REMOVAL OF METHYLENE BLUE DYE USING OIL CAKE (KARANJA)

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In partial fulfilment of the requirements of

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By

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CERTIFICATE:

This is to certify that the thesis entitled, "REMOVAL OF METHYLENE BLUE DYE USING OIL CAKE (KARANJA)", submitted by Ritam Biswas, Roll No.-109CH0468, in partial fulfilments for his requirements for the award of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela is prepared by him under my supervision and guidance.

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NOMENCLATURE

°C : Degree Celsius

BET : Brunnauer Emett Teller

nm : Nanometer

HCl : Hydrochloric acid

NaOH : Sodium hydroxide

UV : Ultra-violet

ASTM : American Society for Testing and Materials

M : Moisture content

A : Ash content

VM : Volatile matter content

q_e : amount of substance adsorbed per unit mass of adsorbent

C_o : initial concentration of methylene blue

C_e : equilibrium concentration at time 't'

ABSTRACT

The feasibility of karanjia oil cake as a precursor for the preparation of activated carbon for the removal of methylene blue was investigated. The effect of various factors such as contact time, temperature, solution pH, amount of adsorbent and the initial dye concentration, was studied. The experimental data were analysed by the Freundlich and Langmuir isotherm models. The adsorption isotherm obtained was described accurately by both the isotherms. The maximum removal of methylene blue was found to be 91.62 %.Two simplified kinetic models, pseudo-first-order and pseudo-second-order equation were selected to follow the adsorption processes. Kinetic studies showed that the adsorption followed pseudo-second order kinetic model. The results in the study indicate that the activated carbon prepared from karanjia oil cake could be used for the removal of methylene blue from aqueous solution.

CHAPTER 1

INTRODUCTION

1. INTRODUCTION

A dye is generally a substance that has an affinity towards the substrate on which it is being applied. It is often applied in an aqueous solution [3]. It appears to be coloured because they absorb some wavelengths of light in particular than other, hence they appear whatever colour they reflect back. The industrialdischarges from textile industries are rich in residual dye content[3, 2]. Some of the residual dyes are non-biodegradable owing to their complex molecular structures which make them more stable and hard to degrade biologically by the action of bacteria, etc.[1, 2]. They cause water pollution and also pose a serious threat to the environment. These coloured compounds along with being aesthetically displeasing also inhibit sunlight penetration into the water bodies and thus affect aquatic ecosystems[3, 2]. Many of these complex compounds are also toxic in nature and can cause direct destruction or affect catalytic capabilities of various microorganisms[1, 2].

The main sources of discharge of dyes are textile industries where they are used to colour products. There are over 1,00,000 dyes which can be commercially used and around 700 tons of dyestuffs are produced annually [1]. The major categories of dyes can be broadly classified as basic dyes, acid dyes, direct dyes, reactive dyes, mordant dyes, azo dyes, disperse dyes and sulphur dyes [1, 2].Most of the dyes are toxic and are carcinogenic in nature. The also inhibit the basic cycles of the aquatic eco-systems, by reducing the biological oxygen demand (BOD). They do not fade in water or by sunlight and owing to their complexity in structures, they cannot be suitably treated in conventional treatment plants for waste waters [2].

There are various harmful effects of dyes on ecosystem such as:

(1) They pose acute as well as chronic effects on most of the exposed organisms. These effects vary depending on the time of exposure and the concentration of dyes [1, 2].

(2) They can absorb or reflect sunlight which enters the water bodies and thus affect the growth of bacteria and cause an imbalance in their biological activities [1, 2].

(3) They are highly visible and even a minor amount may cause abnormal colouration of water bodies which appears displeasing to eyes [1, 2].

(4) They have complex molecular structures which makes them difficult to treat with common municipal treatment operations.

(5) They consume dissolved oxygen and affect the aquatic ecosystem [2].

Methylene blue is a widely used dye in the textile industry and also it has some medical uses as well. However, it has adverse effects on aquatic life and the eco-system. In humans,

excessive amount of methylene blue causes cardiovascular disorders like hypertension, malfunctioning of the central nervous system such as dizziness, fever, headache and mental confusion, skin irritations, nausea, abdominal pain and anaemia. Thus, removal of this dye is of necessary.

There are various methods to remove dyes from wastewater discharges like coagulation, electrochemical process, membrane separation process, chemical oxidation, reverse osmosis and aerobic and anaerobic microbial degradation. Many of these processes have their limitations such as economic disadvantages and inefficiency. Coagulations and chemical and electrochemical oxidations have low feasibility on large scale plants. Adsorption is preferred over these processes and is widely used due to low cost and high performance.

Adsorption is a process by which molecules are attached upon a surface preferentially. The substance being adsorbed is called adsorbate and the substance on whose surface the adsorbate attaches itself are called adsorbent. The process of adsorption is a surface phenomenon. Adsorption phenomena can be classified broadly into two categories – physic-sorption and chemisorption. Physic-sorption depends on intermolecular forces of attraction between adsorbent and adsorbate molecules.

Some of the common adsorbents used are activated carbon, zeolites, silica gel and certain metal hydroxides. Economic advantages,performance efficiencies and environment are the main concerns when selecting an adsorbent. Thus, activated carbon being chief and efficient is most widely used for treatment of wastewater and effluents in industries.

1.1 OBJECTIVE

The purpose of this project work is:

- To study the effectiveness of removal of methylene blue using oil cake (karanjia) and determine its potential for the use of the oilcake as a precursor for an adsorbent.
- To study effect of various experimental process on the adsorption process and study various models of adsorption isotherms and kinetics study of the process.

1.2 SCOPE

Study of effects of various experimental parameters on adsorption like

- Effect of contact time
- Effect of temperature
- Effect of pH
- Effect of adsorbent dose
- Effect of initial concentration of methylene blue

Study of the adsorption kinetics and adsorption isotherms.

1.3 PROBLEM STATEMENT

In recent times, there has been an ever increasing demand for activated carbon; hence it is a matter of interest among the researchers to find a better substitute or a better source for the production of cheap and efficient activated carbon. Karajia oil cake are an agricultural waste which has no further use and it is available in abundance in India. Thus it can be a potential precursor for preparation of an effective adsorbent.

CHAPTER 2

LITERATURE REVIEW

2. LITERATURE REVIEW

For the production of activated carbon, a wide variety of raw materials have been used over the years. Extensive studies have been undertaken by various scholars and researchers for the synthesis and characterization of adsorbents from different agricultural based precursors.

The following table gives a brief review of the various raw materials that have so far been used for the production of activated carbons.

Table 1: List of raw materials which have been used for the production of activated carbon

Raw materials	**Authors**
Walnut shells	Aygün A. ,Yenisoy-Karakaş S. [9]
Coir pith	Kavitha D. , Namasivayam C. [10]
Apricot stones	Aygün A. , Yenisoy-Karakaş S. [9]
Almond shell	Aygün A. ,Yenisoy-Karakaş S. [9]
Hazelnut shell	Aygün A. ,Yenisoy-Karakaş S. [9]
Silk cotton hull	Kadirvelu K., Kavipriya M. [11]
Maize cob	Kadirvelu K., Kavipriya M. [11]
Coconut coir dust	Macedo J. S., Júnior N. B., Almeida L. E. [12]
Peach stones	Caturla F., Molina-Sabio M., Rodríguez-Reinoso F. [13]
Sugarcane bagasse	Girgis B.S., Khalil L.B., Tawfik T.A.M. [14]

In the production of activated carbons from walnut shells, the walnut shells were first carbonized then mixed with KOH solution and the mixture was activated thermally in absence of air. The products were washed with distilled water and dried to get the final activated carbon. The effect of activation temperature, activation time and KOH/char ratio on the development of micro porosity were studied [15].

In the production of activated carbon from palm cob, the cobs were first pre-treated with 60% (w/W) ZnCl solution and then carbonized at 600-700 °C. The adsorbate concentration at625nm was determined using a spectrophotometer. The investigation revealed that adsorption capacity of the carbon adsorbents produced on thermal temperature treatment and duration, high temperature and low residence time enhance micro porosity.[16]

In 2005 B.H.Hameed, A.T.M.Din, A.L.Ahmad carried out adsorption of methylene blue by bamboo-based activated carbon. Bamboo was used to make activated carbon by physiochemical activation with potassium hydroxide and carbon dioxide. Adsorptiobn models and kinetic studies were also conducted and it was found that pseudo-second-order model best described the process [7].

