

**Department of Chemical Engineering  
Faculty of Science and Engineering**

**Removal of Methylene Blue Contaminant by Natural and Modified  
Low Cost Agricultural By-Product**

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**This thesis is presented for the Degree of  
Doctor of Philosophy  
of  
Curtin University**

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# DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Signature: .....

Date: .....

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This work is dedicated to my mother and father for their loving support

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## **PUBLICATIONS**

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## ABSTRACT

The removal of dyes from wastewater is a matter of great interest in the field of waste water treatment. The effluents from many industries often contain one or more toxic dyes. Methylene blue (MB) is one of the most common water-soluble dyes. Therefore, an increased interest has been focused on removing such dyes from wastewaters. In general, several methods are used for the removal of dyes from wastewater. Among the treatment methods, adsorption is comparatively superior. Agricultural wastes are renewable and available abundantly at no or low costs. Due to the abundant availability at no or low costs, little processing cost and ability to biodegrade pine cone and pine leaves materials, an agricultural by-product, were identified as a potential adsorbent material for wastewater treatment in this study. The raw pine tree materials, however, needs to be modified, chemically by pre-treating with either sodium hydroxide or hydrochloric acid. Generally, the treatment with NaOH and HCl increases the negatively charged sites on pine tree material surfaces. In this study, six different adsorbents were prepared, raw pine cone (PC), pre-treated with different concentrations of sodium hydroxide (0.1 and 0.05 M) (PC1 and PC2), raw pine leaves (PL), pine leaves modified with (0.1 M ) of hydrochloric acid (PLAT) and pre-treated raw pine leaves with (0.1 M ) sodium hydroxide (PLBT).

Several techniques were employed to characterize pine cone and pine leave materials to understand the properties of raw and modified pine tree materials as well as to study the effects of modification on the textural and surface properties of the raw pine cone and pine leaves. For the chemically modified pine cone and pine leaves, higher BET surface areas were observed. Higher bulk density of treated pine cone and pine leaves was due to the chemically modified pine tree material surfaces. The scanning electron microscopy SEM of all the prepared adsorbents showed the highly irregular shapes and sizes. The treatment with base and acid solutions partly removed the protective thin wax on pine material surfaces. The chemically modified surface appeared to be rough, indicating that the surface had been covered with organic

molecules. FT-IR spectra of raw and treated pine tree materials (PC, PC1, PC2, PL, PLAT, and PLBT) did not show any radical changes indicating that the treatment with mild base and acid solutions did not significantly alter the chemical properties of the raw pine materials. Two new bands lying at about 2901.4 and 2879.56  $\text{cm}^{-1}$  on both PC1 and PC2, 2921.7 and 2922.6  $\text{cm}^{-1}$  on both PLBT and PLAT were observed.

The experimental study showed the effectiveness of the prepared adsorbents for the removal of methylene blue MB dye from its aqueous solution. The batch adsorption tests performed using raw and treated pine cone on methylene blue MB dye showed low removal percentage of dyes by both raw and treated pine cones. The batch study also revealed that the adsorption was a function of initial dye concentration, contact time, solution pH, salt concentration, agitation speed, adsorbent dosage, and system temperature. Adsorption capacity of MB dye uptake by raw and treated pine cone biomass increased with increase in initial dye concentration, contact time, and solution pH but decreased with increase in, salt concentration and system temperature. The kinetic experiments revealed that adsorption of dyes were rapid at initial stage followed by a slower phase where equilibrium removal was achieved. Based on kinetic study of adsorption of PC, PC1, and PC2 on methylene blue (MB) dye, the pseudo second- order model best fitted the kinetic data. The experimental isotherm data of dye adsorption on raw and modified pine cone indicated that the adsorption was well fitted by both the Langmuir and the Freundlich isotherm models within the initial dye concentration range. The Langmuir batch adsorption capacities of MB dye was 129.87 mg/g occurred at pH of 9.02 for an initial dye concentration of 10 mg/L by raw pine cone, whereas for treated pine cone with two different NaOH concentrations PC1 and PC2 the values were 142.25 mg/g and 139.23 mg/g respectively at the same experimental conditions. Desorption experiments also showed that the dye loaded pine cone materials was stable at low solution pH. A single-stage batch adsorber design for the MB adsorption onto pine cone and modified pine cone was presented based on the Langmuir isotherm model equation, and the thermodynamic parameters, such as standard Gibbs free energy ( $\Delta G^{\circ}$ ), standard enthalpy ( $\Delta H^{\circ}$ ) and standard entropy ( $\Delta S^{\circ}$ ), also showed adsorption process is spontaneous, exothermic and physical in nature.

In the same manner to pine cones, the applicability of the prepared pine leaves (PL, PLAT, and PLBT) in removing methylene blue (MB) dye from its aqueous solution was studied. These adsorption tests were performed by using all three adsorbents (PL, PLAT, and PLBT) by batch adsorption under various conditions such as initial dye concentration, contact time, solution pH, salt concentration, agitation speed, adsorbent dosage, and system temperature. Kinetic experiments clearly indicated that adsorption of MB on both pine leaves biomass is a three step process: a rapid adsorption of dye onto the external surface followed by intra-particle diffusion into the interior of adsorbent which has also been confirmed by intra-particle diffusion model. The kinetic study revealed that equilibrium time was short and the pseudo second- order model provided the best correlation for the kinetic adsorption data of methylene blue MB dye on PL, PLAT, and PLBT. The isotherm data for sorption of methylene blue MB dye onto raw and treated pine leaves indicated that the Langmuir model fitted better than the Freundlich isotherm model within the initial dye concentration range with the maximum adsorption capacities of MB dye at 126.58 mg/g by raw pine leaves, whereas for acid and base treated pine leaves the maximum adsorption went up to 140.84 and 131.58 mg/g for PLAT and PLBT respectively under the same experimental conditions. Desorption experiments also showed that desorption of methylene blue decreased as the pH increased. However, in contrast to pine cone, the thermodynamic analysis indicates that the process was endothermic and physical in nature in the case of pine leaves.

The applicability of the adsorbents for methylene blue MB dye removal by pine cones was also tested in a fixed bed column study. The breakthrough curves indicated the favourable performance of pine cones for the removal of methylene blue MB dye and it strongly depended on the flow rate, initial MB dye concentration, and bed height. The results showed that the amount of total sorbed dye, equilibrium dye uptake, mass transfer zone, and total percent removal increased with increasing initial MB dye concentration. Also when flow rate increased the breakthrough time decreased and with the increase in the height of the bed, the breakthrough increased, and the total percent removal increased from 38.9% to 46.1% when the height of the bed increase from 10 cm to 15 cm. To determine the column kinetic parameters of fixed bed columns, the Thomas, Yoon–Nelson, and Bed Depth Service Time models

were used for fitting the experimental data obtained from dynamic studies. Thomas model showed that the value of maximum solid-phase concentration ( $q_0$ ) decreased when the flow rate and the height of the bed increased but increase with increasing initial methylene blue MB dye concentration and the value of Thomas rate constant ( $K_{Th}$ ) increased with higher flow rate but decreased with increasing initial methylene blue MB dye concentration and the height of the bed. Yoon–Nelson model showed that the time required to achieve 50% adsorbate breakthrough  $\tau$  fitted well with the experimental data ( $\tau_{50\% \text{ exp}}$ ) in the entire column adsorption system and that the rate constant  $K_{YN}$  increased with both increasing flow rate and initial MB dye concentration but decreased with increasing bed height. The Bed Depth Service Time (BDST) model showed that the rate constant ( $K_0$ ) decreased when both the bed heights and the initial MB dye concentration increased, but increased with higher flow rate and the value of the volumetric sorption capacity of the bed ( $N_0$ ) increased with increasing flow rate, initial MB dye concentration, and bed height. On the whole, all three models fitted the experimental data very well.

