491	2.542	2.631	2.374	2.901
6	0.579	2.586	2.64	2.390	2.940
7	0.663	2.619	2.651	2.404	3.018
8	0.744	2.644	2.659	2.418	3.064
9	0.822	2.664	2.666	2.431	3.100
10	0.898	2.680	2.673	2.443	3.119
20	1.511	2.755	2.714	2.540	3.127
30	1.929	2.780	2.739	2.615	3.138
40	2.214	2.793	2.756	2.678	3.206
50	2.409	2.801	2.769	2.734	3.232
60	2.542	2.807	2.782	2.784	3.236
80	2.695	2.813	2.798	2.874	3.256
100	2.766	2.817	2.81	2.952	3.269
120	2.799	2.820	2.822	3.023	3.276
150	2.819	2.823	2.835	3.120	3.283

Table A-9: Freundlich adsorption isotherm values at different temperatures

293 K		303 K		313 K	
ln C_e	ln q_e	ln C_e	ln q_e	ln C_e	ln q_e
0.4028	0.2245	0.3452	0.4252	0.2948	0.4325
1.6852	1.1921	0.7812	1.1721	0.623	1.0712
2.0012	1.4823	1.1501	1.591	0.7512	1.621
2.412	1.4212	1.4021	1.84001	1.1042	1.8192

Table A-10: adsorbent adsorption capacity by different adsorption isotherm at 303 K

Ce (mg/l)	q_e (mg/g)		
	Langmuir isotherm	Freundlich isotherm	Experimental
1.160	1.537	1.875	1.589
1.768	2.066	3.006	2.857
2.107	2.311	3.894	3.159
4.399	3.404	7.486	6.450

Table A-11: % removal of dye for different amount of adsorbent dose

Time (minute)	% Removal of dye			
	0.5 (g)	1.0 (g)	1.5 (g)	2.0 (g)
0	0	0	0	0
10	43.855	84.231	80.964	92.048
40	58.313	87.564	92.753	96.609
80	71.325	88.569	95.856	97.690
120	76.626	90.542	97.079	99.289
150	79.518	75.662	97.831	99.430

Table A-12: % removal of dye for different dye concentration

Time (minute)	% Removal of dye			
	25 (mg/l)	50 (mg/l)	75 (mg/l)	100 (mg/l)
0	0	0	0	0
10	68.342	73.903	76.461	75.252
40	82.143	89.608	85.363	84.778
80	89.742	94.807	88.619	87.049
120	92.683	97.406	90.883	89.802
150	95.134	98.592	91.222	89.889

Table 13: % removal of dye at different temperatures

Time (minute)	% Removal of dye		
	293 K	303 K	313 K
0	0	0	0
1	59.081	91.156	66.988
2	70.897	92.590	73.253
3	75.273	93.068	76.144
4	76.149	93.371	82.891
5	76.586	93.721	87.499
6	80.963	94.150	88.675
7	81.838	94.421	91.036
8	82.533	94.701	92.426
9	83.151	94.957	93.647
10	84.026	95.050	94.070
20	86.054	95.797	94.317
30	88.933	96.403	94.634
40	90.772	97.336	96.703
50	91.028	98.315	97.454
60	91.466	98.735	97.590
80	92.050	99.294	98.207
100	92.900	99.458	98.583
120	94.166	99.691	98.811
150	96.066	99.7613	99.007