In 2007, R.A.Shawabkeh and E.S.M. Abu-Nameh performed study of adsorption of phenol and Methylene Blue by activated carbon from pecan shells. Activated carbon was prepared from pecan shells by chemical activation with phosphoric acid. Then it was treated with sodium dodecyl sulfate to prepare the surface for adsorption. The results indicated good removal of phenol and Methylene Blue dye by pecan shells.[17]

The removal of methylene blue using treated and untreated activated carbon was investigated by Yasin, Hussein and Ahmad{yaminuitm}. The effects of various experimental parameters like contact time, pH of the solution and adsorbent dosage were studied. It was found that the amount of methylene blue removal increased with the increase in contact time, solution pH and amount of adsorbent used. The data obtained best fitted the Langmuir isotherm plot. [18]

The adsorption of methylene blue onto dehydrated wheat bran (DWB) was investigated by Ozer A, Dursun G., at temperatures (25-45 °C), initial methylene blue (MB) concentrations (100-500 mg/L) and adsorbent dosage at the given contact time for the removal of dye. The pseudo first order and pseudo second order kinetic model were applied to the data and it was found that pseudo second order best described the data obtained.[19]

In another instance, jute fibre was used to prepare activated carbon using phosphoric acid. It was found that at a fixed carbon concentration, the decrease in particle size increased the dye uptake and decreased the equilibrium time. The per cent adsorption decreased with increase in the initial methylene blue concentration, but the actual amount of methylene blue adsorbed per unit mass of carbon increased with increase in methylene blue concentration. The Langmuir equation gives an accurate description of the experimental data.[6]

The adsorption of methylene blue (MB) from aqueous solution using a low-cost adsorbent, rejected tea (RT), was studied by batch adsorption technique. The adsorption experiments were carried out under different conditions of initial concentration (50-500 mg/L), solution pH 3-12, RT dose (0.05-1g) and temperature (30-50 °C). The equilibrium data were fitted to Langmuir and Freundlich isotherms and the equilibrium adsorption was best described by the Langmuir isotherm model with maximum monolayer adsorption capacities found to be 147, 154 and 156 mg/g at 30, 40 and 50 °C, respectively. Three kinetic models, pseudo-first-order, pseudo-second-order and intra-particle diffusion were employed to describe the adsorption mechanism. The experimental results showed that the pseudo-second-order equation is the best model that describes the adsorption behaviour with the coefficient of correlation $R^2 \geq 0.99$. The results suggested that RT has high potential to be used as effective adsorbent for MB removal.[7]

Activated carbon prepared from non-wood forest product waste (rattan sawdust) has been utilized as the adsorbent for the removal of methylene blue dye from an aqueous solution. The rattan sawdust was collected from a local furniture factory. It was washed with hot distilled water to remove dust like impurities, dried and the material was finally sieved to discrete sizes. The raw material was then carbonized at 700 °C under nitrogen atmosphere for 1 h. A certain amount of produced char then was soaked with potassium hydroxide (KOH) at impregnation ratio of 1:1. The mixture was dehydrated in an oven overnight at 105 + 1 °C, then pyrolysed in a stainless steel vertical tubular reactor placed in a tube furnace under high-purity nitrogen (99.995%) flow of 150 cm^3/min to a final temperature of 850 °C and 2 h soaking. Once the final temperature was reached, the nitrogen gas flow was switched to carbon dioxide and activation was continued for 2 h. The activated product (RSD-AC) was then cooled to room temperature and washed with deionized water to remove remaining chemical.[8]

Adsorption isotherms

Adsorption is generally described through isotherms, that are amount of adsorbate on the adsorbent as a function of pressure (for gases) or concentration (for liquids) at a constant temperature.

Freundlich isotherm:

It is an adsorption isotherm which relates concentration of solute on the surface of the adsorbent to the concentration of the solute in the liquid with which it is in contact. This model assumes that adsorption takes place on heterogeneous surface.

The linear form can be written as:

$\log q_e = \log k_f + (1/n) * \log C_e$

Where, k_f and n (dimensionless constants) are the Freundlich adsorption isotherm constants, which indicate the capacity and intensity of the adsorption, respectively.

Langmuir isotherm:

It relates the adsorption of molecules on a solid surface to gas pressure or concentration of a medium above the solid surface at a fixed temperature. It is based upon the fact that adsorption process occurs in monolayers.

The linear form of Langmuir expression:

$1/q_e = 1/Q_o + 1/(bQ_oC_e)$

Where Ce is the equilibrium concentration of dye solution (mg/L), qe is the equilibrium capacity of dye on the adsorbent (mg/g), qo is the monolayer adsorption capacity of the adsorbent (mg /g), and b is the Langmuir adsorption constant (L/mg) and is related to the free energy of adsorption.

CHAPTER 3

MATERIALS AND METHODS

3. MATERIALS AND METHODS

3.1 Chemicals

Methylene blue dye, chemical formula, $C_{16}H_{18}N_3ClS$ and molecular weight of 319.5 was used for the initial adsorption experiments. Other chemicals such as NaOh and HCl were used for preparing solutions of varying pH. The chemicals were provided by the department laboratory.

3.2 Instrumentation

An orbital shaker was used for all the adsorption experiments. A UV-ray spectrophotometer was used to determine the absorbance. Afurnace was used to dry the sample. The pH meter was used to measure the pH of solution. Glass wares were used to handle the solutions. A meter balance was used to weigh the samples.

Figure 1 The orbital shaker used for the experiments.

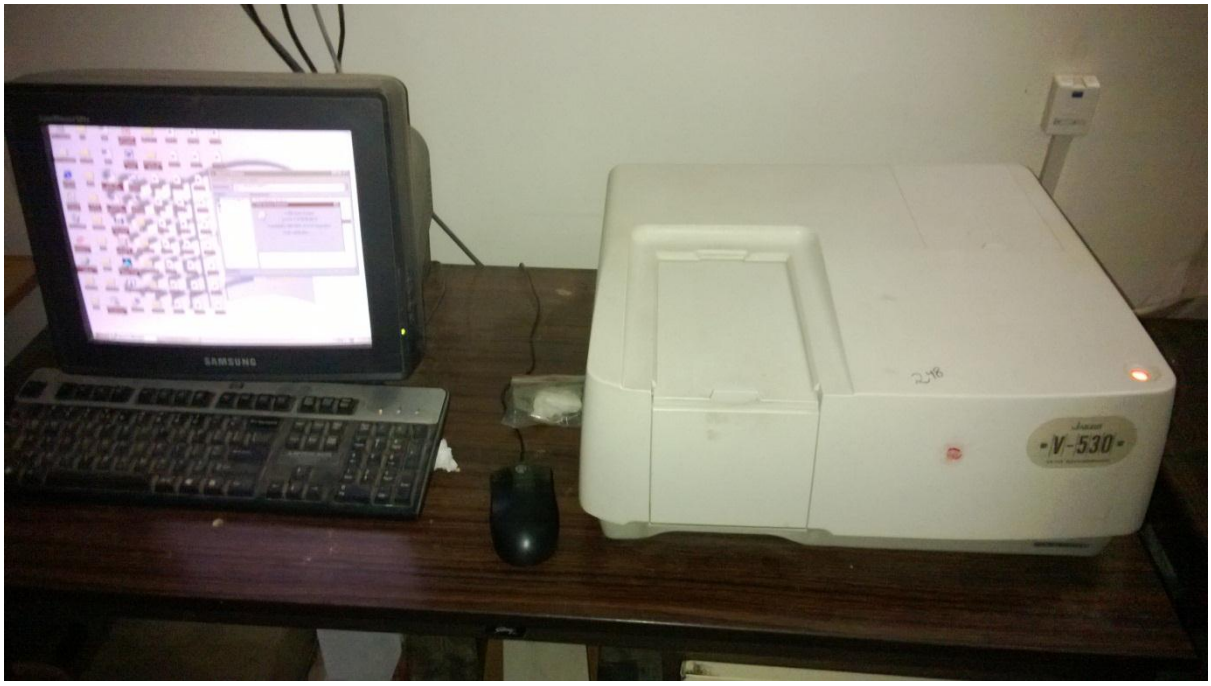

Figure 2 the UV-spectrophotometer used for determining the % absorbance.

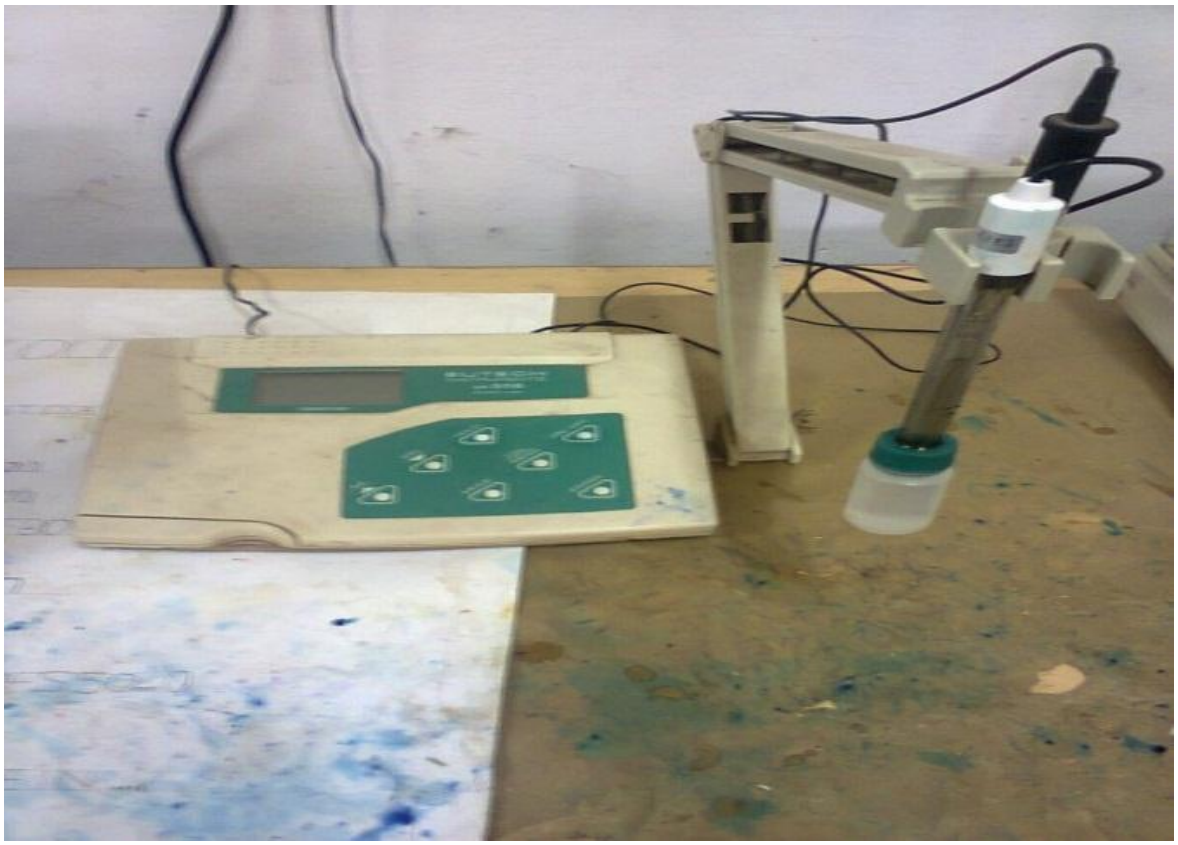

Figure 3 the pH meter used to determine the solution pH

Figure 4 the glasswares used to handle the chemicals and carryout the experiment

3.3 Biomass Raw Material

The karanja oil cake was obtained from Krishi Kendra, Aambagan, Rourkela.

