

# **Bio-waste derived adsorbent materials for waste water treatment**

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A Dissertation Submitted to  
Indian Institute of Technology Hyderabad  
In Partial Fulfillment of the Requirements for  
The Degree of Master of Science

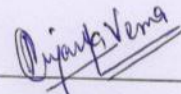


Department of Chemistry

April, 2014

## Declaration

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## Approval Sheet

This thesis entitled **Bio-waste derived adsorbent materials for waste water treatment** by Priyanka Verma is approved for the degree of Master of Science from IIT Hyderabad.



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Finally, I am forever indebted to my parents for their understanding, endless patience and encouragement from the beginning.

## **Dedication**

Dedicated to my parents, teachers and friends.

## Abstract

Corn cobs were used as a source to prepare activated carbon by physical and chemical activation methods. The physical activation was employed with CO<sub>2</sub> and steam at high temperature of 1,173K while chemical activation with nitric acid and hydrogen peroxide at ambient temperature. The adsorption studies of a basic dye, methylene blue, on the activated carbon were investigated. The effects of various experimental parameters like contact time, adsorbent dosage, MB concentration, temperature and pH were studied using batch adsorption experiments. The characterization of the activated carbon was accomplished by using BET-N<sub>2</sub> adsorption, Temperature programmed decomposition (TPD) and Thermogravimetric analysis (TGA). The results obtained from adsorption studies follow Langmuir adsorption isotherm with maximum monolayer capacity of 94.33 mg/g for CCC, 64.93 mg/g for SCC, 7.02 mg/g for NCC and 4.04 mg/g for PCC. The kinetics of adsorption was analyzed by different kinetic models like pseudo first order, pseudo second order, intraparticle diffusion and Evolich. Among these, pseudo second order was found to be the most appropriate to study the adsorption of MB on physically activated carbon. The process was found to be endothermic with enthalpy change,  $\Delta H$  (kJ mol<sup>-1</sup>) of 43.27 (CCC), 38.45 (SCC), 151.63 (NCC) & 72.29 (PCC) and entropy change,  $\Delta S$  (kJ mol<sup>-1</sup>) of 1.57 (CCC), 1.33 (SCC), 5.09 (NCC) and 2.41 (PCC) for a temperature change of 300-330 K. The negative value of  $\Delta G$  (kJ mol<sup>-1</sup>), of -29.92 (CCC), -11.14 (SCC), -7.09 (NCC) and -2.14 (PCC), suggests the spontaneous adsorption of MB on activated carbon.

## **Nomenclature**

AC	Activated Carbon
CC	Corn Cob
PCC	Peroxide treated Corn Cob Carbon
NCC	Nitric acid treated Corn Cob Carbon
CCC	Carbon dioxide treated Corn Cob Carbon
SCC	Steam treated Corn Cob Carbon
BET	Brunauer Emmett Teller
MB	Methylene Blue
nm	nanometer
UV	Ultra Violet
TPD	Temperature Programmed Decomposition
TGA	Thermogravimetric analysis
TCD	Thermal Conductivity detector
MS	Mass spectrometer
PZC	Point of zero charge

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# Chapter 1

## 1. Introduction

### 1.1 Waste water

Water from textile industries is a cause of serious environmental concern, since they generate large amount of waste water in various steps of dyeing and finishing processes. According to an estimate, about 20% of industrial water pollution is caused due to treatment and dyeing of textiles. The water is found to be rich in colour and consists of residues of reactive dyes (intermediates) and a large number of different compounds [1]. Dyes released from various sources, e.g., textile industries, cosmetics, pharmaceuticals, paper and pulp industries are regarded as one of the potent pollutants being added to the natural water resources [2, 3]. The textile industry is believed to be the major polluter of clean water by the usage of about more than 8000 chemicals in various processes of dyeing and printing. During these processes a major proportion of dye dissipates into the water stream, which makes the discharge distinctly colored which cannot be removed by traditional water treatment methods [1]. Since majority of dyes possess high water solubility, they pass through drains and rivers and hence affect the quality of water, making it unfit for consumption.

The presence of dyes in water is unenviable, not only because of their color but also due to their hazardous effects on human health and environment [4, 5]. Some adverse effects on human health include respiratory sensitization, allergic problems like dermatitis, irritation to eyes, mucous membrane and respiratory tract. Their degraded products are found to be toxic, carcinogenic and mutagenic due to presence of carcinogens like benzidine, toluidine and several other aromatic compounds [1]. Moreover, their presence can interfere with aquatic ecosystem by depleting the level of dissolved oxygen (DO) that can endanger the life of aquatic plants and animals.

The various methods available for the treatment of dye contaminated water are chemical precipitation, membrane filtration, ion exchange, carbon adsorption and co-precipitation/adsorption [6]. However, chemical and biological methods cannot be used because of the non biodegradable nature of most of the dyes [7]. Hence adsorption using

activated carbon is the most preferred process for removal of dyes from aqueous solutions with respect to methodology and efficiency [8]. This is due to its highly porous structure and high surface area to volume ratio [9].

## 1.2 Activated Carbon

Activated carbon (AC) is being used in various industrial processes especially for environmental applications. They are microporous structures with very high surface area and porosity. Due to their high surface area, they are largely being used as adsorbents for the removal of organic and inorganic pollutants from air and water [10-12].

Activated carbon is prepared by the carbonization of the raw materials in inert atmosphere at high temperature. The selection of suitable activated carbon depends on the physical and chemical properties of the substance to be adsorbed. Pores present on the surface of carbon are classified on the basis of their size into macro, meso and micropores. The range of size of pores has been shown in Table 1.1.

**Table 1. 1:Pore size range on the surface of carbon**

Pores	Size range (nm)
Macropores	>50
Mesopores	2-50
Micropores	< 2

The quality of activated carbon depends on the surface area, porosity and the surface functional groups. Depending on the size of activated carbon produced, it is classified into powdered, granular, extruded, bead and impregnated carbon. Today, activated carbon is being used in various applications like colour removal from pharmaceuticals and food products, as electrodes in batteries and as pollution control devices for industrial and automobile exhaust [13-15]. According to an estimate, about 500,000 tons/annum of activated carbon are produced globally. The cost and the non-regenerability of the activated carbon hamper its use on large scale as an adsorbent. Hence there is an urge to develop tailor made low cost activated carbon using agricultural and other bio-waste materials [16-18].

### 1.3 Biowaste material

The main reason of using agricultural waste for preparation of carbon is their large availability [8]. Low cost efficient adsorbents can be developed due to high content of their lignocellulosic materials like cellulose, hemicellulose and lignin [8]. Cellulose containing materials show potential adsorption capacity. The main advantages of using bio waste materials include low cost, regenerability, biodegradable nature and high efficiency. They are economic and eco-friendly materials that can be used to prepare diversity of adsorbents which after processing can give functional carbonaceous materials. Agricultural and bio-waste materials which have been used for the production of activated carbons are rice husk [19], peanut shell [8], fruit shell [20], sawdust [21], palm tree cobs and ground nutshells [22], sugarcane bagasse [23], coffee beans [24] etc. The carbon developed from these agricultural wastes can be used to remove toxic metal ions, dyes, organic pollutants from water [13]. Modifications can be done in the carbon prepared from agricultural waste to make them more efficient and applicable at industrial scale. The present study utilized maize corn cob as a source of raw material to prepare activated carbon.

### 1.4 Corn Cobs

India is the fifth largest producer of corn in the world with an average production of about 22 million tons every year, and thousands of tons of corn cobs continue to exist as agricultural waste in fields and factories. They are known to have highest residual to product ratio (RPR) of 4.3 among all the agricultural waste. Thus, they possess a great potential to be used as raw material for the production of activated carbon.

Corn cobs contain 32.3-45.6% cellulose, 39.8% hemicelluloses and 6.7-13.9% lignin. The proximate analysis of corn cob, as shown in Table 2, was done in order to determine the moisture, volatile content, ash and fixed carbon content.

**Table 1. 2 Proximate analysis of Corn cob**

Properties	CC
Ph	6.3-8.2
Moisture (%)	8.63
Volatile content (%)	66.1
Ash content (%)	8.9
Fixed carbon content (%)	16.37

The present study demonstrates the use of corn cob, a bio waste material obtained from maize/corn, for the production of activated carbon by physical and chemical activation methods. Chemical activation was performed by using nitric acid ( $\text{HNO}_3$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) while physical activation was done by employing steam ( $\text{H}_2\text{O}$ ), ozone ( $\text{O}_3$ ), carbon dioxide ( $\text{CO}_2$ ) and a mixture of steam and carbon dioxide ( $\text{CO}_2 + \text{H}_2\text{O}$ ) to the raw carbon [18].

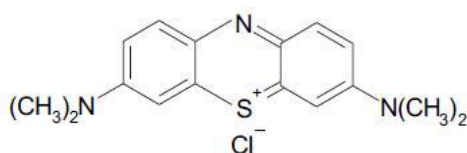
The main objective of present study is to develop activated carbon from agricultural waste, corn cobs and to test the efficacy of carbon to remove dye from waste water. The present study differs from the earlier reports due to the fact that a systematic approach of activation was followed by both physical and chemical methods. The correlation of surface area and the surface functionality of the carbon prepared was estimated by nitrogen adsorption and temperature programmed decomposition. In order to ensure the effectiveness of the activation steps, a model dye methylene blue, is selected as a prototype for assessing the potential of corn cob carbon to remove dye from waste water. The impact of various parameters like temperature, contact time, pH, different concentrations of adsorbent and adsorbate was studied in detail. The equilibrium data thus obtained was interpreted to study the kinetics, adsorption isotherms and thermodynamic parameters.