# **CHAPTER 1**

## **INTRODUCTION**

## 1.1 General overview

Freshwater is already a limiting resource in many parts of the world (Ahalya et al., 2005). It will become even more limiting due to increased population, and climate change. This limitation will be caused not just by increased demand for water, but also by pollution in freshwater ecosystems. Pollution decreases the supply of used water and increases the cost of purifying it. Major water pollutants are organic and inorganic in nature. As most of the industrial processes are to be found close to the water bodies, they are increasingly polluted by a number of organic and inorganic materials. Potential pollutants are affecting human health and interfere with industrial or agricultural water use. Dyeing industry effluents are one of the major problematic wastewaters to be treated not only for their high chemical oxygen demand, but also for colour, which is the first contaminant apparent to the human eye. Dyes may affect the photosynthetic activity in aquatic life and may also be toxic to some aquatic life due to the presence of aromatics, metals, etc. in them (Ramachandra, 2008, Ramachandra et al., 2002). Dyes have created much concern regarding its use, due to its toxic effects. It has been reported to cause carcinogenesis, mutagenesis, chromosomal fractures, and respiratory toxicity. Table 1 presents the source colour concentrations, their limits and quantum of water generated from industries.

**Table 1.1** Colour concentrations limits and quantum of water generated from industries (Anjaneyulu et al., 2005)

<i>No</i>	<i>Industry</i>	<i>Quantum of water generated standards m<sup>3</sup>/Ton</i>	<i>Colour concentration hazen units</i>	<i>Colour limits hazen units (USPHS)*</i>
1	Sugar	0.4 m <sup>3</sup> /Ton cane crushed	150-200	5-10
2	Pulp and paper			
	Large	175 m <sup>3</sup> /Ton of paper	100-600	0-10
	Small	150 m <sup>3</sup> /Ton of paper		
3	Textile	120 m <sup>3</sup> /Ton of fibre produces	1100-1300	0-25
4	Tannery	28 m <sup>3</sup> /Ton of Raw hide	400-500	10-50
5	Kraft mill	40 m <sup>3</sup> /Ton	2100-2300	10-40
6	Brewery	0.25 m <sup>3</sup> /kl Beer produces	200-300	5-10
7	Distillery	12 m <sup>3</sup> /kl alcohol produces	200-300	5-10

\* *USPHS*: United States Public Health Services.

The effluents from many industries such as cosmetic, textiles, leather , printing, plastics , paper, rubber , dye manufacturing, and food processing contains various types of toxic dyes (Ayyappan et al., 2005, Dawood and Sen, 2012). Meanwhile, about 10,000 different commercial dyes and pigments exist, most of which are difficult to biodegrade due to the complex aromatic structure and synthetic origin. Over 700,000 metric tons of dye are produced annually worldwide, while 10-15% of the dyes were estimated to be lost in the effluent during dyeing process (Yu et al., 2009). Water is particularly vulnerable to the contamination from discharge of wastes from these industrial activities. The random discharge of untreated or partially treated effluents into the natural environment makes a major ecological problem.

Methylene blue (MB) is the most common soluble dye in water, in general used for cotton, dyeing leather, medicinal purposes, printing, and tannin (Gupta et al., 2004). Even though this dye is not significantly toxic to human being, it can cause eye irritation, and skin irritation (Sen et al., 2011, Tsai et al., 2009). Methylene blue (MB) may cause vomiting, nausea, diarrhoea , profuse sweating, mental confusion, and gastritis and it can make difficult breathing (Sen et al., 2011). Thus, removal of such dyes from the wastewater effluents is essential.

Numerous methods such as reverse osmosis, ion exchange, membrane filtration, conventional coagulation, chemical precipitation, and adsorption are the common practices for the removal of dyes from wastewater (Mahmoode et al., 2011, Dawood and Sen, 2012). Among all of these methods adsorption is a reasonably superior technique because of high quality of treated, ability to treat dyes more concentrated from other techniques and low cost(Mahmoode et al., 2011, Sen et al., 2011). The common adsorbents used are activated carbons, because it has high adsorption capacity for a large number of organic/inorganic contaminates. However, uses of commercial activated carbon are not cost effective and regeneration remains a problem.

## **1.2 Research motivation**

Toxic Coloured wastewater discharged with industrial effluents usually find their way into water bodies such as lakes, rivers and streams and therefore increasing the intensity of these pollutants in such water bodies (Ofomaja et al., 2009). It, therefore, becomes necessary to remove these contaminants from these wastewaters by an appropriate treatment before releasing them into the environment. Removal of dyes before it is discharged into the environment can be accomplished by a number of processes such as chemical precipitation, sedimentation, solvent extraction, reverse osmosis and ion exchange (Ahmad et al., 2009). Adsorption is the process through which a substance, originally present in one phase, is removed from that phase by accumulation at the interface between that phase and a separate phase. Adsorption can occur at any solid fluid interface, gas-solid interface or liquid-solid interface, substance thus adsorbed on the surface is called the adsorbate and the substance on which it is absorbed is known as adsorbent (Dabrowski, 2001).

Adsorption has been found to be superior to other techniques for water reuse in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants without resulting in the formation of harmful substances (Kumar et al., 1998).

Activated carbon is a very well known material that is used for this purpose. However, activated carbon is relatively expensive which limits its application. Many studies have been undertaken to investigate the use of alternative low-cost adsorbents such as peat, bentonite, steel plant slag, fly ash, china clay, maize cob, wood shavings, silica, agricultural by product such as rice husk, palm kernel, cocoa shell, etc. for colour removal. However, agricultural wastes offer advantages such as abundantly available, inexpensive, simplicity in technology. Due to these reasons, agricultural wastes have been chosen as an adsorbent to remove dye from its solutions. Development of low cost adsorbent materials based on agricultural by-products as an alternative to activated carbon is another motivation of this study.

### **1.2.1 Significance of current study**

Many industrial and agricultural processes as well as mining activities have increased the concentration of toxic contaminants in water and wastewaters around the world. Removal of these potential pollutants from water and wastewater is very important for public health reasons. Adsorption has been observed to be an effective process for colour removal from dye wastewater. Use of activated carbon has been found to be effective, but it is too expensive and regeneration makes its limitation.