3.4 Pre-treatment of Raw Material

The oil cake was crushed using a grinder and the powder form was left to dry in an oven at 60°C for 24- 36 hours. Then a quantity of the powdered raw material was kept in a beaker which was filled with water in order to submerge it completely for 3-4 hours. This was done to wash the raw material and remove any impurities which might affect the adsorption process like cellulose and other plant wastes. The raw material was filtered out using a clean cotton cloth and kept in an oven at 60°C to remove all the residual moisture. The raw material was left in the oven overnight to dry.

3.5 Proximate Analysis

The proximate analysis of coal is used to determine the distribution of products obtained when the coal sample is heated under specific conditions. It is defined by ASTM D 121; and separates the products into four groups:

(1) Moisture: water content present in the sample

(2) Volatile matter: gases and vapours driven off from the sample during the heating process

(3) Fixed carbon: non-volatile fraction of sample (basically the carbon content of the sample)

(4) Ash: inorganic residue remaining after combustion (inert matter present in the sample)

To determine the four products on heating, the sample is subjected to specific conditions for each test.

3.5.1 Moisture Content

According to this test the sample was heated in a petri dish at 105°C for 1hour 30 minutes in an oven. The weight of the sample before heating and after heating was determined. This specifies the amount of moisture content present in the sample.

The moisture content $M = 100(B-F)/ (B-G)$

B= Mass of crucible with lid + original sample

F= Mass of crucible with lid + dried sample

G= Mass of crucible with lid

3.5.2 Volatile Matter Content

The procedure implies that the sample was heated at 925 °C ± 25°C in a closed crucible for 7 minutes 30 seconds. The heating was done in a muffle furnace. The weight of the sample before heating and after heating was used to determine the amount of volatile matter present in the sample. Larger weight loss of the substance implies greater volatile matter content.

Volatile matter on dry basis $VM=100[100(B-F)-M (B-G)]/ [(B-G) (100-M)]$

B= Mass of crucible, lid and sample before heating

F= Mass of crucible, lid and contents after heating

G= Mass of empty crucible and lid

M= % of moisture as determined above

3.5.3 Ash Content

To determine the ash content, the sample was heated at 725 °C ± 25°C in an open crucible for 1 hour 30 minutes in a furnace. The weight of the sample before heating and after heating was used to determine the amount of ash content present in the sample. In this test, the amount of residual substance is equal to the ash present in the sample.

The ash content A= 100(F-G)/ (B-G)

G= Mass of empty crucible

B=Mass of crucible + dried sample

F=Mass of crucible + ash sample

3.5.4 Fixed Carbon Content

The fixed carbon content is determined by subtracting the sum of percentage compositions of moisture content, volatile matter content, and ash content form 100. The value obtained is the amount of fixed carbon present in the sample expressed in percentage.

Fixed carbon, FC=100-(volatile matter + ash content)

3.6 BET

BET stands for Brunauer, Emmett and Teller-the men who proposed a theory to measure the surface area of solid particles like porous powders. The basic principle involved is the adsorption of gas molecules to the surface of the solid whose surface area is required. From the area of each molecule, the whole area of the solid can be calculated.

BET theory is based on multilayer adsorption with the following assumptions [23]:

· Gas molecules can be physically adsorbed on the solid surface and form infinite layers

· There is no interaction between the layers

· Langmuir theory is applied to each layer

The BET equation is given by:

$1/v\ [(P^0/P)-1] = (c-1)\ (P/P^0)/\ (v_m c) + 1/\ (v_m c)$

P^0= Saturation pressure of the adsorbate

P= Equilibrium pressure of the adsorbate

v= Volume of gas adsorbed

v_m= Volume of gas adsorbed in the monolayer

c= BET constant given by exp (E1-EL)/RT

E1= Heat of adsorption for the first layer

EL= Heat of adsorption for higher layers

A plot of $1/v\ [(P^0/P)-1]$ v/s (P/P^0) is obtained from the BET analysis. From the slope and intercept of the line, v_m and c are obtained. Surface area S of the solid sample is given by

$S= (v_m Ns)/ (VX)$

N= Avogadro's number

s= adsorption cross-section of the gas being adsorbed

V= molar volume of the gas being adsorbed

X= mass of the adsorbent

A small amount of the sample was taken in the tube and the tube was placed in a dewar containing liquid nitrogen. Initially the sample was degasified to remove the impurities and gases. Then gaseous nitrogen was passed through the sample and based on adsorption of the gas, the surface area of the sample was calculated.

3.7 BULK DENSITY

In a cylindrical vessel of known volume sample up to a specific height was taken and then its masswas measured.

Thus, bulk density =mass/volume

3.8 EXPERIMENTAL WORK

3.8.1 CONTACT TIME STUDY

A solution of methylene blue having concentration of 10mg/l was prepared. 1 gm. of the pre-treated sample was taken in a 100ml conical flask along 100ml of the prepared methylene blue solution. This was then kept in a shaker at a temperature of 35°C and vibrating at 115 rpm. Same experiment was repeated for the prepared sample.

Samples were collected at 5 minutes intervals for the first 30 minutes and then at 25 minutes interval for a total of 130 minutes, for the raw sample.

For the prepared sample, samples of the solution were collected at every 5 minute interval for 60 minutes and then at 30 minute intervals for a total of 120 minutes.

The % absorbance of UV at 670nm was determined for the samples.

3.8.2 EFFECT OF TEMPERATURE

A 100ml solution of methylene blue of 10ppm concentration was taken in a conical flask to which 1 gm of the prepared sample was added. The conical flask was kept in a shaker at 115rpm and at a temperature of 35 °C. The same experiment was repeated at 25 °C and 45 °C.

Samples were collected at 10 minute intervals for 60 minutes. The %absorbance of UV at 670nm was found out using a spectrophotometer.

3.8.3 EFFECT OF pH OF THE SOLUTION

Methylene blue solution of concentration of 10 ppm but of pH varying as 5, 5.5, 6.6.5, 7, 7.5 and 8 were prepared. 1 gm of the prepared sample was taken as adsorbent dose for the 100ml solutions prepared.

Samples were collected at 10 minute intervals for first 40 minutes and then at 60 minutes. The % absorbance at 670nm was found out using a UV-spectrophotometer.

3.8.4 EFFECT OF ADSORBENT DOSAGE

2 gm and 3 gmof raw samples and prepared samples were taken in conical flasks containing 100ml of 10ppm methylene blue solution. The flask was put in a shaker at 115rpm and 35°C.

Samples were collected at 10 minute intervals for 60 minutes. The % absorbance at 670nm was found out using a UV-spectrophotometer.

3.8.5 EFFECT OFCONCENTRATION OF METHYLENE BLUE

100ml of Methylene blue solution of concentrations 25ppm, 50ppm and 100 ppm were taken in conical flasks, to which 1 gm of raw sample was added and shaken in a shaker at 115rpm and 35 °C. The experiment was repeated for 1 gm of prepared sample.

Samples were collected at regular intervals for 120 minutes. The % absorbance at 670nm was found out using a UV-spectrophotometer.

3.8.6 ADSORPTION ISOTHERM STUDIES

100ml of methylene blue solution of concentrations 20ppm, 40 ppm, 60ppm, 80ppm and 100pm were prepared. 1 gm of the prepared sample was taken in conical flasks containing the solutions. The flasks were shaken at 115rpm and 35°C for 120 minutes.

At the end of 120 minutes, samples were collected from each flasks and %absorbance of UV at 670nm was determined using a spectrophotometer.

CHAPTER 4

RESULTS AND DISCUSSIONS

4. RESULTS AND DISCUSSIONS

4.1 PROXIMATE ANALYSIS

The proximate analysis of the samples yielded the following results

Table-2 proximate analysis of the samples.

Content	Raw sample	Prepared sample
Moisture content %	2.25	1.36
Ash content %	3.73	3.84
Volatile matter content %	79.32	18.78
Fixed carbon %	14.7	76.02

4.2 BULK DENSITY

The bulk density of the sample was found to be =0.4512 g/ml=451.2 kg/m^3.