# Chapter 2

## Methods and materials

### 2.1 Methylene Blue Dye

Dye is a colored organic substance that imparts color to various substrates. It is classified on the basis of nature of chromophore present, acidic and basic groups, nature of origin, chemical composition and application. Methylene blue is a heterocyclic basic dye which containing three water molecules in hydrated form which is commonly employed in textile industries for dyeing purposes. The dye has molecular formula of  $C_{16}H_{18}N_3SCl \cdot 3H_2O$  with the structure shown in Fig. 2.1.



**Figure 2. 1:Chemical structure of Methylene blue**

Methylene blue has also found use in medical applications for staining tissues and as an antidote for cyanide poisoning. At therapeutic doses, it can treat *methemoglobinemia*, which decreases the oxygen carrying capacity of hemoglobin in body. Continuous research is going on to find its potential role for the treatment of malaria and alzheimer's disease. It also exhibits antiseptic properties against bacterial infection. Apart from these medical applications, its presence in water can affect human health in various ways. It is one of the most commonly used cationic dyes for dyeing cotton, wool and silk. Although the dye is not strongly hazardous, still it can generate some negative effects on human health. Chronic exposure to skin can cause discoloration, redness or dryness. Exposure to eyes induces irritation, watering and burning sensation to eyelids, or may lead to permanent damage in humans and animals. Ingestion may lead to irritation of gastrointestinal tract along with symptoms of headache, dizziness, nausea and vomiting. It may give rise to convulsions, cyanosis, confusion and sweating, if inhaled. Its degradation products like toluidine, benzidine and other aromatic components induce several chemical and biological changes in

body; can lead to cancer and mutations. Hence, it is prerequisite to remove methylene blue from waste water.

Methylene blue ( $C_{16}H_{18}N_3ClS$ , molecular weight 319.85 g/mol) was selected as an adsorbate for carrying out the adsorption studies on prepared activated carbon. It has absorption maxima at 668nm. The 1000ppm (1000mg/L) stock solution of dye was prepared by dissolving 1g of Methylene blue in 1L of deionised water (taken from Direct-Q 3 MILLIPORE water purification system). Required initial concentrations of the dye were prepared by diluting the stock solution in accurate proportion. The concentration of methylene blue in solution was monitored before and after adsorption using a double beam UV spectrophotometer (Shimadzu, Japan). The solutions of known concentration of methylene blue were used for calibration curve.

## 2.2 Preparation of activated carbon

The following scheme, as shown in Fig.2.2, depicts the steps followed in the preparation of carbon using corn cobs as a source of raw material.



**Figure 2. 2:Schematic representation for the preparation of activated carbon**

The carbonization and activation of carbon were carried out independently. Corn cobs used in the present study were obtained from the nearby market. It was washed and cut into small pieces and kept overnight in oven to remove moisture content. It was then subjected to carbonization in furnace at 1,173K under N<sub>2</sub> atmosphere for 6h. The flow of nitrogen gas and the heating rate was kept constant at 100 mL/min and 10 K/min respectively. After completion of treatment, sample was allowed to cool down at room temperature with continuous supply of N<sub>2</sub> gas through the sample. The produced carbon was collected and used for further activation processes.

## 2.3 Activation of Carbon



All activation methods of carbon fall under two categories of physical and chemical activation. Chemical activation includes treatment with acids, bases and salts in solutions which are easy to carry out since it requires lower temperature than physical activation methods. Physical activation involves the use of gaseous activation agents like carbon dioxide, steam or air that generally necessitates high temperature conditions.

### **2.3.1 Chemical activation**

Chemical activation involves the infusion of chemical reagents onto the precursor i.e. carbon. The degree of chemical activation can significantly change the properties of the produced carbon. In comparison to physical activation, chemical activation is preferred due to its lower temperature requirement, less time of activation and high yield. But this process adds on an additional step of washing of activated carbon to remove the excess of chemical reagent intact with the carbon. There has been observed a change in the dimensions of the precursor during chemical activation which is necessary to assimilate the reagent inside the precursor which led to the formation of microporous structure. The porous structure is developed on the surface of carbon, which makes it suitable to be used as an adsorbent. Various chemical activating agents are being used like alkali metal hydroxides (KOH, NaOH), alkali metal carbonates, nitric acid, hydrogen peroxide, potassium permanganate etc.

In the present study,  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  were used as chemical reagents for activation. The usual method of activation involves the washing of carbon with distilled water followed by treatment with oxidising agent in the ratio of 50:50 (v/v %). The first method of activation involves the treatment of sample with chemical reagents under constant stirring for about 3h. The sample was then filtered and rinsed with deionised water followed by drying in oven at 393K. These samples are named as ambient temperature nitric acid-treated corn cob (ANC) and ambient temperature peroxide-treated corn cob (APC). In the other method of activation, the sample mixed with reagents was taken in a crucible wrapped with aluminium foil and kept in furnace at 673K for about 10 min. After several washing with deionised water, it was dried in oven at 393K and named as nitric acid-treated corn cob (NCC) and peroxide-treated corn cob (PCC).

### **2.3.2 Physical activation**

In this method, carbon is allowed to interact with oxidising gases like steam,  $\text{CO}_2$  and air. It involves the development of molecular porous structure with high surface area in the

presence of high temperature of about 600-800°C. Physical activation increases the pore structure due to partial oxidation of carbon by oxidizing gases like CO<sub>2</sub> and steam. Some combined activation processes have also been studied which involves physical after chemical activation. These processes made it possible to synthesize microporous structures with very high surface area of upto 4000 m<sup>2</sup>/g. Since the activation of carbon by physical methods demand very high temperature, a loss of carbon amount is expected. One of the advantages of physical over chemical activation is the preservation of the microstructure in the activated carbon which is not possible in chemical activation.

This method of activation can be considered as eco-friendly since it doesn't produce waste water; however consumption of large amount of energy and time can be called as its negative impact. Due to high temperature requirements and low reaction rate between the oxidizing gas and the sample, usually low product yield is obtained through physical activation.

The process was initiated by packing raw carbon, CC, in quartz tube with gun cotton followed by placing it into furnace. The inlet of the tube was affixed with N<sub>2</sub> generator and furnace was switched on. N<sub>2</sub> gas was passed through the sample till the furnace temperature reached to the required set value in order to ensure the complete absence of oxygen. For all activation process the flow rate of N<sub>2</sub> gas and the heating rate of furnace were kept constant at 100 mL/min and 10K/min respectively. After the attainment of the required temperature, the N<sub>2</sub> generator was switched off and CO<sub>2</sub> gas was passed through for 2 h at 700°C. After completion of the treatment, again N<sub>2</sub> generator was switched on and the sample was allowed to cool down. Finally, the sample was collected and used for further analysis.

The same process was followed for the other physical activation treatments. In addition, N<sub>2</sub> gas was bubbled through water for steam treatment while CO<sub>2</sub> was bubbled through water for a combination of CO<sub>2</sub>+steam activation.

## **2.4 BET surface area**

The specific surface area, pore volume distribution, micropore surface area were determined by using a surface area analyzer, Quantachrome Nova 2200 which is based on the principle of multilayer adsorption of N<sub>2</sub> as a function of relative pressure. Before analysing the sample in BET, it was kept for de-gassing at 573K for 3h to detach any gaseous impurities within the sample.

The most widely used BET equation is:

$$\frac{p}{V_{\text{total}}(p_0 - p)} = \frac{1}{V_{\text{mono}}C} + \frac{(C-1)p}{V_{\text{mono}}C p_0}$$

Where,

$V_{\text{mono}}$  : Volume of the gas required to form one complete monolayer of adsorbate on the surface of the adsorbent.

$V_{\text{total}}$ : Total volume of gas adsorbed on the surface of the adsorbent, at the given temperature and pressure.

$p_0$ : Saturated vapour pressure of the gas at temperature T and  $p$  is the pressure of the gas.

C: a constant, at given conditions which depends on the nature of the gas for a particular adsorbate- adsorbent pair.

$C = \exp\left(\frac{E_1 - E_L}{RT}\right)$  where  $E_1$  is heat of adsorption in the first layer and  $E_L$  is second and higher layers and is equal to the enthalpy of liquefaction. It is an indication of the magnitude of the adsorbent/adsorbate interactions.

## 2.5 TGA

Thermogravimetric analysis (TGA) is an essential analytical technique used for the characterization of sample. Since TGA can quantitatively analyze any class of materials, it has found widespread use in almost every field of science and technology. In this technique, thermal stability of sample is monitored by observing the percentage of weight loss as a function of temperature. The sample is heated in a controlled temperature programme in an inert atmosphere of helium, argon or nitrogen. It consists of a sample pan along with a reference pan kept in a furnace which is heated or cooled during the analysis. Apart from recording the weight change, some instruments measure the temperature difference between the sample and the reference pan known as differential thermal analysis, DTA. The heating rate and the sample size play an important role in TG analysis. The other factors that affect the analysis are particle size, packing of sample, crucible shape and flow rate of gaseous atmosphere. Usually around 50 mg of sample is used for analysis with a temperature ramp of 10°C/min. Buoyancy effect of sample container, furnace and temperature effects are the various sources of error that should be avoided during analysis. A derivative of TGA curve i.e. the rate of weight change (dW/dt) as a function of temperature is known as DTG, Differential Thermal analysis, to clearly pinpoint the maximum of weight change.