Adsorption techniques are widely used to remove certain classes of contaminants from wastewaters, especially those that are not easily biodegradable such as dyes. Decolourisation is a result of two mechanisms: adsorption and ion exchange, and is influenced by many physio-chemical factors such as dye/sorbent interaction, sorbent surface area, particle size, temperature, solution pH, concentration, and contact time (Sulak et al., 2007). Adsorption of dyes is dependent on dye properties such as molecular structure and type, number and position of substituent's in the dye molecule (Reife and Freeman, 1996). Natural materials, or the wastes/by-products of industries, or synthetically prepared materials, which are inexpensive and can be used directly or partial treatment as adsorbents, are generally called low-cost adsorbents. The major advantage of this adsorbent in treatment include low cost, high efficiency, minimization of chemical and biological sludge, regeneration of adsorbent and possibility of dye recovery (Das et al., 2006). Adsorption is increased by the presence of hydroxyl, nitro and azo groups in the dye molecule (Reife and Freeman, 1996). The presence of variety of functional groups in the sorbents makes them selective and highly capable of sorption of dyes from wastewater.

The removal of dyes and organics in an economical way remains an important problem although a number of systems have been developed with adsorption technique. A commonly used commercial activated carbon adsorbent is effective in the removal of dye or other organic/inorganic from aqueous solution due to their structural characteristics. But some of its disadvantages are the high cost and difficulty to regenerate which gives the increase in the cost of the wastewater treatment. Thus there is demand for alternative adsorbents which are made up of inexpensive material and locally available such that the adsorption process will become economically viable. Therefore, the significance of this study are:

- To find an alternative cost effective agricultural by-product based novel adsorbent in the removal of dye from its aqueous solution. This study was undertaken to utilize raw and treated agricultural wastes pine cone and pine leaves in the removal of cationic dye Methylene Blue in a more economical way.
- This developed pine cone and pine leaves adsorbents may also be useful in the removal of other inorganic/organic from industrial effluents.
- Adsorption mechanism depends on biomass adsorbents origin and structure characteristics. Therefore this present study will explore the mechanism of adsorption and adsorption kinetics of dye by raw and treated pine biomass.

## 1.3 Research Methodology

This work was conducted by the following sequence;

### 1.3.1 Materials and Adsorbent

#### 1.3.1.1 Collection and preparation of adsorbent and adsorbate

##### a. Collection and preparation of adsorbent

##### 1. Pine Cone (*Pinus Radiate*)

Pine cones hang singly or in groups from branches near the top of pine trees. They have 50 to 80 scales, usually found in spiralling rows of five. Cones are cylindrical when closed. They are six to 20 centimetres long and about 2.5 centimetres wide. Soon after the cones mature, they open and release winged seeds (figure 1.1).



Figure 1.1 Pine cone

Pine cones were collected locally from Curtin University campus (Australia). The pine cone materials were washed several times with distilled water to remove impurity and then dried in an oven at 60 °C for 24 h. Dried pine cone was grounded by using a crusher. The resultant powders were passed through British Standard Sieves and particles below 100 µm were collected in a plastic container and were used as adsorbent for adsorption experiments.

## 2. Pine Leaves

Pine leaves (needles) are 6 to 12 centimetres long and clustered in groups of five. The needles are straight, flexible, soft to touch, dark blue-green in colour with finely toothed edges. They stay on trees for two or three years turning brown and falling off in the autumn (figure 1.2).

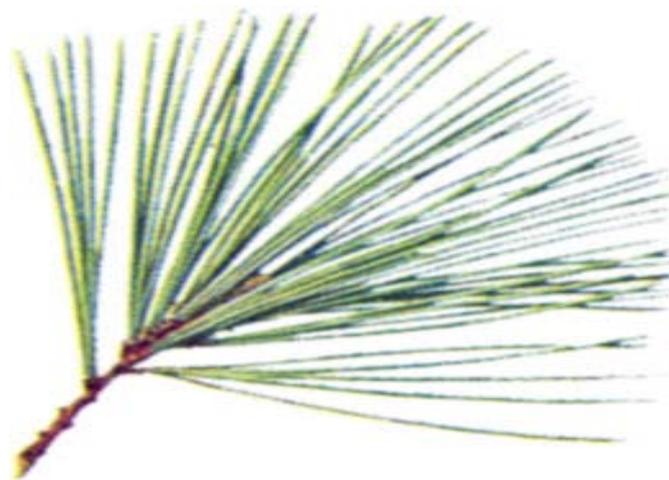


Figure 1.2 Pine leaves

The pine leaves were collected locally from Curtin University campus (Australia). The leaves were washed several times with distilled water to remove impurity such as sand then dried in an oven at 65°C for 1day. Dried pine leaves were cut into pieces (2.0 cm) then ground by using a crusher. The resultant powders were passed through British Standard Sieves and particles below 350µm were collected in a plastic container and used as adsorbent for adsorption experiments.

## 3. Modification of raw pine cone and raw pine tree leaves

Base and acid modified pine powder materials used as adsorbent was prepared by mixing 10 g of raw pine materials powder with 100 ml of 0.1M NaOH solution and with 100 ml of 0.1 M HCl solution. The whole reaction mixture was stirred in a magnetic stirrer for a period of 24 hr and then the powders were filtered and repeatedly washed with distilled water. The washed powders were then oven dried overnight at 50 °C and was used as adsorbent.

### b. Preparation of adsorbate

The basic cationic dye, Methylene Blue (MB), was tested as the model dye adsorbate in this study. The formula of methylene blue is  $C_{16}H_{18}N_3S^+Cl^- \cdot 3H_2O$ , and molecular weight as 319.85 g. The chemical structure of this dye is shown in Fig (1.3). It was supplied by Sigma-Aldrich Pty. Ltd., NSW, Australia, and of analytical grade. It was used without further purification. The stock dye solution was prepared by dissolving 1g of methylene blue in 1000 ml distilled water. The experimental solutions were obtained by diluting the stock dye solution with deionised water to give the appropriate concentration of the experimental solutions. The pH of the experimental solutions was adjusted by addition of either dilute 0.1 M HCl or 0.1 M NaOH solutions.

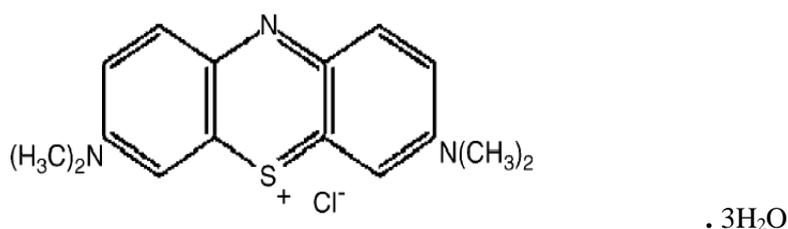


Figure 1.3 Chemical structure of Methylene Blue

#### 1.3.1.2 Characterisation of adsorbent

The surface morphology of adsorbent was found by scanning electron microscopy (SEM). The surface area of the adsorbent was measured by Brunaur Emmett Teller (BET). The zeta potential of the adsorbent was determined by Zeta potentiometer. The Fourier Transform Infrared spectroscopy (FTIR) was used to obtain the functional groups of the adsorbent. Bulk density of raw and modified pine biomass were determined.