4.3 BET SURFACE AREA

The BET surface area of the samples were found to be as follows

Table 3 BET surface area data

samples	BET surface area (m^2/gm)
Raw sample	49
Prepared sample	179

4.4 CALIBRATION PLOT

The calibration plot for methylene blue at 670nm was obtained as follows

Table 4 calibration data

concentration(mg/l)	% absorbance
2.5	0.3466
5	0.662
10	1.324
15	1.9908

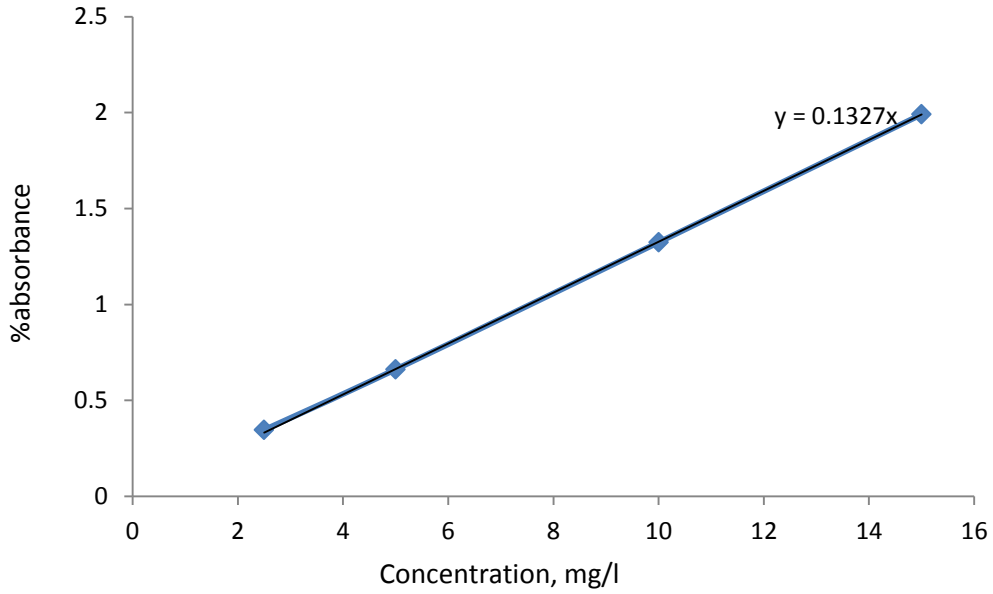

Figure 5 calibration plot

From the graph the slope is found to be 0.1327

Thus, equilibrium concentration at time 't', C_e= (absorbance)/(0.1327)

4.5 CONTACT TIME STUDY

The dependence of adsorption on time was studied from the data.

The amount of substance adsorbed per unit weight of adsorbent, q_e, was calculated.

$q_e = \{(C_o - C_e)/ w\}*V$

Where, C_o is the initial concentration of the solution

C_e is the equilibrium concentration at time 't'

W is the weight of adsorbent taken

V is the volume of the solution taken

w/V = X , amount of adsorbent per unit volume of solution

Table 5 contact time study data for raw sample

time	absorbance at 670nm	concentration(mg/l), Ce	q=(Co-Ce)/X
0	-	10	0
5	1.0019	7.5501	0.2449
10	0.8826	6.651	0.3349
15	0.7734	5.8281	0.4171
20	0.5646	4.2547	0.5745
25	0.4567	3.4415	0.6558
30	0.3835	2.8899	0.711
55	0.3469	2.6141	0.7385
80	0.3122	2.3526	0.7647
105	0.2994	2.2562	0.7743
130	0.2867	2.1605	0.7839

The graph between $q_e$and time was plotted from the data obtained for the raw sample.

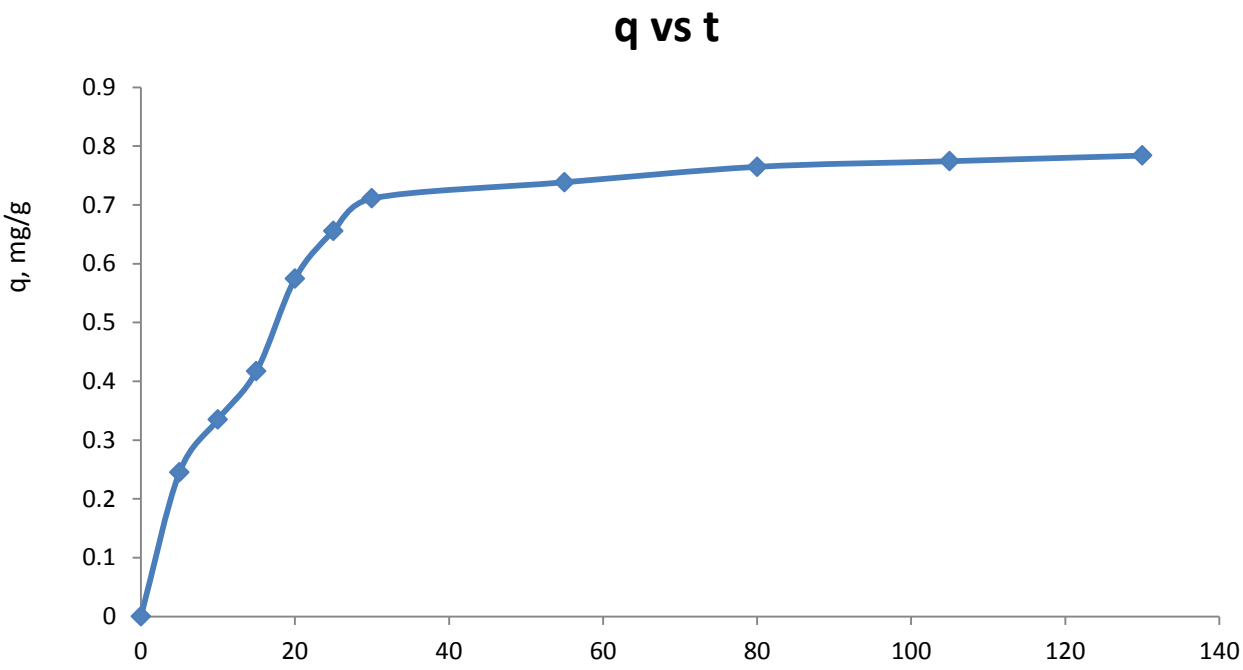

Figure6 plot of q vs t for the raw sample

Table 6 contact time study data for prepared sample

time	%absorption at 670nm	Ce, mg/l	q=(Co-Ce)/X
0			0
5	0.4318	3.2539	0.6746
10	0.3662	2.7596	0.724
15	0.3223	2.4287	0.7571
20	0.269	2.027	0.7973
25	0.2495	1.8801	0.8119
30	0.2399	1.8078	0.8192
35	0.2157	1.6254	0.8374
40	0.1997	1.5048	0.8495
45	0.1852	1.3956	0.8604
50	0.1689	1.2727	0.8727
55	0.1558	1.174	0.8826
60	0.1458	1.0987	0.8901
90	0.1198	0.9027	0.9097
120	0.1112	0.8379	0.9162

The graph between qe and time was plotted from the data obtained for the prepared sample.

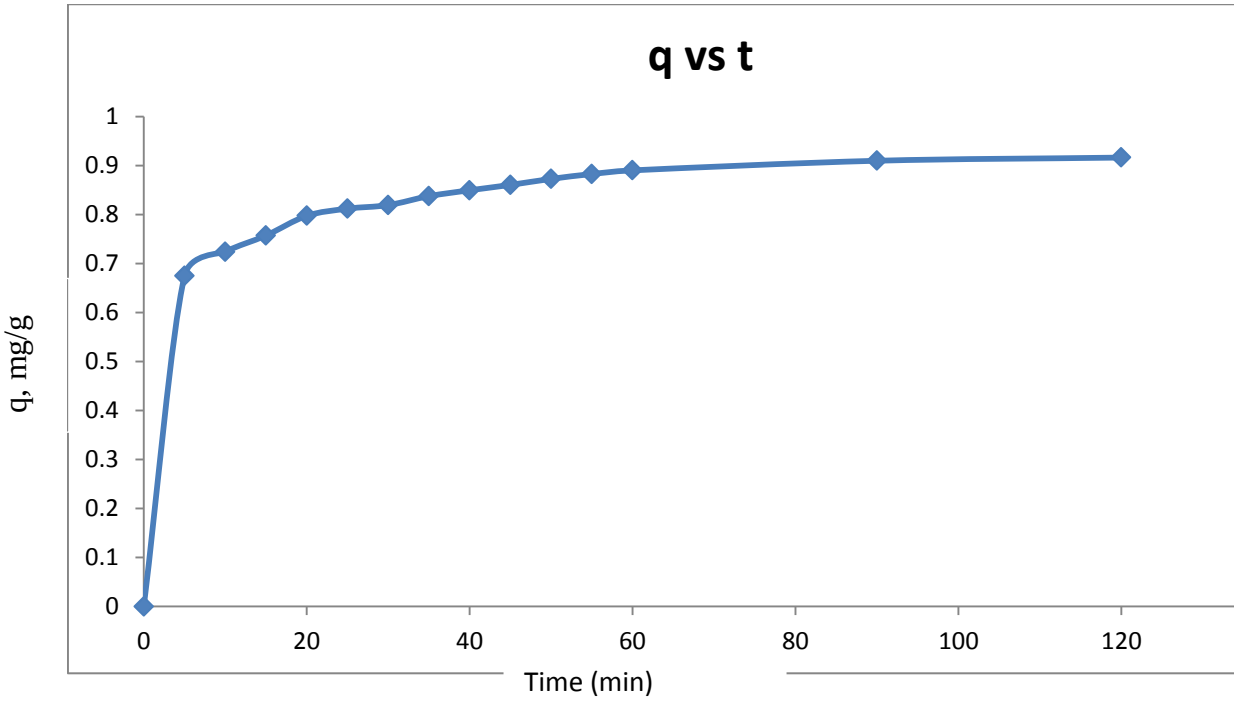

Figure7 plot of q vs t for prepared sample

The comparison between the contact times for the raw sample and prepared sample is given.