## 2.6 TPD

Temperature programmed decomposition (TPD) has been used to study the surface functionality of the carbons. On-line mass spectrometry was used to measure the decomposition products (CO and CO<sub>2</sub>). A Quadrupole Mass Spectrometer is an instrument for measuring concentrations of atoms and molecules by separating atomic and molecular ions according to their mass-to-charge ratios (m/z).

The TPD-MS studies were performed in a quartz reactor by using Quantachrome gas sorption analyzer. For the TPD-MS study, the sample was purged with He for 30 min at room temperature and then was heated at 10°C/min upto 1000°C with simultaneous monitoring of the m/e 2, 4, 15, 18, 28, 30, 32, and 44 species by using mass spectrometer (RGA PRIS MA PLUS 200 AMU featuring a smaller detectable mass range from 1 to 200 amu) calibrated with gas mixtures of known compositions.

## 2.7 PZC

The point of zero charge (pH<sub>PZC</sub>) is the pH at which the surface exhibits net zero charge. pH<sub>PZC</sub> was determined by batch equilibration method in which five different solutions were prepared having pH values ranging from 2-10. At first 20 cm<sup>3</sup> of distilled water was kept in several beakers and their pH values were adjusted by adding varying amounts of 0.1mol/dm<sup>3</sup> of NaOH or HNO<sub>3</sub> solution. Then a portion of carbon sample (50mg) was added into beakers and kept for equilibration at room temperature. After 24h, the final pH was measured and plotted as a function of initial pH values. The final pH value in the curve where a common plateau is obtained is the pH<sub>PZC</sub> of the carbon. The same procedure was repeated for all activated carbons.

# Chapter 3

## Experimental section

### Adsorption studies

Several batch adsorption experiments were carried out using activated carbon (adsorbent) and aqueous solutions of methylene blue (adsorbate) at 300K. The adsorption experiments were carried out to study the effects of varying initial MB concentration, carbon amount (0.1, 0.15 and 0.2 g) and temperature (300, 313 and 333K). The studies were carried out by varying one of the parameters while keeping others constant. The concentration of dye was monitored after fixed interval of time (15min) using UV-Visible spectrophotometer at absorption maxima of 668nm. The amount of dye adsorbed at equilibrium,  $q_e$  (in mg/g) and the percentage of adsorption can be evaluated by the following expression [18]:

$$q_e = (C_o - C_e) V / W$$

$$\text{Percentage (\%)} \text{ of adsorption} = (C_o - C) / C_o \times 100$$

Where  $C_o$  and  $C_e$  represent initial and equilibrium concentrations of adsorbate,  $V$  the volume of solution,  $W$  is the weight of adsorbent, and  $C$  is the concentration of the dye at the end of adsorption.

### 3.1 Effect of contact time

Various batch experiments were kept for equilibration with initial MB dye concentration of 10, 15, 20 mg/L (NCC, PCC) and 100, 150 and 200 mg/L (SCC, CCC). The amount of dye getting adsorbed on the surface of activated carbon increases with increasing contact time till a plateau is obtained. It represents the state of dynamic equilibrium in which the amount of dye adsorbed onto the adsorbent is in equilibrium with that of dye present in solution. This equilibrium was observed at around 90 min for physically treated carbon and 120 min for chemically treated carbon. The attainment of equilibration takes a bit longer time due to a complex mechanism involved in the adsorption of dyes on macro and micro pores of activated carbon. The mechanism entails the confrontation of dye molecules to the boundary

layer before diffusing onto the surface of adsorbent and then finally entering into the porous structure of carbon.

On increasing the methylene blue concentration, the amount of dye adsorbed per unit mass of carbon (unit adsorption capacity) increases while it decreases with increase in the adsorbent dosage due to unsaturation of adsorption sites.

### 3.2 Effect of adsorbent mass

Set of experiments conducted to study the effect of adsorbent mass on methylene blue adsorption by varying the amount of adsorbent from 100, 150 and 200 mg for different concentrations of methylene blue at constant temperature (300K) and pH (7.0). On increasing the adsorbent dosage from 100 to 200 mg, the percentage of adsorption increased with shorter equilibrium time. This can be ascribed to the increased surface area and availability of more adsorption sites.

### 3.3 Adsorption isotherm

Adsorption isotherm is the study of equilibrium relationship between adsorbate adsorbed on the surface of adsorbent and adsorbate remained in solution, if they are kept in contact with each other for longer periods of time. It correlates the equilibrium concentration of a solute on the surface of an adsorbent,  $q_e$ , to that of the concentration of the solute in the solution phase,  $C_e$ , at a particular temperature. Moreover, the isotherm models enable us to calculate the maximum adsorption capacity of adsorbate for a given adsorbent at a particular temperature. There are various mathematical models to predict the distribution of adsorbate at equilibrium, but the Langmuir model is the most accepted one for the application of activated carbon in waste water treatment. This model assumes the monolayer formation on the surface of adsorbent which implies the more specific binding of adsorbate. It further assumes that all sites on the surface of adsorbent are equivalent and there occurs no interaction between adsorbate and adsorbent molecules.

The linear form of Langmuir isotherm is represented as [25]:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L}$$

Where  $C_e$  represents the concentration of dye in aqueous phase (mg/L) at equilibrium,  $q_e$  (mg/g) is amount of dye adsorbed at equilibrium,  $Q_m$  (mg/g) is the maximum monolayer adsorption capacity of adsorbent and  $K_L$  (L/mg) is associated with the energy of adsorption. A linear plot of  $C_e/q_e$  versus  $C_e$  shows the validity of Langmuir model. Langmuir constants,  $Q_m$  and  $K_L$ , can be calculated from the slope and intercept of the linear plot respectively.

The favorability of adsorption was established by the calculation of a separation factor  $R_L$ , which can be defined as [8]:

$$R_L = \frac{1}{1 + bC_0}$$

Where  $b$  is Langmuir adsorption constant,  $C_0$  (mg/L) is the initial concentration of dye. It has been observed that value of  $R_L$  is the deciding factor to determine the type of adsorption. Its value in between 0 to 1 suggests favorable adsorption. For all values of  $R_L > 1$ , adsorption is unfavorable while  $R_L = 0$  indicates irreversible adsorption.

### 3.4 Adsorption kinetics

The kinetics of adsorption was studied by carrying out set of experiments for adsorption of MB on activated carbon, by varying the initial concentration of dye from 10-20 mg/L (NCC & PCC) and 100-200 mg/L (SCC & CCC) and the adsorbent dosage (0.1-0.2 g/100mL of solution) at constant temperature. To understand the mechanism and the rate of adsorption, various kinetic models were investigated like first order, second order, pseudo first order, pseudo second order, intra particle diffusion and Evolich. A linear plot of these models confirms their validity. Quantitative confirmation can be done by comparing their correlation coefficient values. The obtained results of adsorption studies were treated with pseudo second order kinetic model. The linear form of equation can be represented as [26]:

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{t}{q_e}$$

Where  $q_e$  (mg/g) is the equilibrium concentration of adsorbate,  $q_t$  (mg/g) is the adsorbate concentration at any time  $t$  and  $k_2$  (g/mg min) is pseudo second order rate constant. A linear plot of  $t/q_t$  versus  $t$  will give the value of  $q_e$  and  $k_2$  from its slope and intercept respectively. It was observed that the values of correlation coefficient were almost ideal ( $R^2 > 0.999$ ) for pseudo second order kinetic model, which shows a good agreement in theoretical and experimental results. Furthermore, a good correlation was observed between  $q_e$  values, calculated using pseudo second order model and the experimental observation.

The kinetic studies of other models were also plotted and a quantitative comparison was made among each other and with that of pseudo second order kinetics.

The linearised form of pseudo first order kinetics is represented as [27]:

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

Where  $q_e$  and  $q_t$  are the sorption capacity (mmol g<sup>-1</sup>) at equilibrium and at time  $t$  respectively,  $k_1$  (L min<sup>-1</sup>) represents the rate constant for pseudo first order kinetics.

In intraparticle diffusion model, a plot of  $q_t$  versus  $t^{1/2}$  is drawn to check the validity of this model. The correlation coefficient values were close enough to the ideal value but don't fit well in comparison to the values of pseudo second order kinetics. It involves the preferential movement of species from bulk of solution to the micropores in solid phase.

The linear form of the equation can be best represented as [26]:

$$q_t = K_d t^{1/2} + C_i$$

Where  $q_t$  is the sorption capacity at time  $t$ ,  $K_d$ ,  $C_i$  are the diffusion and intraparticle diffusion constant calculated from the slope and intercept respectively.

For Evolich model,  $q_t$  versus  $\ln t$  was plotted in accordance with the linear form of the equation as mentioned below:

$$q_t = a + b \ln t$$

Where  $q_t$  is the sorption capacity at time  $t$ ,  $a$  &  $b$  are the Evolich constants determined from slope and intercept of the plot respectively.