### **1.3.2 Experimental procedure**

Adsorption measurement was determined by batch experiments of known amount of the adsorbent with 50 ml of aqueous methylene blue solutions of known concentration in a series of 250 ml conical flasks. The mixture was shaken at 150 rpm in a constant temperature at 30°C for 240 min. At predestined time, the bottles were withdrawn from the shaker, and the residual dye concentration in the reaction mixture was analysed followed by centrifuging the reaction mixture and then measuring the absorbance of the supernatant at the wavelength that correspond to the maximum absorbance of the sample. Dye concentration in the reaction mixture was calculated from the calibration curve. The pH value of suspension can be adjusted with either dilute HCl or NaOH solution. Adsorption experiments were conducted by varying initial solution pH, contact time, adsorbent dose, initial methylene blue dye concentration, temperature and salt concentration under the aspect of adsorption kinetics, adsorption isotherm and thermodynamic study.

### **1.3.3 Desorption study**

A desorption study helped to explain the mechanism and recovery of the adsorbate and adsorbent and it is important for the determination of the amount of dye that will possibly be washed out when it is exposed to the environment. The dried adsorbent was agitated with distilled water at different pH values of 3, 7 and 9 for the predetermined equilibrium time and then the desorbed dye was measured by UV spectrophotometer.

### **1.3.4 Column studies**

Since batch processes are usually limited to the treatment of small amounts of wastewater, a more practical alternative to eliminate dye from aqueous solution on a larger scale is required. Therefore, column experiments were performed in order to evaluate the removal and recovery of dye ions under various process conditions such as flow rate, bed height, dye concentration etc. Breakthrough plots were determined under various conditions.

## 1.4 Scope of this Study

The overall objectives of this study is to develop a cost-effective environmentally sustainable agricultural by product based on adsorbent and test its effectiveness in the removal of cationic dye, methylene blue (MB) from aqueous solution under various physiochemical conditions. The specific objectives are:

- Collection and characterization of natural agricultural by-product pine cone (*Pinus radiata*) and pine tree leaves which are locally available.
- Synthesis and characterization of modified pine cone and pine leaves adsorbents.
- Selection of adsorbate Methylene Blue (MB) as model pollutant dye.
- To study batch adsorption of methylene blue on raw and modified pine tree materials under various physiochemical parameters such as initial solution pH, contact time, adsorbent dose, initial methylene blue dye concentration, temperature and salt concentration.
- To find the optimum process parameters on MB adsorption.
- To explain the adsorption kinetics, thermodynamic and mechanism of methylene blue by raw and modified pine tree materials.
- To find the application characteristics of various kinetics models and isotherm models under a range of conditions.
- To study desorption of methylene blue.
- To perform column study experiments to find out various breakthrough plots under various process conditions.
- To apply various kinetic mass transfer models to column study.

## 1.5 Organization of Thesis

This thesis has been organized into seven chapters as outlined below and the structure of the thesis is summarized in Figure 1.4.

*Chapter 1* provides introductory information about the research project which includes the background and progress in this area, the significance of the study and brief research methodology.

*Chapter 2* covers the detailed literature overview and current state of the developments on sources for inexpensive materials to remove dye and determination of research gap.

*Chapter 3* establishes the characteristics of the raw and modified pine tree materials.

*Chapters 4 and 5* generally discuss the treatment of dye wastewater, using the prepared (raw and modified pine cone) and (raw and modified pine leaves) respectively. The discussions include the findings in batch experiments. The appropriate models were also employed to fit the experimental data.

*Chapter 6* presents the results of laboratory column experiments. In this chapter, emphasis has been given to examine the conditions such as influent flow rate, amount of pine cone, which leads to remove methylen blue.

Finally, in *Chapter 7*, an overview of the major conclusions of this work is presented along with some suggestions for further work.