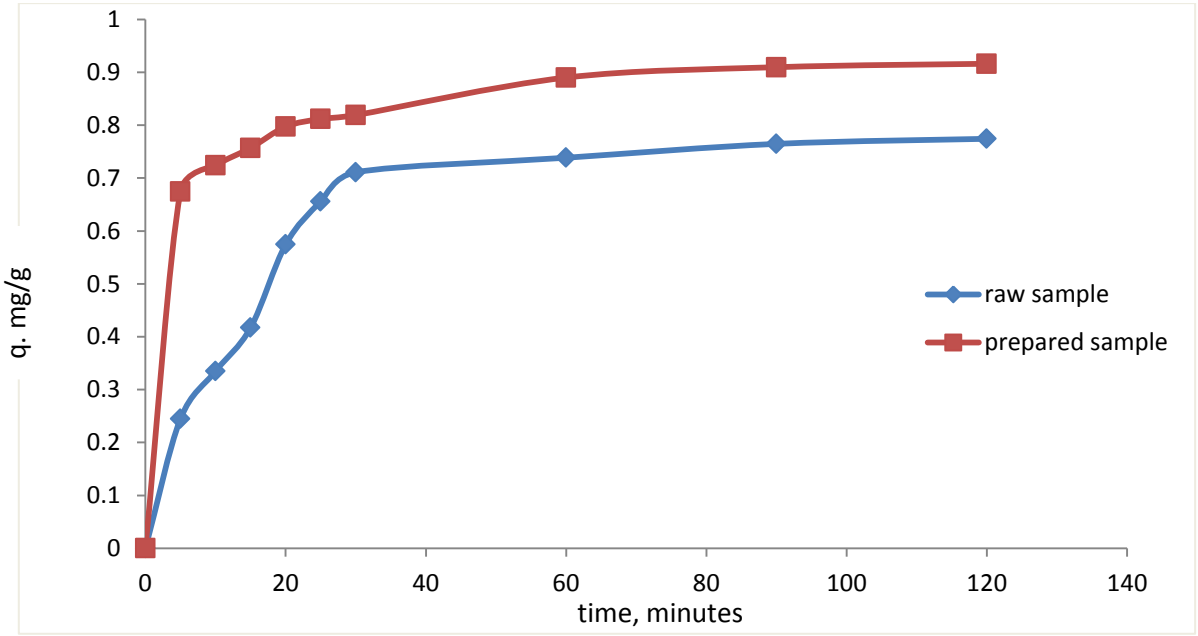

Figure8comparison of the two contact time studies

It was found that the value of q_e rapidly initially, but reached a saturation as time progressed. The major part of adsorption occurred within the first 10 minutes, where the concentration was almost halved. This may be explained by the fact that initially, the adsorbent surface was

available for adsorption. As time passed, the adsorption rate slowed down until a saturation point was reached, where rate of adsorption was very slow. At this point, there was no surface available for adsorption. Thus adsorption equilibrium was reached.

It was observed that equilibrium was reached within the first 60 minutes of the experiment. Thus 60 minutes would be taken as optimum time for further adsorption studies.

The adsorption rate of the prepared sample was found to be higher.

4.6 STUDY OF EFFECT OF TEMPERATURE

The %absorbance data for the samples collected at different intervals of time was used to calculate the equilibrium concentration C_e and the amount of substance adsorbed per gm of adsorbent, q_e.

The following datawere obtained for temperatures 25°C, 35 °C and 45 °C temperatures.

Table 7 q_e for different temperatures

Temperature , °C	C_e, mg/L	q_e, mg/g	% removal of methylene blue, {{Co-Ce}/Co)*100
25	1.1175	0.8882	88.82
35	1.0987	0.8901	89.01
45	1.0192	0.8890	88.90

The relation between the amounts of substance adsorbed per gm of adsorbent, q_e and temperature is shown below.

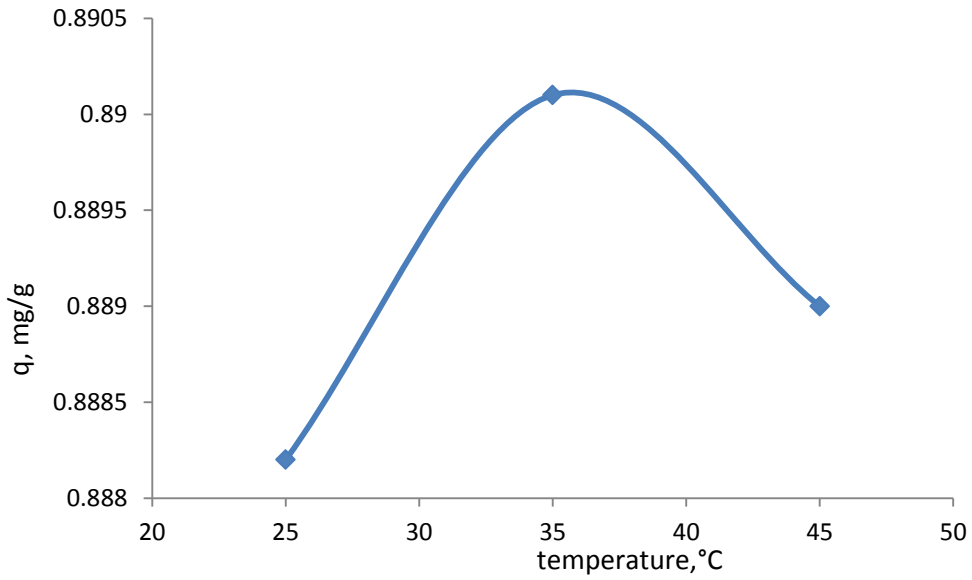

Figure 9 plot of q vs. temperature

It was observed that the amount of substance adsorbed per unit mass of adsorbent is highest at a temperature of 35 °C.

.The relation between %removal of methylene blue and temperature is shown below.

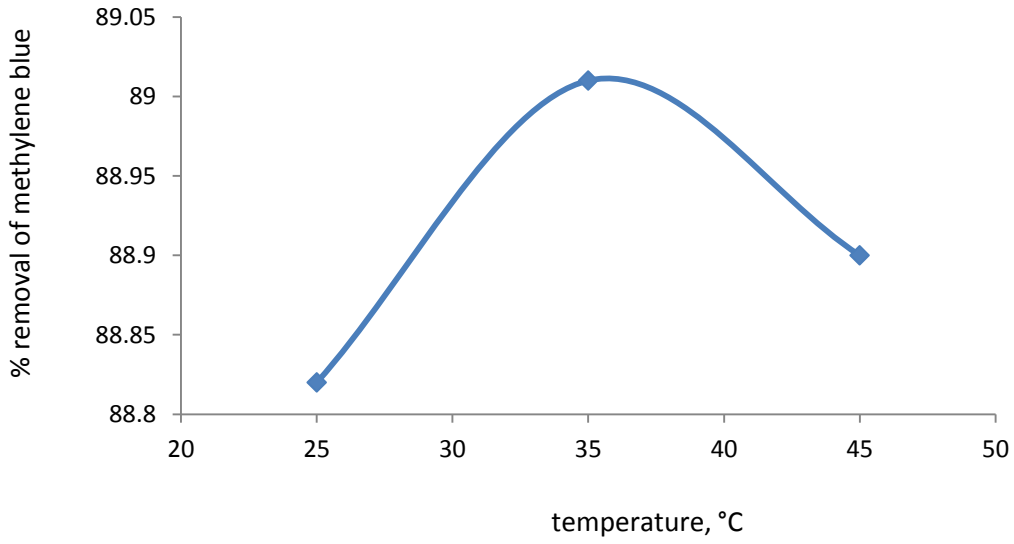

Figure 10 plot of % removal of methylene blue vs temperature

The percentage of removal of methylene blue is highest at 35°C, although the variation was not quite great. Hence, 35°C was taken as optimum temperature for further adsorption processes.

4.7 STUDY OF EFFECT OF pH ON ADSORPTION

The effect of variation of pH on adsorption rates were studied from the data and the graph obtained between q_e vs. pH.

Table 8 effect of pH on q_e and % removal of methylene blue

pH	qe, mg/g	%removal of methylene blue
5	0.823	82.4%
5.5	0.829	82.9%
6	0.8261	82.61%
6.5	0.8543	85.43%
7	0.8838	88.38%
7.5	0.8901	89.01%
8	0.8750	87.50 %

The reason for choosing these pH values were that from the literature it was evident that the adsorption of methylene blue was highest in the neutral range.

The plot of variation of q_e with pH is shown below.

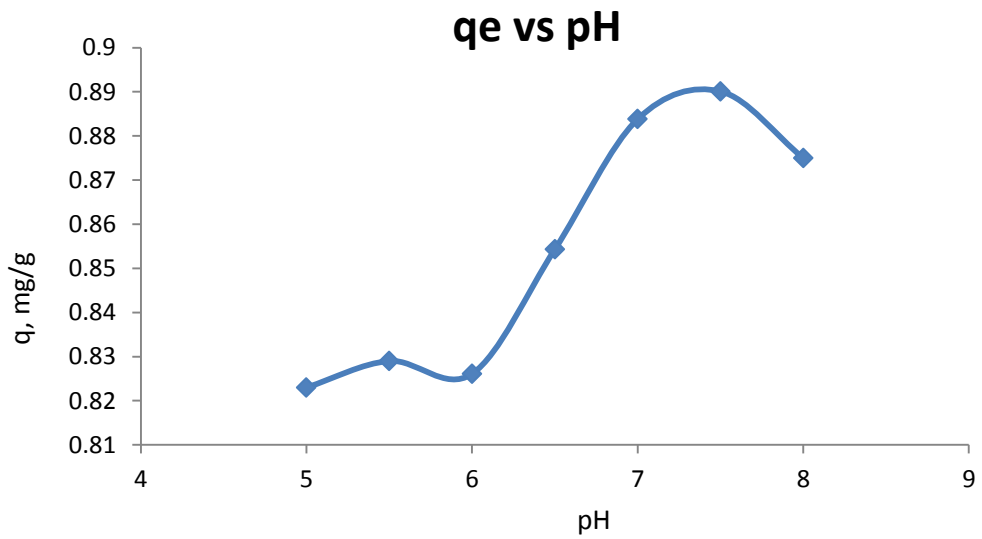

Figure 11 plot of q_e vs pH

The plot of % removal of methylene blue and pH is given below.