### 3.5 Determination of Thermodynamic parameters

The knowledge of thermodynamic parameters gives clues to predict the feasibility of a process at a given temperature. Thermodynamic parameters like Gibb's free energy change,  $G^\circ$ , enthalpy change,  $H^\circ$ , and entropy change,  $S^\circ$  can be calculated by using the following expressions[16]:

$$K_e = C_{\text{solid}} / C_{\text{liquid}}$$

$$G = -RT \ln K_e;$$

$$\ln K_e = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

Where  $C_{\text{solid}}$  (mg/L) is the dye concentration in solid phase, i.e., on the surface of adsorbent,  $C_{\text{liquid}}$  (mg/L) is the dye concentration in liquid phase, i.e., in solution,  $R$  ( $8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ) is the universal gas constant and  $T$  (K) is the absolute temperature. The spontaneity of the process can be predicted on the basis of negative sign of Gibb's free energy change,  $G$ . From the present study, it has been observed that the values of  $G$  becomes more negative with increase in the adsorbent dosage and less negative with increasing concentration of dye.  $H$  and  $S$  can be calculated from the slope and the intercept of the linear plot (negative slope) of  $\ln K_e$  versus  $1/T$  respectively.



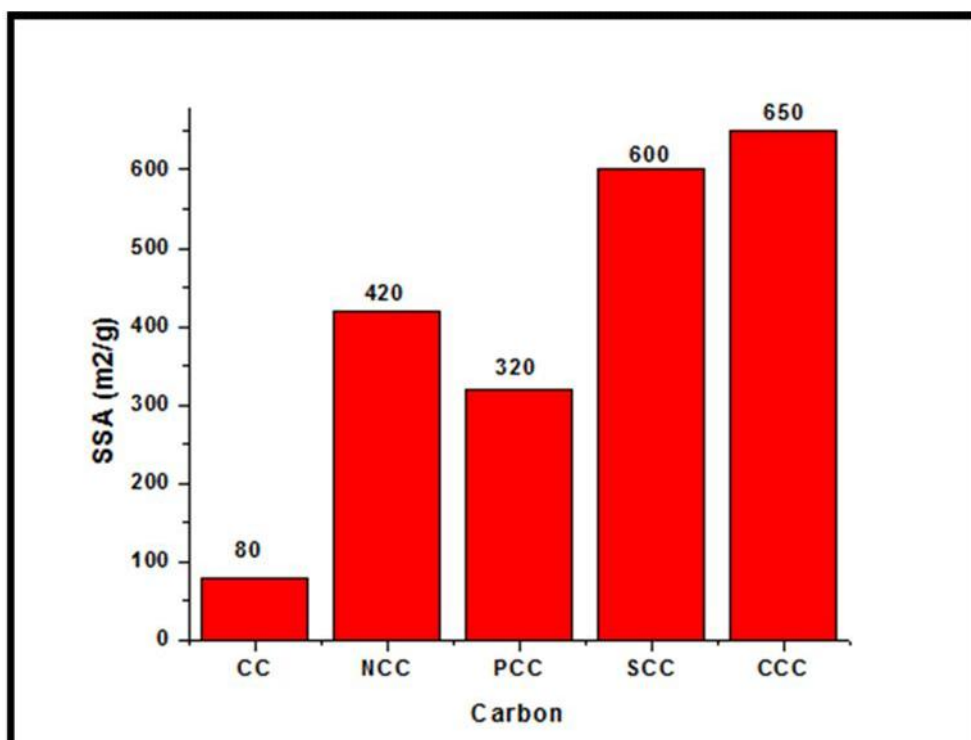
# Chapter 4

## Results & Discussions

### 4.1 Characterization

#### 4.1.1 BET

Surface area is one of the important parameters in deciding the quality and efficiency of activated carbons. The raw carbon prepared by the carbonization of corn cob showed the BET surface area of 80 m<sup>2</sup>/g. It was observed that among chemically activated carbons, NCC (420 m<sup>2</sup>/g) showed higher surface area than PCC (320 m<sup>2</sup>/g). While CCC (650 m<sup>2</sup>/g) showed better activity than SCC (600 m<sup>2</sup>/g) among physically treated carbon as shown in Fig. 4.1. The difference in the efficacy of these carbons proved the importance of type of treatment on the properties of activated carbon. The calculated physicochemical properties of activated carbons have been summarized in Table 4.1.



**Figure 4. 1: BET surface area of activated carbons**

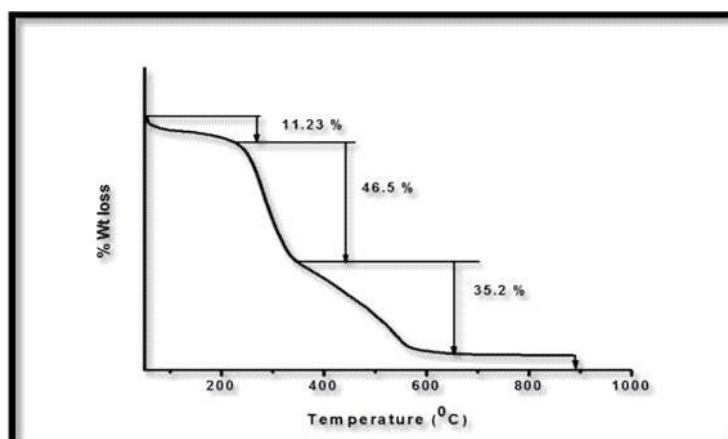
**Table 4. 1:Physico-chemical properties of activated carbons**

Sample	BET surface area (m <sup>2</sup> /g)	Micropore surface area (m <sup>2</sup> /g)	External surface area (m <sup>2</sup> /g)	Micropore Volume(cc/g)	CO (mmolg <sup>-1</sup> )	CO <sub>2</sub> (mmolg <sup>-1</sup> )	Total (CO+CO <sub>2</sub> ) (mmolg <sup>-1</sup> )	PZC
CC	80	63	17	0.03	0.24	0.62	0.86	6.4
SCC	600	428	172	0.39	3.63	5.46	9.09	5.1
CCC	650	495	155	0.52	4.14	9.23	13.37	6.9
NCC	420	331	89	0.29	2.12	3.87	5.99	6.2
PCC	320	206	114	0.17	1.87	2.93	4.80	5.3

#### 4.1.2 TGA

5 mg of carbon was taken for analysis and heated at a constant rate of 10°C/min till 900°C.

Fig. 4.2 shows the percentage of weight loss for CC as a function of temperature. It can be seen from the curve that decomposition takes place in three stages.

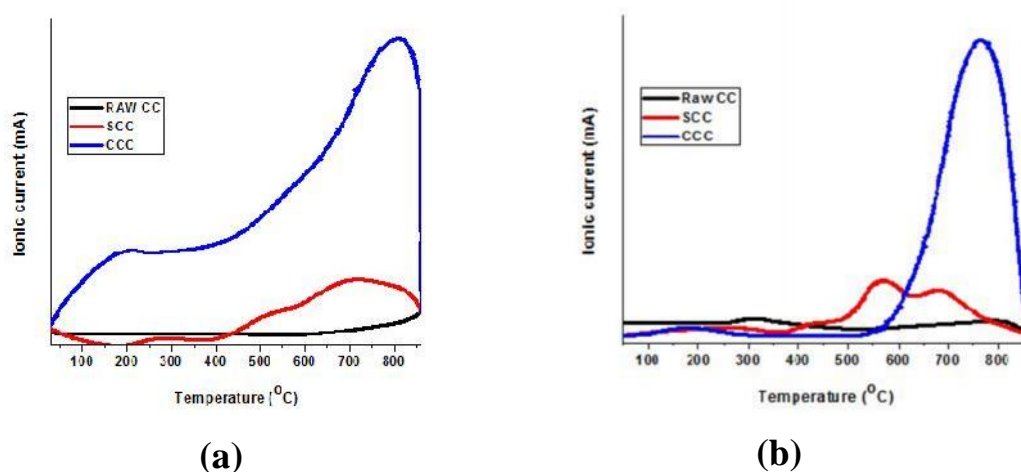


**Figure 4. 2:Thermogravimetric analysis of corn cob**

The first stage comes in the range of 323 to 383K with a weight loss of about 11.23%, which accounts for the loss of moisture from the sample. The second stage can be referred to as the major stage of decomposition, since 46.5% of weight loss takes place within the temperature range of 383-673K. This loss can be attributed to the decomposition of chemically bound water, cellulose, hemicelluloses, and lignin. On heating further at a temperature greater than 673K, 35.2% of weight loss can be assigned to the formation of volatile products like CO, CO<sub>2</sub> etc.

### 4.1.3 TPD

The porosity of the carbon plays an important role in its catalytic activity. It is well known that the surface functionalities are also important in determining the adsorption of molecules on carbon surfaces. The overall process of TPD analysis can be abridged as the translation of functional groups like carboxylic, ketonic and alcoholic into CO<sub>2</sub> and CO on heating. The analysis is based on the generalization that groups releasing CO<sub>2</sub> show acidic nature while those releasing CO show basic character. It was observed that physically activated carbon displayed more amount of CO<sub>2</sub> & CO in comparison to raw carbon. In CO<sub>2</sub> profile, the maximum in the temperature range of 580-640 K is assigned to carboxylic groups. Maximum around 880-1030 K is due to anhydrides or lactones. In CO profile, a maximum peak above 1100 K is attributed to anhydrides or phenols, ethers, carbonyls or quinones.