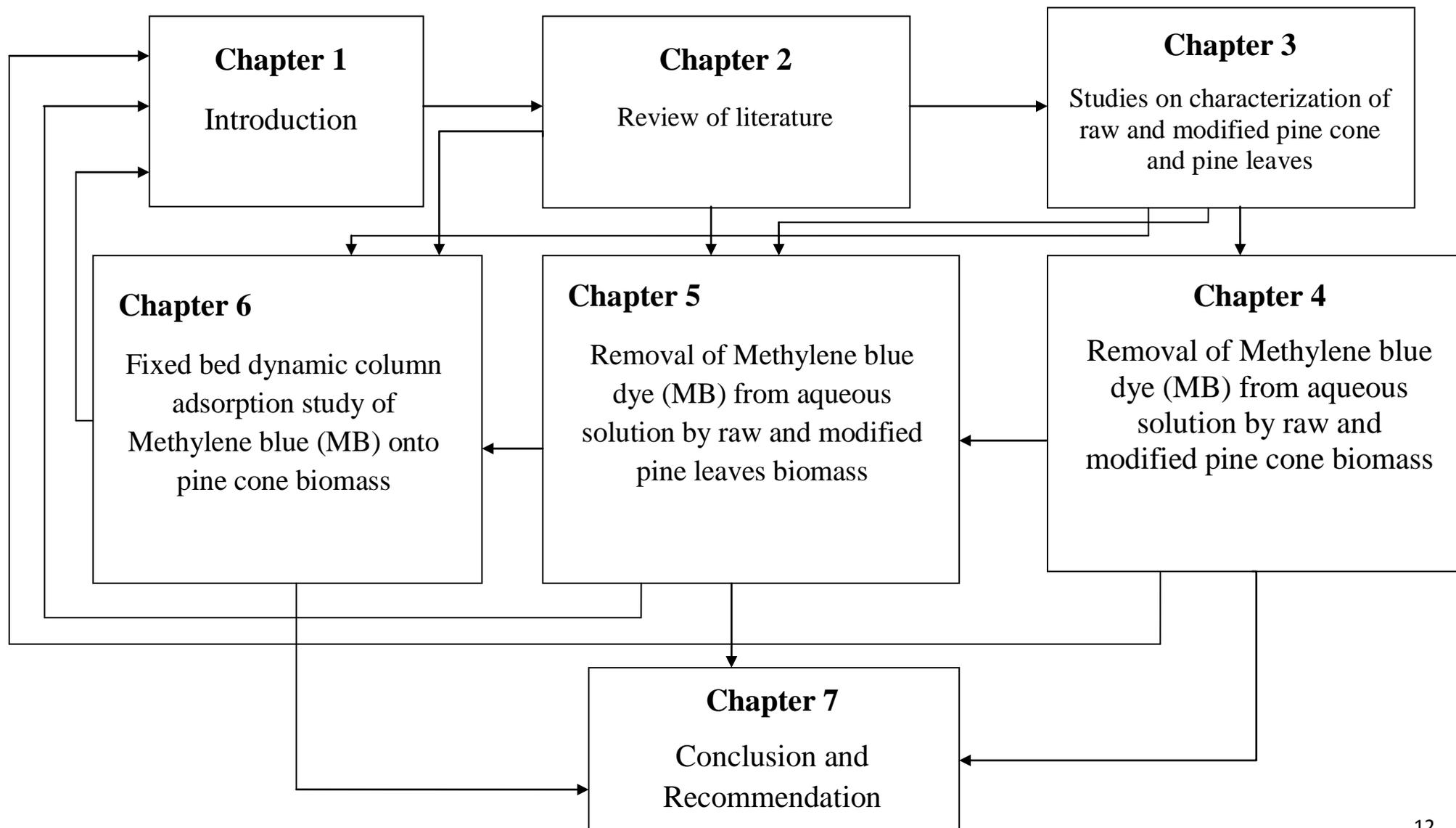


Figure 1.4 Thesis mapping

# **CHAPTER 2**

# **LITERATURE REVIEW**

## 2.1 Dyes in the Aquatic Ecosystems and Its Removal

Dyes are basically chemical compounds that can connect themselves to surfaces or fabrics to impart colour. The majority of dyes are complex organic molecules and are required for being resistant to many things such as the action of detergents. Synthetic dyes are widely used in industry, e.g., in various kinds of the textile industry (Gupta et al., 1992, Sokolowska-Gajda et al., 1996), in paper manufacture (Ivanov et al., 1996), agricultural sector (Kross et al., 1996, Cook and Linden, 1997), leather tanning industry (Kabdaşlı et al., 1999, Tünay et al., 1999), food technology (Bhat and Mathur, 1998), light-harvesting arrays (Bensalah et al., 2009), photo electrochemical cells (Wróbel et al., 2001), and in hair colourings (Scarpi et al., 1998). Synthetic dyes are also employed in ground water tracing (Field et al., 1995), for the determination of specific surface area of activated sludge (He and Tebo, 1998), sewage (Morgan-Sagastume et al., 1997) and wastewater treatment (Hsu and Chiang, 1997, Orhon et al., 1999), etc.

The exact quantity of dyes produced in the world is not identified. Exact data on the amount of dyes discharged in to the environment are also not available. However, the release of essential amounts of synthetic dyes to the environment has posed challenges to environmental scientists. Various methods such as adsorption, coagulation, advanced oxidation, membrane separation, etc are used in the removal of dyes from wastewater (Gupta, 2009). Study of recovery of dyes reveals adsorption as an efficacious process. Many textile industries use commercial activated carbon for the treatment of dye waste. The current research is focused on the need of alternatives to commercial activated carbon as the cost effective, potential adsorbent. Many researchers have reported the feasibility of using low cost adsorbents derived from natural materials, industrial solid wastes, agricultural by-products and biosorbents as precursors. The lignin cellulosic biomass behave as good adsorbents (Rehman et al., 2012). Different physical or chemical treatment may also be given to the raw biomass adsorbents for improving adsorption capacity.

## 2.2 Classification of Dyes

There are several ways for classification of commercial dyes. It can be classified in terms of structure, colour and application method (Clarke and Anliker, 1980). However, due to the complexities of the colour nomenclature from the chemical structure system, the classification based on application is often favourable (Gupta, 2009). The classification based on chemical structure for the common class of the dyes is presented in Table 2.1 whereas Table 2.2 represents the different applications based on chemical types (Hunger, 2007). Other than the above, dyes are also usually classified based on their particle charge upon dissolution in aqueous application medium (dye bath) (Mishra and Tripathy, 1993, Purkait et al., 2005) such as cationic (all basic dyes), anionic (direct, acid, and reactive dyes), and non-ionic (dispersed dyes).

**Table 2.1.** Classification of dyes according to the chemical structure adopted from (Ali, 2010)

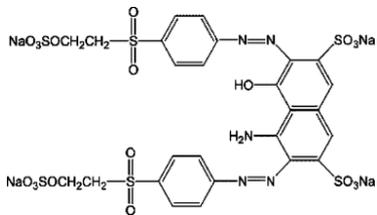
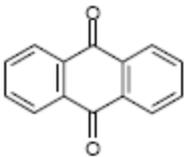
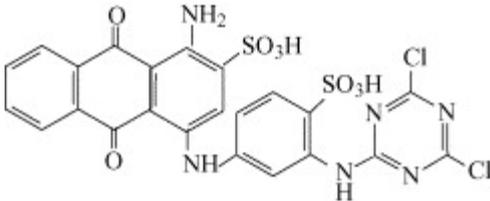
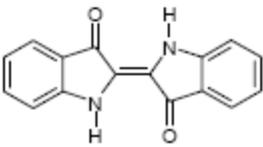
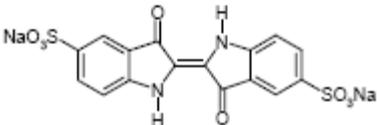
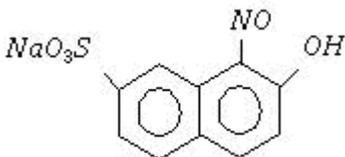
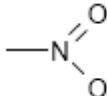
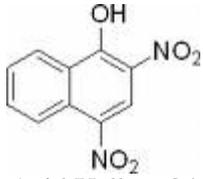
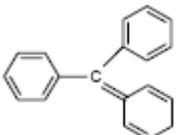
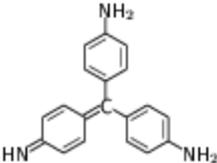
<i>Class</i>	<i>Chromospheres</i>	<i>Example</i>
<b>Azo dyes</b>		 <p>Reactive Black 5</p>
<b>Anthraquinone dyes</b>		 <p>Reactive Blue 4</p>
<b>Indigoid dyes</b>		 <p>Acid Blue 71</p>
<b>Nitroso dyes</b>		 <p>Acid green 1</p>
<b>Nitro dyes</b>		 <p>Acid Yellow 24</p>
<b>Triarylmethane dyes</b>		 <p>Basic red 9</p>

Table 2.2 Classification of dye based on their chemical nature adopted from (Hunger, 2007)

<i>Class</i>	<i>Substrate</i>	<i>Method of application</i>	<i>Chemical types</i>
<b>Acid</b>	Wool, nylon, silk, inks, leather and paper.	Generally from neutral to acidic bath.	Anthraquinone, xanthene, azo (including, nitroso, premetallized), nitro, and tryphenylmethane.
<b>Basic</b>	Inks, paper, polyacrylonitrile, treated nylon, and polyester	Applied from acidic dye baths.	Hemicyanine, azo, cyanine, diazahemicyanine, azine diphenylmethane, xanthene, triarylmethane, acridine, anthraquinone and oxazine.
<b>Direct</b>	Nylon, rayon, paper, leather and cotton.	Applied from neutral or a little alkaline baths containing additional electrolyte.	Phthalocyanine, azo, oxazine, and stilbene.
<b>Disperse</b>	Polyamide, acrylic polyester, acetate, and plastics	Fine aqueous dispersions often applied by high temperature/pressure or lower temperature carrier methods; dye maybe padded on cloth and thermo fixed.	Benzodifuranone, azo, anthraquinone, nitro, and styryl.
<b>Reactive</b>	Wool, cotton, silk and nylon.	Reactive site on dye reacts with functional group on fibre to bind dye covalently under influence of heat and pH.	anthraquinone, formazan, phthalocyanine, Azo, oxazine and basic.
<b>Sulphur</b>	Rayon and Cotton.	Aromatic substrate vatted with sodium sulphide and reoxidized to insoluble sulfur-containing products on fibre	Indeterminate structures
<b>Vat</b>	Wool and cotton.	Water-insoluble dyes solubilised by dropping with sodium hydrogensulfite, then exhausted on reoxidized and fibre.	Indigoids and Anthraquinone.