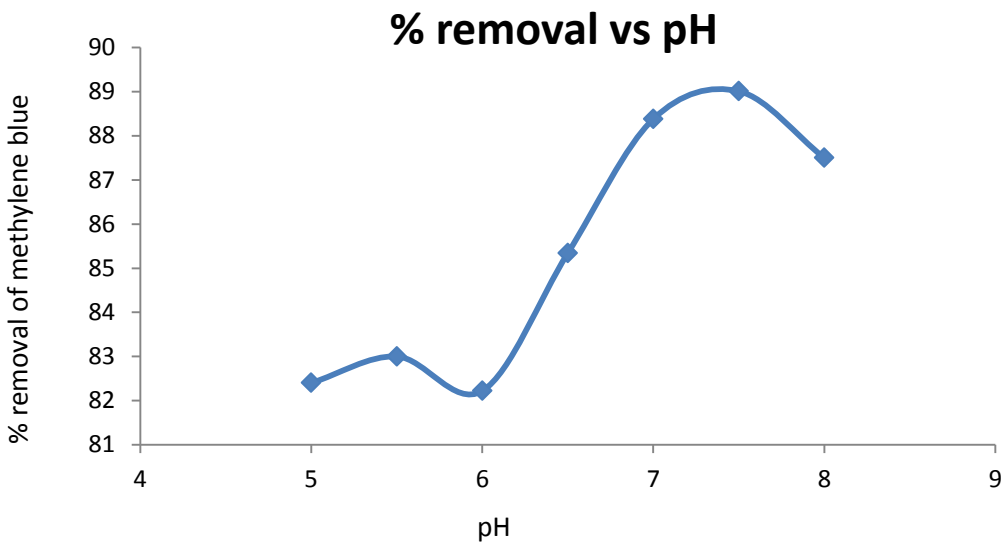

Figure 12 plot of %removal vs pH

The optimum pH was found to be at 7.5. The amount of substance adsorbed onto the surface of the adsorbent was more in case of neutral and slightly basic pH.

4.8 STUDY OF EFFECT OF ADSORBENT DOSAGE

The amount of dosage was varied between 0.5 gm, 1gm, 2gm and 3gm of the prepared sample.

The amount of substance removed per unit mass of adsorbent and the % removal of methylene blue for different dosage are given below.

Table 9 variation of equilibrium concentration, q_e and % removal of methylene blue with dosage of adsorbent

Dosage of the sample, gm	Equilibrium concentration after 1 hour, mg/L	q_e , mg/g	% removal of methylene blue
0.5	2.304	0.2304	76.96
1	1.0987	0.8901	89.01
2	1.0489	0.4475	89.50
3	0.9780	0.3007	90.22

The graph of q_e vs dosage was obtained as follows.

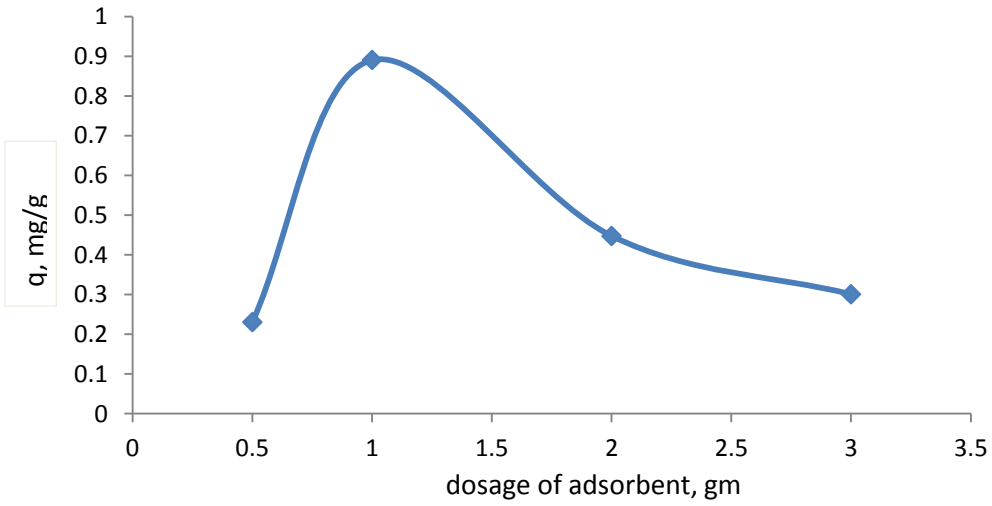

Figure 13 the plot of q vs dosage of sample.

The graph of % removal vs. dosage was obtained as shown below.

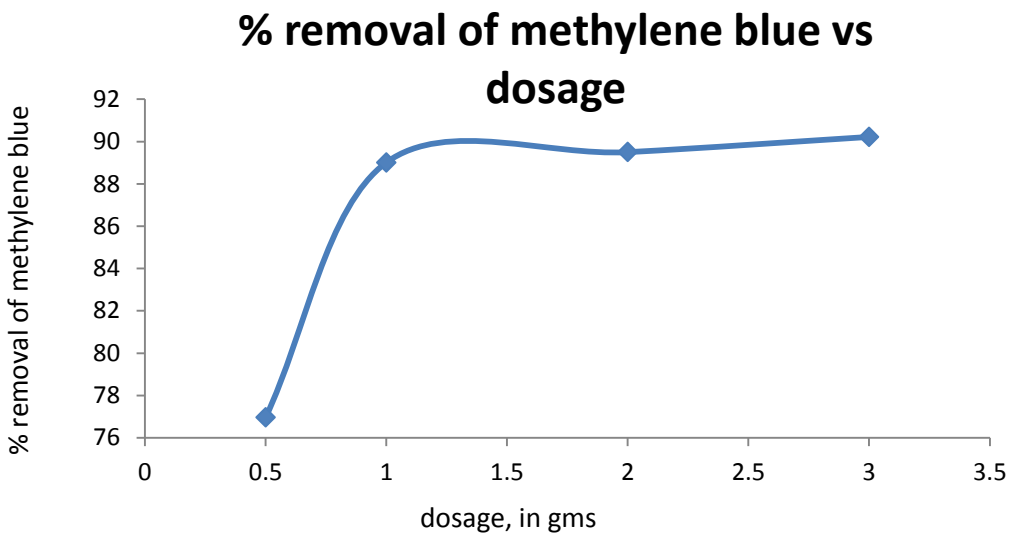

Figure 14 the plot of % removal of methylene blue vs. dosage of the adsorbent

It was observed from the graphs that increasing the dosage decreases the value of q_e but the % of removal of methylene blue increases. As there was no drastic increase in the adsorption rate on increasing the dosage of adsorbent, hence, from economic point of view, 1gm was taken as optimum dosage amount for removal of methylene blue.

4.9 STUDY OF EFFECT OF CONCENTRATION OF THE METHYLENE BLUE SOLUTION

The adsorption of methylene blue onto the prepared sample was studied for different concentrations of 25ppm, 50ppm and 100 ppm of methylene blue solution. The data obtained are provided in the table below.

Other parameters were taken as optimum values, that is, 1gm dosage, 35°C and a pH of 7.5.

Table 10 absorbance, equilibrium concentration and q for different concentrations of MB

time In mins	Initial concentration 25mg/l			Initial concentration 50mg/l			Initial concentration 100mg/l		
	absorbance	Concentration in mg/l, Ce	q_1=(Co-Ce)V/W	absorbance	Ce ,in mg/l	q_2=(Co-Ce)V/W	absorbance	Ce,in mg/l	q_3=(Co-Ce)V/W
0	-	0	0	-	0	0	-	0	0
10	1.0846	8.1733	1.6826	2.1003	15.8274	3.4172	2.6686	20.11	7.9890
20	0.9014	6.7927	1.8207	1.2463	9.3918	4.0608	2.4276	18.2938	8.1706
30	0.7788	5.8688	1.9131	0.9098	6.8560	4.3144	2.2098	16.6526	8.3347
60	0.6149	4.6337	2.0366	0.6944	5.2328	4.4767	1.9893	14.9909	8.5009
90	0.4634	3.4920	2.1508	0.4769	3.5938	4.6406	1.9662	14.8168	8.5183
120	0.3861	2.9095	2.2090	0.4601	3.4672	4.6532	1.9355	14.5855	8.5414

The plot between the concentration and time was obtained as given below.