**Figure 4. 3:TPD profiles of various CC samples before and after treatments:(a) CO evolution, (b) CO<sub>2</sub> evolution**

As seen from the Fig. 4.3, In the CO<sub>2</sub> profile of CCC & SCC, the peak observed at around 323-523 K corresponds to the presence of carboxylic groups. The maxima in the temperature range 673-1073 K can be assigned to anhydrides or lactones [28]. The CO<sub>2</sub> treated carbon (CCC) accounts for the maximum oxygen functional groups on surface. The presence of carbonyl, phenol, ethers was confirmed by the CO profile of CCC & SCC, which gave maxima above 673 K. Among the three carbons, CCC (13.37 mmol g<sup>-1</sup>) showed the maximum amount of surface functional groups followed by SCC (9.09 mmol g<sup>-1</sup>) and CC (0.86 mmol g<sup>-1</sup>).

#### 4.1.4 PZC

The PZC of various samples of CC, shown in Table 4.2, activated by different treatments were determined using the standard procedure already mentioned in chapter 3.

**Table 4. 2:PZC of activated CC carbons**

Carbon	PZC
CC	6.4
NCC	5.1
PCC	6.9
SCC	6.2
CCC	5.3

## 4.2 Adsorption studies

### Percentage of adsorption & adsorption capacity

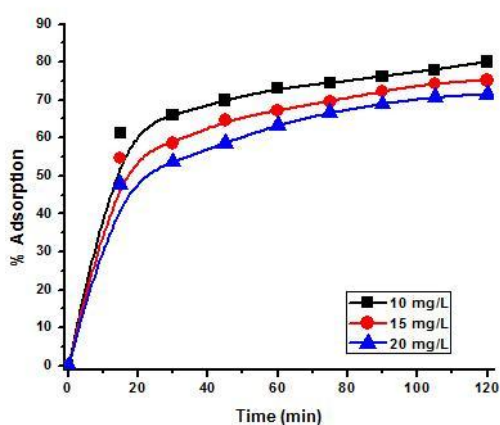
The percentage of adsorption and the amount of dye adsorbed,  $q_e$ , was calculated for all activated carbons. Among chemical activation, NCC showed 78% removal of MB with a  $q_e$  of 7.8 mg/g and PCC removed 60.6% of MB with  $q_e$  of 6.06 mg/g which can be seen from Table 4.4. Physically activated carbon performed better, which can be shown by 92% MB removal by SCC and 100% by CCC, as observed from the following Table 4.3. The % adsorption and unit adsorption capacity are plotted as a function of time by varying adsorbent dose and MB concentration for NCC, PCC, CCC and SCC as shown in Fig.4, Fig.5, Fig.6, and Fig.7 respectively.

**Table 4. 3:Equilibrium parameters  $q_e$  and % adsorption of MB onto physically activated carbons**

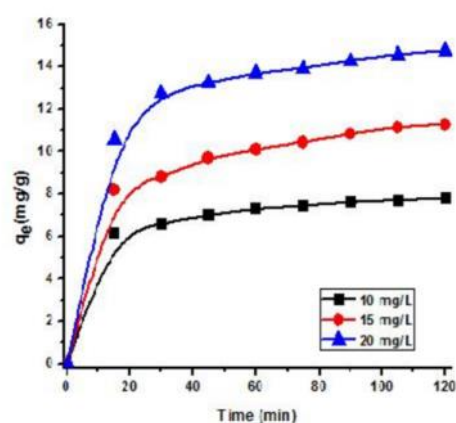
Sample	100ppm		150ppm		200ppm	
	$q_e$ (mg/g)	% adsorption	$q_e$ (mg/g)	% adsorption	$q_e$ (mg/g)	% adsorption
CCC100	92	92	135	90	165	82.5
CCC150	66.7	99.99	100	100	130	97.25
CCC200	50	99.99	100	99.99	99.2	99.2
SCC100	100	100	131	87.6	135	67.5
SCC150	66.7	100	90	90	106.6	80
SCC200	50	100	69.5	92.6	82.5	82.5

**Table 4. 4:Equilibrium parameters  $q_e$  and % adsorption of MB onto chemically activated carbons**

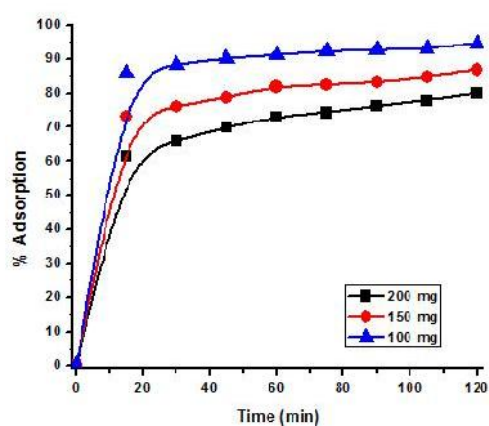
Sample	10ppm		15ppm		20ppm	
	$q_e$ (mg/g)	% adsorption	$q_e$ (mg/g)	% adsorption	$q_e$ (mg/g)	% adsorption
NCC100	7.8	78	11.3	75.1	14.3	71.5
NCC150	5.79	86.8	8.31	83.1	10.4	78.5
NCC200	4.73	94.6	6.76	90.1	8.4	84
PCC100	6.06	60.6	8.15	54.3	10.11	50.5
PCC150	4.6	69.1	6.19	61.9	7.52	56.4
PCC200	3.52	70.4	5.28	70.4	6.73	67.35



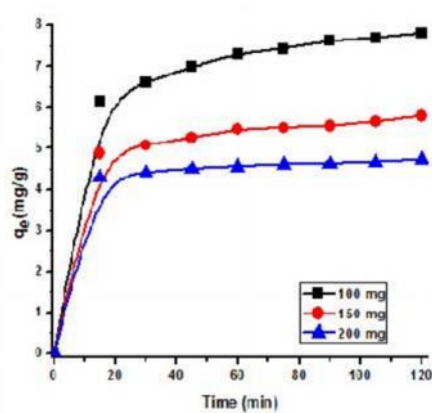
(a)



(b)

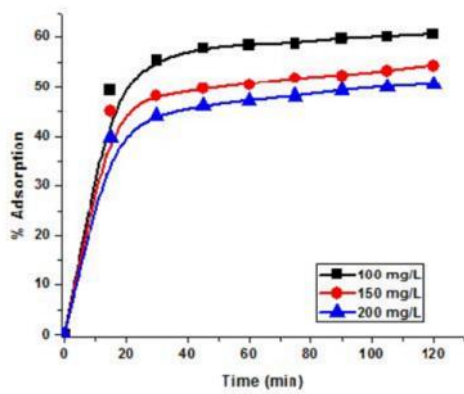


(c)

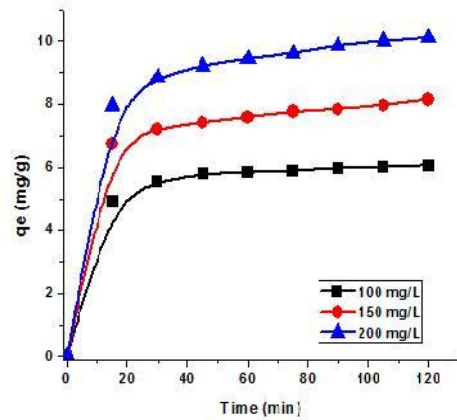


(d)

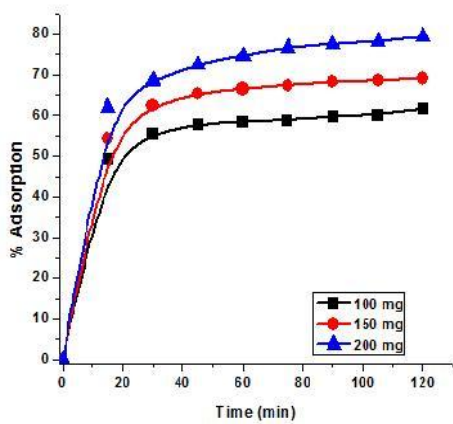
**Figure 4. 4:Performance of NCC: ( a ) % adsorption with 100 mg adsorbent dose (b) Unit adsorption capacity for 100 mg of adsorbent dose (c) % adsorption for 10 mg/L MB conc. (d) unit adsorption capacity for 10 mg/L MB conc.**