Several industries such as dyestuff, textile, paper, printing, carpet, plastic, food and cosmetic industry use dyes to provide colour to their products. These dyes are always present in industrial waste and consequently discharged generally to the water resources (Forgacs et al., 2004, Muthukumar and Selvakumar, 2004, Crini, 2006, Ong et al., 2007). Table 2.3 indicates the relative fixation of acid and reactive dyes (Easton, 1995).

**Table: 2.3** Estimation of degree of fixation and loss to effluent for different dye (Easton, 1995)

<i>Dye class</i>	<i>Fibre</i>	<i>Degree of fixation (%)</i>	<i>Loss of effluent</i>
<b>Acid</b>	Polyimide	89 – 95	5 - 20
<b>Basic</b>	Acrylic	95 – 100	0 - 5
<b>Direct</b>	Cellulose	70 –95	5 - 30
<b>Disperse</b>	Polyester	90 – 100	0 - 10
<b>Reactive</b>	Cellulose	50 – 90	10 -50
<b>Sulphur</b>	Cellulose	60 – 90	10 - 40
<b>Vat</b>	Cellulose	80 – 95	5 - 20

## 2.3 Toxicity Effects of Dyes

Basic dyes have high intensity of colours and are greatly visible even in very little concentration (Clarke and Anliker, 1980, Banat et al., 1996, Mittal and Gupta, 1996, Fu and Viraraghavan, 2001, Chu and Chen, 2002, Fu and Viraraghavan, 2002c). The complex dyes are generally chromium based, which is carcinogenic (Clarke and Anliker, 1980, Gupta et al., 1990, Mishra and Tripathy, 1993, Banat et al., 1996). Dyes may affect the photosynthetic activity in aquatic life due to decreased light penetration and may also be toxic to some aquatic life due to the presence of metals, aromatics, etc. (Clarke and Anliker, 1980, Gupta et al., 1990, Mishra and Tripathy, 1993, Banat et al., 1996, Mittal and Gupta, 1996, Fu and Viraraghavan, 2001, Lazar, 2005). Furthermore, dyes are also carcinogenic, mutagenic, or teratogenic in various microbiological, fish species. Additionally it also can cause severe damage to human beings such as dysfunction of kidney, reproductive system, liver brain and central nervous system (Kadirvelu et al., 2003). Table 2.4 shows the disadvantages according to different dye class

**Table 2.4** Disadvantages of different dye class (Robinson et al., 2001)

<i>Dye class</i>	<i>Disadvantages</i>
<b>Basic dyes</b>	It has high brilliance and intensity of colours and is highly visible even in a low concentration.
<b>Azo groups</b>	Their reductive cleavage of azo linkages is responsible for the formation of toxic amines in the effluent.
<b>Anthraquinone-based dyes</b>	It is most resistant to degradation due to their fused aromatic ring structure and thus remains coloured for a longer time in wastewater.

Due to the dyes toxic effects, dyes have generated much concern regarding its use. It is known informed to cause mutagenesis, chromosomal fractures, carcinogenesis, and respiratory toxicity. The mutagenic activity of textile wastewater effluents, using the salmonella assay and contributed the maximum percentage of mutagenic effluents (McGeorge et al., 1985). Textile effluent is graded second in toxicity, among eight industrial sectors (Costan et al., 1993). Therefore, focus on specific methods and a technology to remove dyes from different kinds of wastewater streams is desired. In view of the toxicological effects of dyes on environment, animals and human beings, it becomes very important to treat these toxic compounds in wastewater effluents before discharged into the environment.

## **2.4 Methods Available for Dye Removal**

There are numerous methods to treat dye bearing effluents. In spite of the availability of many techniques to remove dye contaminants from wastewaters, such as coagulation, chemical oxidation, membrane separation process, electrochemical and aerobic and anaerobic microbial degradation, and each of these methods have inherent limitations. The technologies can be divided into three categories: physical, chemical and biological (Ghoreishi and Haghghi, 2003). All of these methods have advantages and disadvantages. Table 2.5 shows the advantages and disadvantages of different dye removal methods.

**Table 2.5** Advantages and disadvantages of dyes removal methods (Salleh et al., 2011).

<i>Methods</i>	<i>Advantages</i>	<i>Disadvantages</i>
<i>Physical treatments</i>		
Adsorption by activated carbon	Good removal of wide variety of dyes	Very expensive
Membrane filtration	Removes all dye types	Concentrated sludge production
Ion exchange	Regeneration: no adsorbent loss	Not effective for all dyes
Irradiation	Effective oxidation at lab scale	Requires a lot of dissolved O <sub>2</sub>
Electrokinetic coagulation	Economically feasible	High sludge production
<i>Chemical treatments</i>		
Oxidative process	Simplicity of application	(H <sub>2</sub> O <sub>2</sub> ) agent needs to activate by some means
H <sub>2</sub> O <sub>2</sub> +Fe(II) salts (Fentons reagent)	Fentons reagent is a suitable chemical means	Sludge generation
Ozonation	Ozone can be applied in its gaseous state and does not increase the volume of wastewater and sludge	Short half-life (20 min)
Photochemical	No sludge is produced and foul odors are greatly reduced	Formation of by-products
Sodium hypochlorite (NaOCl)	Initiates and accelerates azo-bond cleavage	Release of aromatic amines
Electrochemical destruction	No consumption of chemicals and no sludge build up	Relatively high flow rates cause a direct decrease in dye removal
<i>Biological treatments</i>		
Decolorization by white-rot fungi	White-rot fungi are able to degrade dyes using enzymes	Enzyme production has also been shown to be unreliable
Other microbial Cultures (Mixed bacterial)	Decolorized in 24–30 h	Under aerobic conditions azo dyes are not readily metabolized
Adsorption by living/dead microbial biomass	Certain dyes have a particular affinity for binding with microbial species	Not effective for all dyes
Anaerobic textile- dye bioremediation systems	Allows azo and other water-soluble dyes to be decolorized	Anaerobic breakdown yields methane and hydrogen sulfide

## 2.4.1 Physical Methods for Dye Removal

Different physical methods are widely used to remove dye, such as membrane-filtration processes (ultrafiltration (UF), reverse osmosis (RO), and nanofiltration (NF)). Membrane technique was applied on a number of applications mainly for the treatment of complex industrial wastewater (Benito et al., 1998). The main disadvantage of the membrane processes is that they have a limited lifetime before membrane fouling occurs and the cost of periodic replacement must thus be included in any analysis of their economic viability. Types of typical membrane is presented in Table 2.6 (Gregory, 2005).