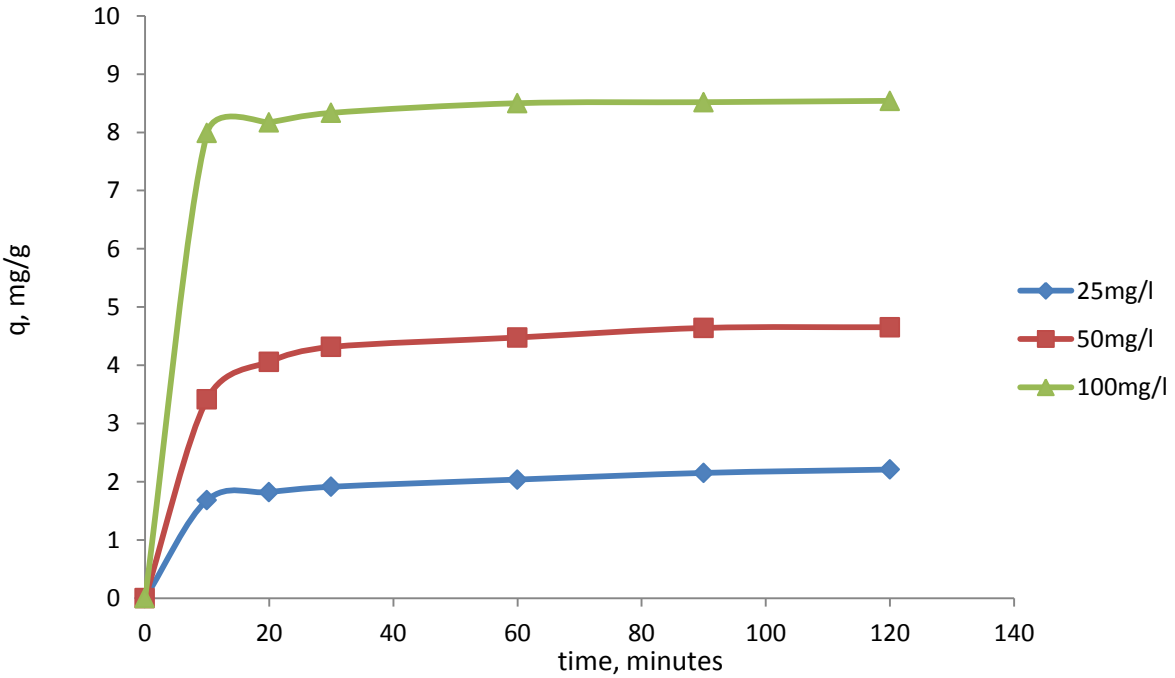

Figure 15 the plot of q vs. time for various concentrations.

From the above graph it can be seen that for higher concentrations of the methylene blue solution, the rate of adsorption is higher and equilibrium is also reached faster. This can be attributed to the higher concentration gradient which acts as a driving force. The saturation in

case of the 100mg/l solution is reached faster as the higher concentration gradient means higher number of particles available for attachment onto the surface. Thus, the surface becomes saturated very quickly and no more adsorption takes place after that. Maximum % removal of methylene blue after 2 hours was found to be 88.36%, 93.06% and 85.41% for 25ppm, 50ppm and 100ppm solutions respectively.

4.10 ADSORPTION ISOTHERMS

Isotherms give an equilibrium relationship between the amounts of adsorbate adsorbed on the adsorbent surface and its concentration in the solution at a constant temperature. Numerous adsorption models are available in the literature to fit the experimental adsorption data. In this study, the data were fitted using Langmuir and Freundlich models. Each of the three models makes use of a parameter qe (i.e. adsorption capacity per unit mass of the adsorbent at equilibrium).

$qe= (C_0-C_e)V/X$

C_0=Initial concentration of solution

C_e=Equilibrium concentration of solution

V=Volume of solution

X=Amount of adsorbent used

4.10.1 LANGMUIR ISOTHERM MODEL

The linear form of Langmuir expression:

$1/qe = 1/Qo + 1/(bQoCe)$

Where Ce is the equilibrium concentration of dye solution (mg/L), qe is the equilibrium capacity of dye on the adsorbent (mg/g), Qo is the monolayer adsorption capacity of the adsorbent (mg /g), and b is the Langmuir adsorption constant (L/mg) and is related to the free energy of adsorption.

Langmuir model was fitted to the experimental data as shown in the figure below.

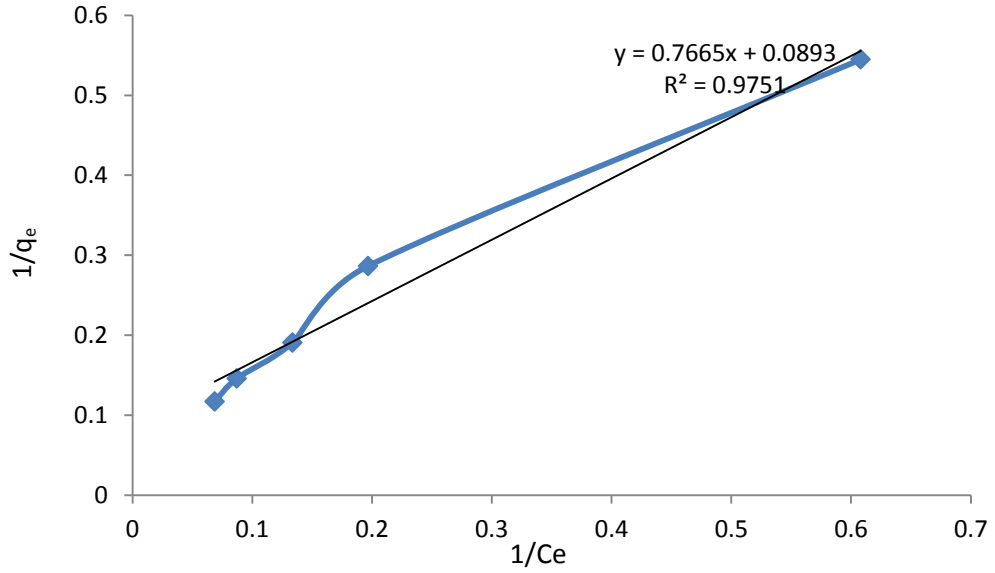

Figure 16 Langmuir model

Form the graph, the slope was found to be 0.7765 which gives us the value of $1/(bQ_o)$.

The y-axis intercept gives the $1/Q_o$= 0.0893

Thus Q_o=11.198 mg/g

And b=0.115 l/mg

R^2=0.975

4.10.2 FREUNDLICH ISOTHERM MODEL

The linear form can be written as:

$\ln q_e = \ln k_f + (1/n)*\ln Ce$

where, k_f and n (dimensionless constants) are the Freundlich adsorption isotherm constants, which indicates the capacity and intensity of the adsorption, respectively.

The Freundlich model was fitted to the experimental data as shown below

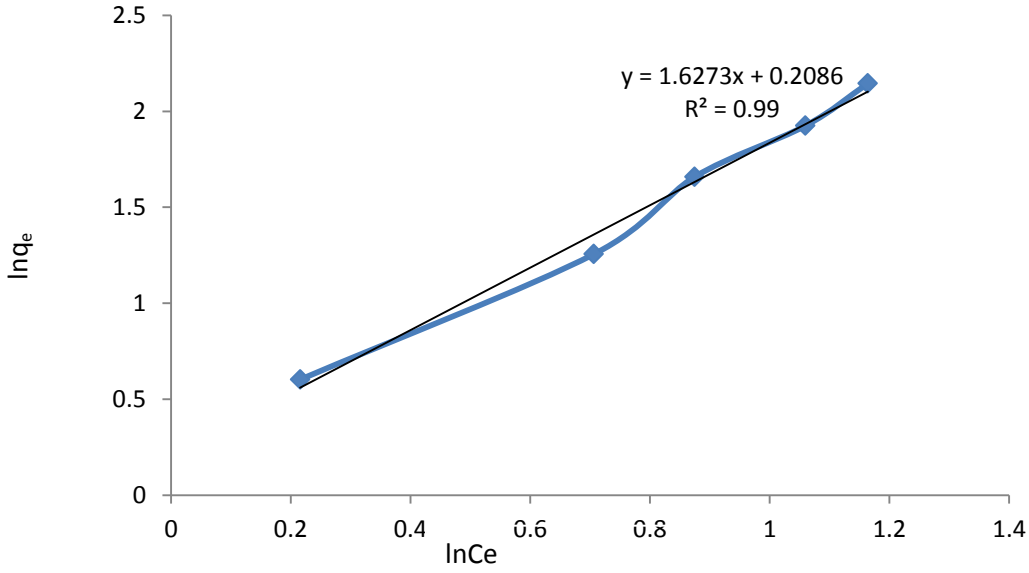

Figure 17 Freundlich model

From the graph the value of n was found to be 1.417 and k_f was found to be 1.23.As the value of 1/n is less than 1, it indicates a favourable isotherm. R^2=0.989

Since the R^2 are fairly close, thus both the models describe the system well.

4.11 ADSORPTION KINETICS STUDY

The kinetics study was made for the prepared sample taking the contact time data for for the prepared sample. The pseudo first order and second order kinetic rate equations were applied.

Table 11 adsorption kinetics study

time	%absorption at 670nm	Ce	q=(Co-Ce)/X
0			0
5	0.4318	3.2539	0.6746
10	0.3662	2.7596	0.724
15	0.3223	2.4287	0.7571
20	0.269	2.027	0.7973
25	0.2495	1.8801	0.8119
30	0.2399	1.8078	0.8192
35	0.2157	1.6254	0.8374
40	0.1997	1.5048	0.8495
45	0.1852	1.3956	0.8604
50	0.1689	1.2727	0.8727
55	0.1558	1.174	0.8826
60	0.1458	1.0987	0.8901
90	0.1198	0.9027	0.9097
120	0.1112	0.8379	0.9162

Pseudo-first-order kinetic model is given by

$dq/dt = k_1 * (q_e - q_t)$

After integration we get;

$\ln(q_e - q_t) = \ln q_e - k_1 t$

Where qe and qt are the amounts of dye adsorbed (mg/g) at equilibrium and at time t respectively. k1 is the rate constant.