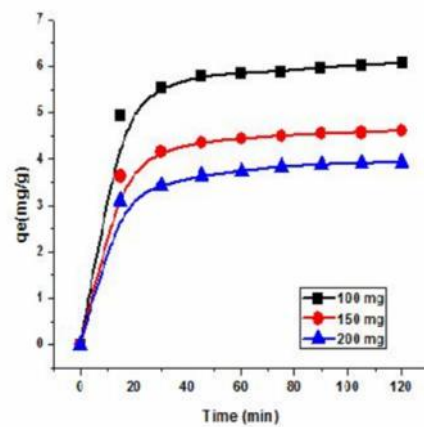
**(a)**



**(b)**

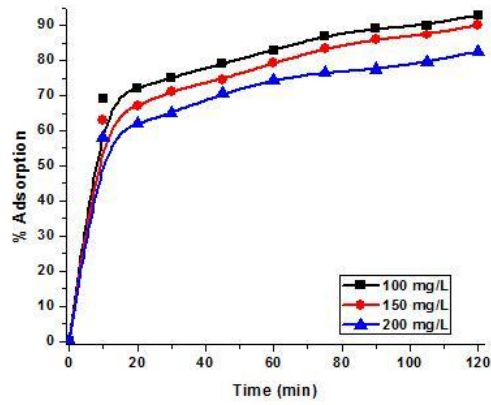


**(c)**

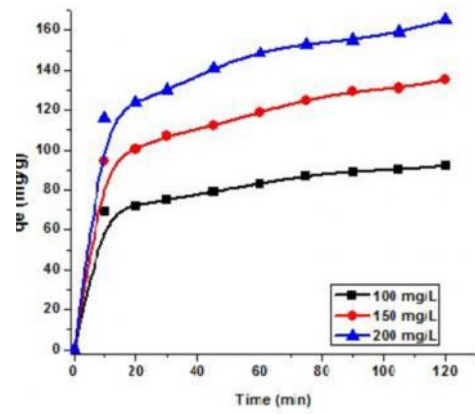


**(d)**

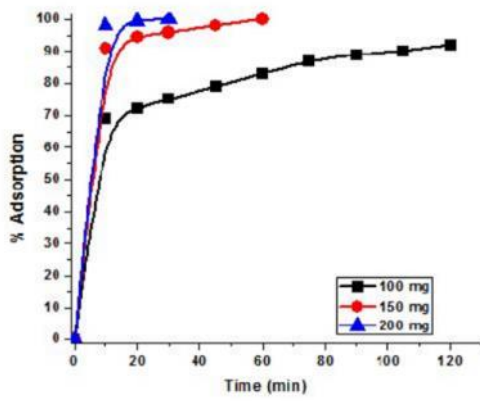
**Figure 4. 5:Performance of PCC: (a) % adsorption with 100 mg adsorbent dosage (b) unit adsorption capacity for 100 mg of adsorbent dosage (c) % adsorption for 10 mg/L MB conc. (d) unit adsorption capacity for 10 mg/L MB conc.**



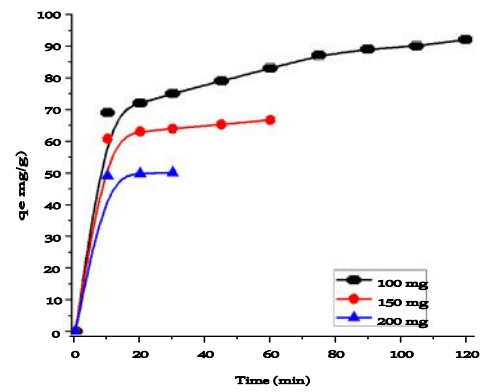
(a)



(b)

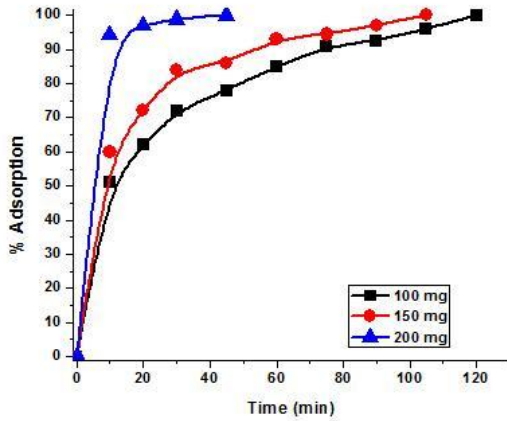


(c)

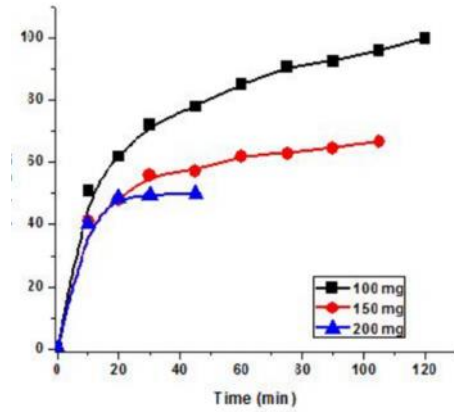


(d)

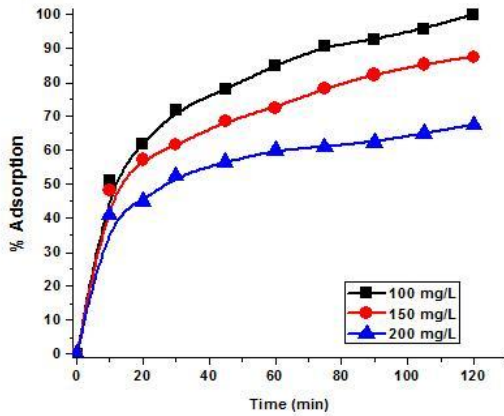
**Figure 4. 6: Performance of CCC: (a) % adsorption with 100 mg adsorbent dosage (b) unit adsorption capacity for 100 mg of adsorbent dosage (c) % adsorption for 100 mg/L MB conc. (d) unit adsorption capacity for 100 mg/L MB conc.**



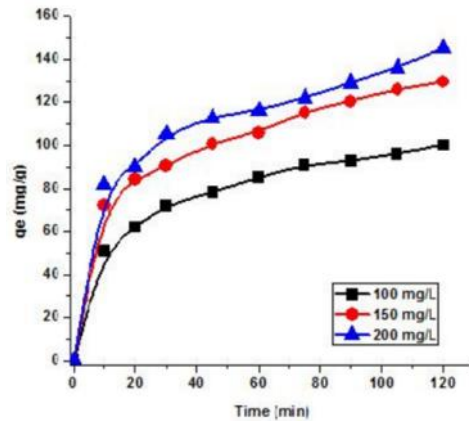
(a)



(b)



(c)



(d)

**Figure 4. 7:Performance of SCC (a) % adsorption with 100 mg adsorbent dosage(b) unit adsorption capacity for 100 mg of adsorbent dosage (c) % adsorption for 100 mg/L MB conc. (d) unit adsorption capacity for 100 mg/L MB conc.**

### 4.3 Adsorption isotherm

Langmuir adsorption isotherm was found to be the best fitted model having correlation coefficient values almost equivalent to 1. A plot of  $C_e/q_e$  v/s  $C_e$  gave a straight line, as seen from Fig. 4.8. The parameters of Langmuir isotherm were calculated using adsorption isotherm equation as shown in Table 4.5 for chemically activated carbon and Table 4.6 for physically activated carbon. The value of  $R_L$  was found to be in between 0 to 1 (as shown in



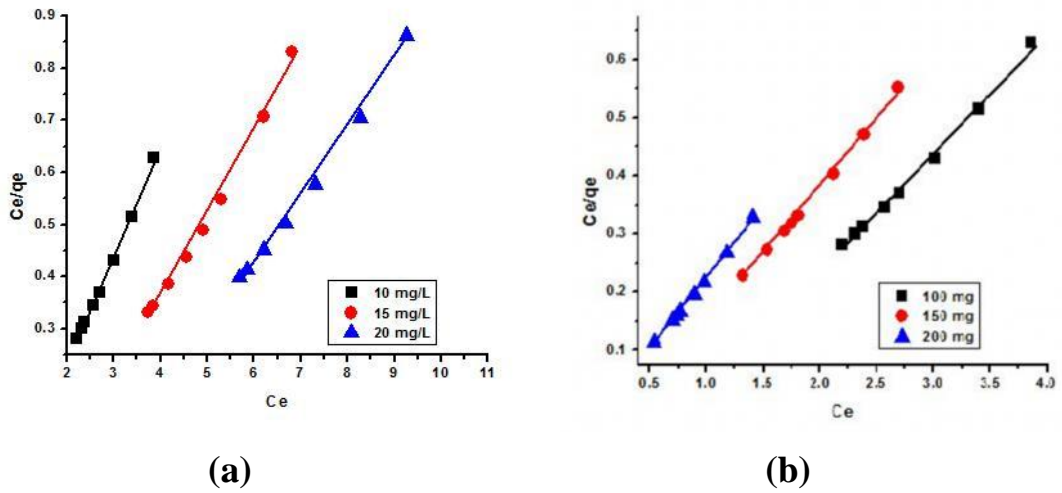
Table 4.5) for the present study which confirms the favorable adsorption of methylene blue on activated carbon under experimental conditions.