**Table 2.6** Classic characteristics of membrane processes (Gregory, 2005)

<i>Process</i>	<i>Operating pressure (Bar)</i>	<i>Pore size (nm)</i>	<i>Size cut-off range (nm)</i>	<i>Molecular weight cut-off range(Dalton)</i>
<b>Ultrafiltration</b>				
(UF)	2–10	10–200	15–200	1,000–1,000,000
<b>Nanofiltration</b>				
(NF)	5–40	1–10	1–100	100–20,000
<b>Reverse osmosis</b>				
(RO)	15–150	<2	<1	<200

The membrane separation process based on a semi-permeable membrane is composed of a thin polymer or ceramic with pores in a certain range (Gregory, 2005). Ultra filtration (UF), nano filtration (NF) and reverse osmosis (RO) are usually applied for drinking water and wastewater treatment. This has been applied for dye removal (Cheremisinoff, 2001, Avlonitis et al., 2008). Each membrane process is best suited for a particular water treatment function (Cheremisinoff, 2001). The main disadvantages are significant energy consumption, high cost of membrane and, high working pressures, and a relatively short membrane life which makes their use limited for treating dye wastewater. Reverse osmosis (RO) are usually applied for dissolved particle such as dissolved salts (Cheremisinoff, 2001). Reverse osmosis (RO) forces water, under pressure, through a membrane that is waterproof to most contaminants. Reverse osmosis is effective decolouring process against the most range of dye wastes, and has been successfully employed for recycling water

(Marcucci et al., 2001, Al-Bastaki, 2004, Šostar-Turk et al., 2005). In general, the usage of membrane technique needs careful considerations as the membrane must own specific features such as chemical and microbial attack and resistant to temperature (Robinson et al., 2001). Other than that, the residue left after separation process may create problems such as disposal, possibility of clogging and replacement of membrane (Mishra and Tripathy, 1993, Xu et al., 1999). Briefly, membrane fouling is the most significant problem with all membrane filters. This is due to formation of chemical precipitates due to chemistry of feed water, damage of membrane due to reacting with chemical substances presence, and build-up contaminants from the feed water deposit on the membrane surface (Gregory, 2005).

#### **2.4.2 Chemical Methods for Dye Removal**

Chemical method is a separation method that separates a material from a sample that contains differences in the chemical properties of the materials. Several methods are commonly used to remove dyes, such as ozonation, chemical coagulation, electrochemical processes etc. These chemical techniques are costly, and a disadvantage is that it produces secondary pollution.

##### **Ozonation**

Ozonation, as an effective oxidation process, has found application in the decolourisation of synthetic dyes (Xu et al., 1999). It was reported that ozone effectively decomposed azo dyes in textile wastewater. Ozone reacts with most organic and several inorganic molecules (Drinan and Spellman, 2012).

Ozonation method is favourable for soluble dyes as it normally attack dye double bonds which are responsible for coloration (Andreozzi et al., 2000), and oxidation takes place. After this process, the effluents become colourless and suitable for to straight discharge to water bodies (Muthukumar and Selvakumar, 2004). Therefore, the major advantage of ozone treatment is ionization of wastewater and sludge volume. Even though ozone is able to rapidly decolorize soluble dyes such as reactive and acid dyes, however, it reacts much slower for non soluble dyes (Gaehr et al., 1994). Furthermore, textile effluent may contain other pollutants such as inorganic salt, surfactant that has a possibility to react with ozone which may subsequently increase ozone consumption. As a result, ozonation process is usually done at final stage treatment (Vandevivere et al., 1999).

### **Chemical coagulation**

Chemical coagulation is a method in which chemicals are added to an aqueous system for the reason of creating fast-settling aggregates out of finely divided, dispersed matter with slow setting velocities. They are generally used to eliminate organic substances from wastewater (Randtke, 1988).

The theory of chemical coagulation is known as destabilization, aggregation, and binding together of colloids. The great, heavier particle flocks settle, and followed by settling and filtration (Drinan and Spellman, 2012). Many inorganic coagulants such as aluminium salts, iron, magnesium and lime are generally used. Various factors, such as coagulant dosage, coagulant types, the solution pH, concentration and nature of organic compounds are known to affect coagulation (Randtke, 1988).

Coagulation is often applied to dye wastewater as a post treatment to compliment other treatment processes or as a main treatment process (Sarasa et al., 1998, Lee et al., 2006, Cañizares et al., 2008). It was reported that, inorganic coagulant are not effective for highly soluble dye (Southern, 1995) removal. Difficulty of disposing the larger amount of sludge produced and high cost of the coagulants limit application of this process (Kurniawan et al., 2006).

### **2.4.3 Enzymatic Decomposition of Dyes**

The character of enzymes in microorganisms that are good for the decomposition of dyes has been widely studied (Ollikka et al., 1993). The attempts have been dedicated to the separation, isolation and testing of these enzymes. Important knowledge of the enzymatic processes that control the decomposition of dyes is significant in the environmental protection both from theoretical and practical aspects (Michniewicz et al., 2008).

The activity of isoenzymes towards decolouring triphenylmethane dyes, heterocyclic dyes, azo dyes and polymer dyes was compared with that of a crude enzyme. Optimum pH values for the decolourisation of dyes by many isoenzymes were noticeably different (Božič et al., 2010).

## **2.4.4 Biological and Microbiological Treatment of Dyes**

### **Biological treatment**

Biological treatment such as aerobic and anaerobic are also used for dye bearing effluents in wastewater treatment plants (Rai et al., 2005). Biological treatment is often the low cost option when compared with other physical and chemical processes. Biodegradation methods such as microbial degradation, adsorption by microbial biomass and bioremediation systems are usually used for the treatment of industrial effluents because of microorganisms such as bacteria, yeasts and algae are capable to accumulate different contaminants (Banat et al., 1996, Fu and Viraraghavan, 2001). However, this treatment requires a large area of land, as well as less flexibility in operation and design, which restricts its use (Crini, 2006). Biological treatment may also be used if toxic materials are present in influents (Suehara et al., 2005).

As dyes were designed to be stable and permanent, therefore it is not easily biodegraded. Thus, the conventional biological wastewater treatment systems are ineffective in treating dye wastewater (Fu and Viraraghavan, 2001). Most of dyes were observed to be non biodegradable under aerobic condition (Rai et al., 2005). This is because majority of dyes are chemically stable and resistant to microbial attacks (Forgacs et al., 2004). Studies also reported that reduction under anaerobic conditions is able to convert azo to aromatic amines; colourless but compounds likely to be harmful, however, can be biologically degradable under aerobic condition (O'Neill et al., 2000, Khehra et al., 2006). The time of treatment may take a few days for biological treatment for high removal. However, the removal efficiency varies for each type of AZO dyes (Rajaguru et al., 2000, Lourenço et al., 2001, Khehra et al., 2006).