The graph between time and $\ln(q_e - q_t)$ was plotted .

From the graph, the kinetic rate constant was found to be 0.0409, and the calculated q_e was 0.3077.

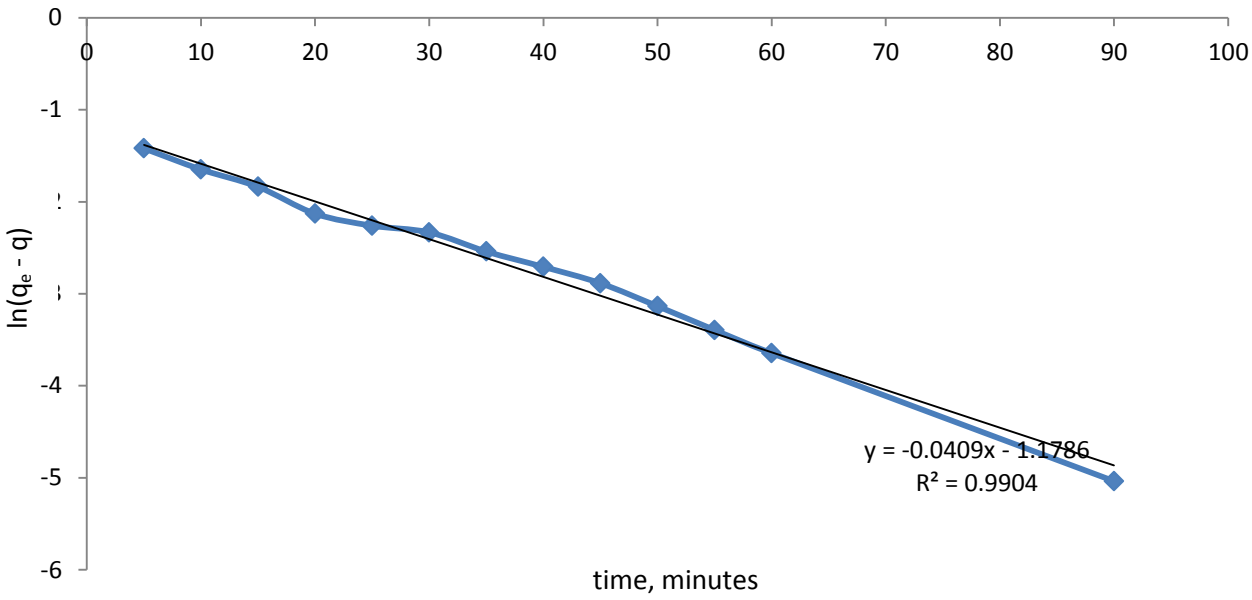

Figure 18 pseudo first order kinetic model

Table 12 parameters of pseudo first order reaction kinetics study.

Co (mg/L)	**$q_{e,exp}$(mg/g)**	**$q_{e,cal}$(mg/g)**	**k_1(1/min)**	**R^2**
10	0.9162	0.3077	.0409	0.9904

In case of pseudo- 2nd order reaction,

$dq/dt = k_2 * (q_e - q_t)^2$

after integration,

$t/q_e = 1/ k_2 q_e^2 + t/q_e$

whereqe and qt are the amounts of dye adsorbed (mg/g) at equilibrium and at time t respectively. k_2 is the rate constant.

The graph between t/q_e and time was plotted.

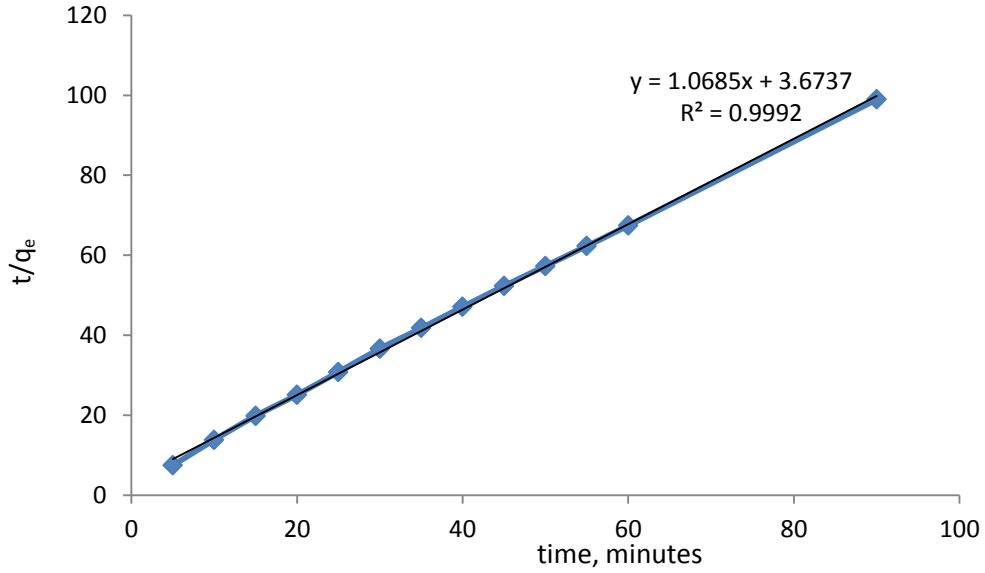

Figure 19 pseudo 2nd order reaction kinetic model.

From the above graph, the value of q_e was found to be 0.9358 which is closer to the experimental value obtained. And the rate constant k_2 was found to be 0.3177

Table 13 parameters for 2nd order reaction kinetics

Co (mg/L)	**$q_{e,exp}$(mg/g)**	**$q_{e,cal}$(mg/g)**	**k_2**	**R^2**
10	0.9162	0.9358	0.3177	0.9992

Thus the pseudo 2nd order describes the adsorption phenomenon more accurately.

Comparison of the data obtained in the present study with some of the other precursors used in other studies.

Table 14 Comparison of adsorption capacities of various adsorbents for MB.

Raw materials	**C_o,initial concentration, mg/l**	**q_e, mg/g**	**References**
Our study(karanjia oil cake)	100	8.54	-
Walnut shells	100	3.53	Aygün A. ,Yenisoy-Karakaş S. [9]
Coir pith	100	5.8	Kavitha D. , Namasivayam C. [10]
Apricot stones	100	4.1	Aygün A. , Yenisoy-Karakaş S. [9]
Almond shell	100	1.3	Aygün A. ,Yenisoy-Karakaş S. [9]
Hazelnut shell	100	8.82	Aygün A. ,Yenisoy-Karakaş S. [9]
Silk cotton hull	100	2.40	Kadirvelu K., Kavipriya M. [11]
Maize cob	100	5.00	Kadirvelu K., Kavipriya M. [11]
Coconut coir dust	100	15.25	Macedo J. S., Júnior N. B., Almeida L. E. [12]
Banana pith	100	4.67	Kadirvelu K., Kavipriya M. [11]

CHAPTER 5
CONCLUSIONS

5. CONCLUSION

From the contact time studies, it was seen that the rate of adsorption was greatest in the initial moments of the experiment. The equilibrium concentration was almost halved in the first 10 minutes of the experiment. This is attributed to the availability of higher surface area for the adsorbate molecules to attach upon. As time progressed, the equilibrium concentration did not vary appreciably with time, thus reaching saturation. It was observed that the equilibrium was reached mostly within 60 minutes as can be seen from the data obtained for both the raw and prepared samples. Thus for optimum operating conditions one hour was taken as operating parameter.

From the temperature studies, it was found that the variation of rate of adsorption and removal of the methylene blue was not very appreciable. The rate of adsorption was only slightly higher in case of 35°C. Thus, 35°C was taken as the optimum operating parameter.

From literature it was found that methylene blue adsorption occurred generally in the neutral pH region. The data obtained from the experiments also supported this. In acidic pH, the adsorption rate was slower and also the amount of removal was also less as compared to neutral pH or basic pH. The maximum adsorption rate and removal of methylene blue was found to be for a pH of 7.5, which was chosen as optimum pH for the rest of the experiments.

On increasing the dosage of adsorbent, the amount of methylene blue removed increased, but the amount of substance adsorbed per unit weight of adsorbent decreased. Also, the removal was not appreciable enough. Hence, from economic point of view, 1gm was taken as optimum dosage for the experiments.

From the study of effect of concentration on the rate of adsorption, it was observed that for higher concentration the rate was very high due to the high concentration gradient. But the % methylene blue removal was slightly lower. This might have been due to the case that the amount of surface area available for adsorption remaining constant, more number of adsorbate atoms is present in the solution, thus the surface gets blocked very quickly. Hence , the time required to reach equilibrium concentration is also less for higher concentrations.Maximum % removal of methylene blue after 2 hours was found to be 88.36%, 93.06% and 85.41% for 25ppm, 50ppm and 100ppm solutions respectively.

From the plot of Langmuir and Freundlich models, it was found that the data obtained fit to both these models quite accurately with a correlation coefficient close to 1. The pseudo 2^{nd} order model of rate kinetics accurately describes the phenomenon of adsorption.

The removal of methylene blue was achieved up to 91.62% for a sample dose of 1gm in a 10ppm solution at a temperature of 35°C and pH of 7.5 at the end of two hours. Thus, it can be concluded that the activated carbon made from the karanjia oil cake can be used for the removal of methylene blue.

CHAPTER 6
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