**Table 4. 5:Langmuir isotherm parameters for chemically activated carbon: NCC & PCC**

Samples	10ppm				15ppm				20ppm			
	Q <sub>m</sub> (mg/g)	K <sub>L</sub> (L/mg)	R <sup>2</sup>	R <sub>L</sub>	Q <sub>m</sub> (mg/g)	K <sub>L</sub> (L/mg)	R <sup>2</sup>	R <sub>L</sub>	Q <sub>m</sub> (mg/g)	K <sub>L</sub> (L/mg)	R <sup>2</sup>	R <sub>L</sub>
NCC100	4.83	1.13	0.995	0.08	6.23	0.565	0.992	0.10	7.02	0.325	0.985	0.13
NCC150	4.22	2.55	0.997	0.03	5.02	0.884	0.991	0.07	5.59	0.441	0.987	0.10
NCC200	4.05	11.15	0.999	0.00	4.95	2.19	0.95	0.02	5.31	0.745	0.992	0.06
PCC100	2.97	0.49	0.969	0.16	3.67	0.26	0.996	0.20	4.04	0.166	0.994	0.23
PCC150	2.50	0.69	0.995	0.12	3.06	0.34	0.995	0.16	3.40	0.065	0.995	0.43
PCC200	2.45	1.17	0.994	0.07	3.02	0.51	0.996	0.11	3.53	0.311	0.993	0.13

**Table 4. 6:Langmuir isotherm parameters for physically activated carbon: SCC & CCC**

Samples	100ppm				150ppm				200ppm			
	Q <sub>m</sub> (mg/g)	K <sub>L</sub> (L/mg)	R <sup>2</sup>	R <sub>L</sub>	Q <sub>m</sub> (mg/g)	K <sub>L</sub> (L/mg)	R <sup>2</sup>	R <sub>L</sub>	Q <sub>m</sub> (mg/g)	K <sub>L</sub> (L/mg)	R <sup>2</sup>	R <sub>L</sub>
CCC100	62.89	0.281	.995	0.03	84.03	0.124	.992	0.05	93.45	0.054	.994	0.08
CCC150	60.6	9.16	.999	0.001	73.52	0.65	.992	0.01	85.47	0.214	.985	0.02
CCC200	49.01	2.15	1	0.004	94.33	13.25	.999	.0005	86.20	2.03	.999	.002
SCC100	50.76	0.209	.968	0.04	64.93	0.070	.969	0.12	53.76	0.022	.986	0.69
SCC150	40.65	0.46	.979	0.02	50	0.104	.978	0.08	53.76	0.042	.983	0.10
SCC200	47.16	26.5	.999	.0003	45.04	5.59	.989	0.001	45.66	0.054	.985	0.08



**Figure 4. 8:Langmuir adsorption isotherm of MB at 300K on NCC: (a) For 100 mg adsorbent dose with different MB conc. (b) For 10 mg/L MB conc with different adsorbent dose.**

#### 4.4 Adsorption kinetics

Various kinetic models were studied to understand the kinetics of the adsorption of MB on activated carbon as already mentioned in chapter 3. The parameters of pseudo first order kinetics were calculated for chemically treated (as shown in Table 4.7) and physically treated (as shown in Table 4.8) carbons. Pseudo second order kinetics was found to be the best fitted model for adsorption of MB on activated carbons on the basis of quantitative comparison made by using correlation coefficient values. The parameters are shown in Table 4.9 and Table 4.10 and a linear plot of  $t/q$  v/s  $t$  in Fig. 4.9.

**Table 4. 7:Parameters for pseudo first order kinetics for NCC & PCC**

Samples	10ppm			15ppm			20ppm		
	$K_1$	$q_e$	$R^2$	$K_1$	$q_e$	$R^2$	$K_1$	$q_e$	$R^2$
NCC100	0.009	5.59	0.682	0.009	9.50	0.768	0.009	13.70	0.806
NCC150	0.004	6.63	0.518	0.005	11.11	0.702	0.004	15.43	0.724
NCC200	0.003	7.05	0.408	0.003	11.39	0.560	0.003	15.95	0.619
PCC100	0.005	6.36	0.518	0.004	10.27	0.521	0.004	14.46	0.557
PCC150	0.003	7.4	0.516	0.0029	11.57	0.507	0.0026	16.02	0.538
PCC200	0.002	7.79	0.449	0.0024	12.11	0.503	0.0023	16.58	0.548

**Table 4. 8:Parameters for pseudo first order kinetics for CCC & SCC**

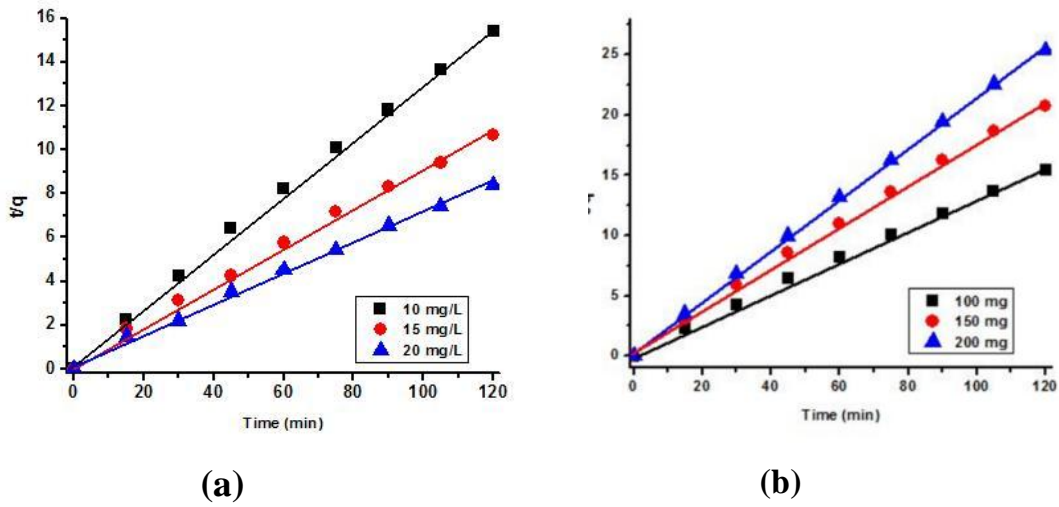
Samples	100ppm			150ppm			200ppm		
	K <sub>1</sub>	q <sub>e</sub>	R <sup>2</sup>	K <sub>1</sub>	q <sub>e</sub>	R <sup>2</sup>	K <sub>1</sub>	q <sub>e</sub>	R <sup>2</sup>
CCC100	0.030	48.98	0.933	0.028	77.61	0.939	0.0261	86.70	0.919
CCC150	0.108	50.50	0.871	0.036	45.69	0.928	0.032	67.69	0.937
CCC200	0.359	61.55	0.941	0.197	115.59	0.900	0.089	64.97	0.913
SCC100	0.049	87.35	0.940	0.025	105.63	0.936	0.011	101.49	0.837
SCC150	0.051	80.64	0.808	0.016	64.71	0.937	0.011	80.64	0.849
SCC200	0.141	27.38	0.893	0.007	64.71	0.751	0.011	56.82	0.813

**Table 4. 9:Parameters for pseudo second order kinetics for NCC & PCC**

Samples	10ppm			15ppm			20ppm		
	q <sub>e</sub> (mg/g)	K <sub>2</sub> (gmg <sup>-1</sup> h <sup>-1</sup> )	R <sup>2</sup>	q <sub>e</sub> (mg/g)	K <sub>2</sub> (gmg <sup>-1</sup> h <sup>-1</sup> )	R <sup>2</sup>	q <sub>e</sub> (mg/g)	K <sub>2</sub> (gmg <sup>-1</sup> h <sup>-1</sup> )	R <sup>2</sup>
NCC100	7.9	0.129	0.991	11.58	0.161	0.994	14.90	0.129	0.991
NCC150	5.79	0.337	0.998	8.53	0.150	0.992	10.66	0.132	0.990
NCC200	4.73	0.653	0.999	6.87	0.242	0.999	8.47	0.175	0.993
PCC100	6.13	0.411	0.999	8.18	0.323	0.998	10.26	0.275	0.998
PCC150	4.67	0.357	0.999	6.23	0.373	0.997	7.61	0.257	0.997
PCC200	3.77	0.881	0.992	533	0.321	0.996	6.74	0.225	0.995

**Table 4. 10:Parameters for pseudo second order kinetics for CCC & SCC**

Samples	100ppm			150ppm			200ppm		
	q <sub>e</sub> (mg/g)	K <sub>2</sub> (gmg <sup>-1</sup> h <sup>-1</sup> )	R <sup>2</sup>	q <sub>e</sub> (mg/g)	K <sub>2</sub> (gmg <sup>-1</sup> h <sup>-1</sup> )	R <sup>2</sup>	q <sub>e</sub> (mg/g)	K <sub>2</sub> (gmg <sup>-1</sup> h <sup>-1</sup> )	R <sup>2</sup>
CCC100	91.74	0.233	0.996	133.3	0.195	0.993	161.29	0.22	0.996
CCC150	66.67	1.25	0.999	101.01	0.310	0.998	131.57	0.225	0.998
CCC200	50	11.11	0.999	100	2.12	0.999	100	0.694	0.998
SCC100	101.1	0.111	0.987	131.57	0.106	0.966	133.33	0.162	0.993
SCC150	68.49	0.168	0.994	93.45	0.108	0.987	107.52	0.130	0.990
SCC200	50.25	2.58	0.999	71.42	0.149	0.993	84.03	0.160	0.995



**Figure 4. 9:Pseudo second order kinetics for MB adsorption on NCC (a) For 100 mg adsorbent dose with different MB conc. (b) For 10 mg/L MB conc with different adsorbent dose.**

Other models which were investigated to study the kinetics of adsorption are intraparticle diffusion and Evolich model. The parameters calculated for intraparticle diffusion model and Evolich model are listed in Table 4.11, Table 4.12, Table 4.13 and Table 4.14.

**Table 4. 11:Parameters for Intraparticle diffusion kinetic model for NCC & PCC**

Samples	10ppm			15ppm			20ppm		
	$K_d$	$C_i$	$R^2$	$K_d$	$C_i$	$R^2$	$K_d$	$C_i$	$R^2$
NCC100	0.255	4.93	0.948	0.454	6.47	0.988	0.697	7.02	0.984
NCC150	0.123	4.41	0.974	0.345	4.62	0.993	0.471	5.29	0.991
NCC200	0.057	4.09	0.975	0.193	4.70	0.991	0.293	5.12	0.994
PCC100	0.476	1.76	0.724	0.628	2.33	0.727	0.802	2.71	0.761
PCC150	0.367	1.28	0.745	0.483	1.73	0.738	0.591	2.03	0.762
PCC200	0.298	1.12	0.207	0.415	1.47	0.742	0.524	1.72	0.772

**Table 4. 12:Parameters for Intraparticle diffusion kinetic model for CCC & SCC**

Samples	100ppm			150ppm			200ppm		
	$K_d$	$C_i$	$R^2$	$K_d$	$C_i$	$R^2$	$K_d$	$C_i$	$R^2$
CCC100	3.12	58.56	0.991	5.38	77.05	0.995	6.26	97.64	0.987

CCC150	1.24	57.061	0.988	2.99	69.78	0.891	4.82	80.18	0898
CCC200	0.44	47.66	0.958	1.76	88.24	0.972	3.10	75.75	0.970
SCC100	6.28	34.43	0.977	7.49	49.67	0.914	6.59	64.50	0.963
SCC150	3.52	32.55	0.926	4.83	38.48	0.995	4.98	51.44	0.992
SCC200	0.81	44.72	0.967	2.97	37.87	0.992	3.53	44.92	0.979

**Table 4. 13:Parameters for Evolich model of kinetics for NCC & PCC**

Samples	10ppm			15ppm			20ppm		
			R <sup>2</sup>			R <sup>2</sup>			R <sup>2</sup>
NCC100	4.64	1.20	0.994	2.27	0.627	0.982	1.08	0.40	0.98
NCC150	8.29	2.28	0.974	2.03	0.825	0.979	1.41	0.60	0.97
NCC200	18.48	4.95	0.985	5.17	1.47	0.983	3.13	0.96	0.96
PCC100	6.42	1.81	0.927	5.05	2.09	0.931	5.17	0.98	0.99
PCC150	7.71	1.54	0.991	6.29	1.78	0.972	5.41	1.36	0.996
PCC200	3.57	2.09	0.667	6.28	2.09	0.990	4.70	1.43	0.970

**Table 4. 14:Parameters for Evolich model of kinetics for CCC & SCC**

Samples	100ppm			150ppm			200ppm		
			R <sup>2</sup>			R <sup>2</sup>			R <sup>2</sup>
CCC100	4.06	0.097	0.961	2.835	0.057	0.969	3.13	0.048	0.978
CCC150	16.54	0.310	0.989	5.01	0.096	0.970	3.11	0.060	0.971
CCC200	49.59	1.05	0.983	19.32	0.231	0.956	7.84	0.120	0.945
SCC100	0.197	0.050	0.996	0.136	0.038	0.897	1.33	0.045	0.984
SCC150	1.274	0.088	0.980	0.839	0.063	0.974	1.55	0.061	0.976
SCC200	21.841	0.511	0.993	2.26	0.102	0.967	2.28	0.086	0.987

#### 4.5 Thermodynamic parameters

The values of thermodynamic parameters ( $\Delta G$ ,  $\Delta H$  and  $\Delta S$ ) showed that all adsorption experiments carried out by using physically and chemically treated carbon are spontaneous. As observed from Table 4.15, for 10 mg/L MB solution,  $\Delta G$  increases from -3.13 to -7.09 kJ mol<sup>-1</sup> for NCC and -1.06 to -2.14 kJ mol<sup>-1</sup> for PCC with increase in the adsorbent dose from 0.1-0.2 g. With increase in the MB concentration from 10-20 mg/L,  $\Delta G$  found to decrease from -3.13 to -2.27 kJ mol<sup>-1</sup> for NCC and -1.06 to -0.054 kJ mol<sup>-1</sup> for PCC. Similarly, for 100 mg/L MB solution, the  $\Delta G$  increases from -6.05 to -28.52 kJ mol<sup>-1</sup> for

CCC and -7.81 to -11.14 kJ mol<sup>-1</sup> for SCC with increase in the adsorbent dose from 0.1-0.2g. The  $\Delta G$  was found to decrease for 0.1 g of adsorbent dose on increasing the MB dye concentration from 100-200 mg/L. It decreased from -6.05 to -3.84 kJ mol<sup>-1</sup> for CCC and -7.81 to -1.81 kJ mol<sup>-1</sup> for SCC as shown in Table 4.16.

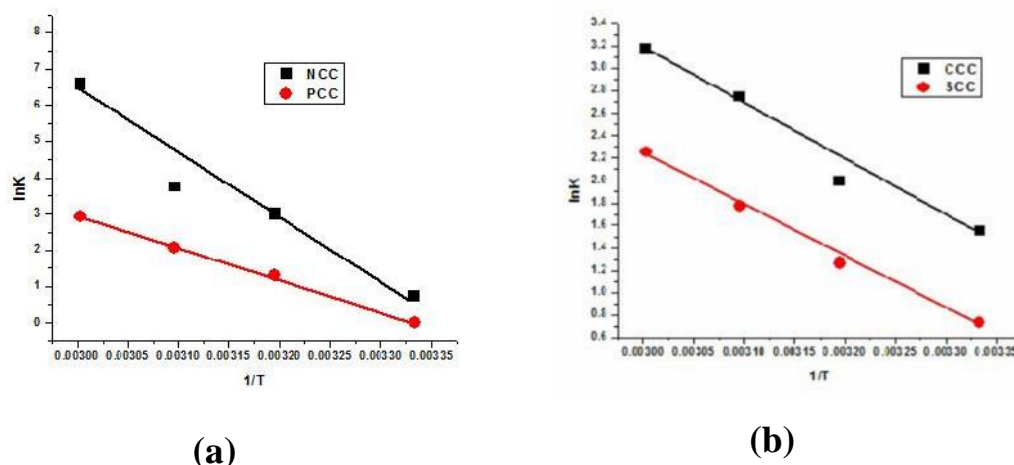
**Table 4. 15:Change in Gibbs free energy for MB adsorption on NCC & PCC**

Samples	G (kJ mol <sup>-1</sup> )		
	10ppm	15ppm	20ppm
NCC100	-3.13	-2.74	-2.27
NCC150	-4.66	-3.95	-3.20
NCC200	-7.09	-5.48	-4.10
PCC100	-1.06	-0.43	-0.054
PCC150	-1.99	-1.20	-0.63
PCC200	-2.14	-2.14	-1.79

**Table 4. 16:Change in Gibbs free energy for MB adsorption on CCC & SCC**

Samples	G (kJ mol <sup>-1</sup> )		
	100ppm	150ppm	200ppm
CCC100	-6.05	-5.44	-3.84
CCC150	-28.52	-11.07	-8.83
CCC200	-29.92	-24.54	-11.94
SCC100	-7.81	-4.84	-1.81
SCC150	-8.61	-5.44	-3.43
SCC200	-11.14	-6.28	-3.84

A linear plot of  $\ln k$  v/s  $1/T$  as shown in Fig. 4.10, was drawn to calculate the thermodynamic parameters, change in enthalpy  $\Delta H$  and change in entropy  $\Delta S$  as summarized in Table 4.17.



**Figure 4. 10:Determination of thermodynamic parameters (a) NCC & PCC (b) CCC & SCC**

**Table 4. 17:Change in enthalpy & entropy for various activated carbons**

Sample	S (kJ mol <sup>-1</sup> )	H (kJ mol <sup>-1</sup> )
NCC	5.09	151.63
PCC	2.41	72.29
SCC	1.33	38.45
CCC	1.57	43.27

#### 4.6 Conclusions

Corn cobs were used as a bio waste source for preparation of carbon, from which activated carbons were developed by both chemical (with nitric acid, hydrogen peroxide) and physical treatments (with carbon dioxide and steam). Nitrogen adsorption studies confirmed the high surface of the carbons and amongst these two treatments, physical treatment resulted the highest surface area (upto 650 m<sup>2</sup>/g). It was interesting to observe that the surface chemistry of carbons also change on varying the type of treatment, where humidified CO<sub>2</sub> treatment resulted carbons with highly acidic surface, as confirmed by temperature programmed decomposition. In order to estimate the performance of these carbons, MB removal from aqueous solutions was studied as a model reaction. Typical results indicated that among chemically activated carbons, nitric acid treated (NCC) sample exhibited greater efficiency

in adsorbing MB than peroxide treated carbon (PCC) while CO<sub>2</sub> treated carbon (CCC) showed the best performance among physically treated carbons. The equilibrium data was in accordance with monolayer Langmuir adsorption isotherm which confirms physisorption followed by chemisorption. The value of  $R_L$  found out to be in between 0-1 for all adsorption studies which further confirms the favorable adsorption of MB on activated carbon. Adsorption kinetics follows pseudo second order model showing maximum interactions within first 120 min. The present study demonstrates a viable approach for the preparation of tailor made carbons from the bio-waste corn cobs and their potential in removing MB from aqueous streams.



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