### **Microbiological treatment**

The application of microorganisms for the biodegradation of synthetic dyes is a simple method of operation. The use of microorganisms for the removal of dyes from industrial waste matters offers considerable advantages. The process is relatively low-cost, the running costs are low and the end products of complete mineralisation are not toxic. The different aspects of the microbiological decomposition of dyes have been reviewed by Stolz (2001). Other methods have been employed in the microbial decolourisation of dyes, beside the traditional wastewater cleaning

technologies (Stolz, 2001). The application of microorganisms for the biodegradation of dyes is a simple and attractive method. Unfortunately, the common dyes are chemically stable and resistant to microbiological assault. The isolation of new strains or the adaptation of existing ones to the decomposition of dyes will probably increase the efficiency of microbiological degradation of dyes in the near future.

#### **2.4.5 Adsorption**

The term adsorption refers to the accumulation of a substance at the interface between two phases (liquid-solid interface or gas-solid interface). The substance that accumulates at the interface is called adsorbate and the solid on which adsorption occurs is adsorbent (Dabrowski, 2001). Adsorption can be classified into two types; chemical sorption and physical sorption. Chemical adsorption or chemisorption is illustrated by the formation of strong chemical associations between molecules or ions of adsorbate to adsorbent surface, which is generally due to the exchange of electrons (Allen and Koumanova, 2005) and thus chemical sorption generally is irreversible (Cooney, 1998). Physical adsorption or physisorption is characterized by weak interparticle bonds between adsorbate and adsorbent (Allen and Koumanova, 2005) and thus reversible in most cases (Cooney, 1998).

Adsorption is one of the most popular methods for the removal of contaminants from wastewater since proper design of the adsorption process will produce a high-quality treated waste matter. This process provides an attractive alternative for the treatment of polluted waters, especially if the sorbent is inexpensive and does not require an additional pre-treatment step before its application (Dabrowski, 2001). As for environmental remediation purpose, adsorption techniques are widely used to remove certain classes of chemical contaminants from waters, especially those that are practically unaffected by conventional biological wastewater treatments (Dabrowski, 2001, Allen and Koumanova, 2005). For water re-use adsorption has been found to be superior to other techniques in terms of flexibility and simplicity of design, initial cost, insensitivity to toxic pollutants and ease of operation. Adsorption also does not produce the harmful substances (Crini, 2006). Factors that influence the adsorption efficiency include adsorbate adsorbent interaction, adsorbent surface area, adsorbent to adsorbate ratio, adsorbent particle size, temperature, pH and contact time (Allen and Koumanova, 2005, Crini, 2006) etc.

## **2.5 Factors Affecting Adsorption of Dye**

There are many factors affecting dye adsorption such as pH, temperature, initial dye concentration, etc. Thus, the effects of these parameters are to be taken into account. Optimization of such conditions will greatly help in the development of industrial-scale dye removal treatment. In this section, some of the factors affecting adsorption of dyes are discussed below:

### **2.5.1 Effect of solution pH**

One of the most important factors affecting the capacity of adsorbent in wastewater treatment is solution pH. The solution pH is a measure of basicity ( $pH > 7$ ) or acidity ( $pH < 7$ ) of an aqueous solution. The effect of pH solution on the adsorption can be determined by preparing adsorbent–adsorbate solution with fixed dye concentration and adsorbent dose but with different pH by adding NaOH (1 M) or HCl (1 M) solutions to adjust pH and then shaken until equilibrium (Salleh et al., 2011). The efficiency of adsorption is dependent on the solution pH, since variation in pH leads to the variation in the degree of ionization of the adsorptive molecule and the surface properties of adsorbent (Nandi et al., 2009b).

(Chowdhury et al., 2011a) studied the effect of solution pH on the adsorption of Basic Green 4 dye by *Ananas comosus* leaf powder and they noticed that at a pH range from 2 to 10, the dye removal ratio was maximum at a pH 10. (Dawood and Sen, 2012c) studied the effect of solution pH on the adsorption of Congo red by pine cone and they noticed that the adsorption was maximum at pH 3.5. (Ibrahim et al., 2010) studied the adsorption of RB4 dye by modified barley straw and they found that RB4 gives a complete removal of 100% at pH of 3 and decreased value below 50% as the pH was increased. Table 2.7 reported different studies on the effect of pH solution on the adsorption process by each adsorbent according to the type of dye.

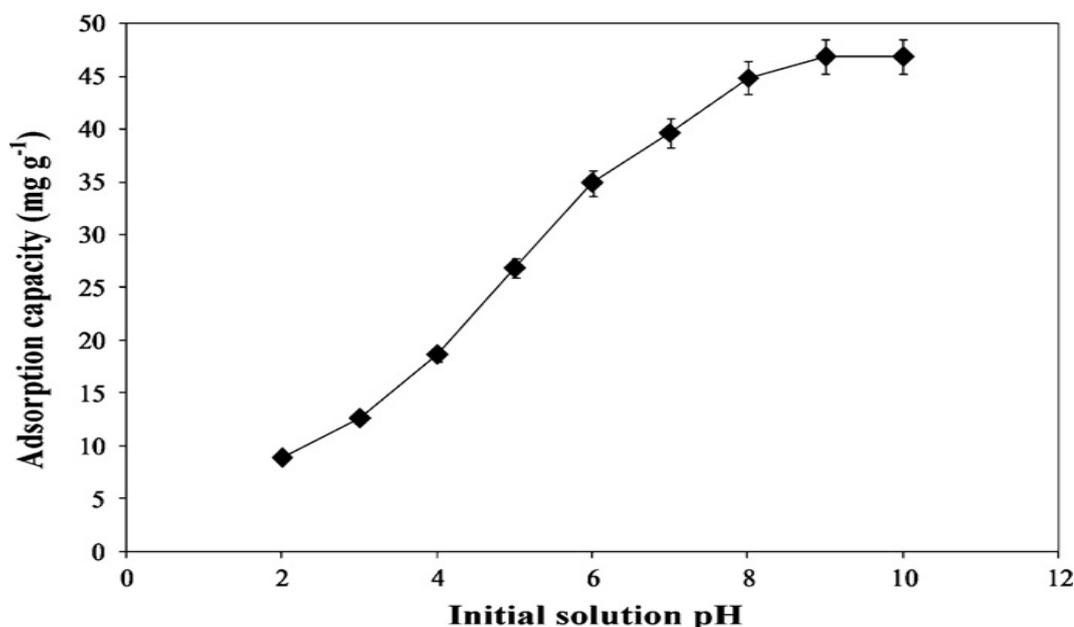


Figure 2.1 Effect of initial solution pH on the adsorption of Methylene Blue (MB) on pine leaves(Chowdhury et al., 2011a).

The adsorption ability of the surface and the type of surface active centres are indicated by the significant factor that is the point of zero charge ( $\text{pH}_{\text{pzc}}$ ) and it determines the linear range of pH sensitivity (Liu et al., 2012). The pH at which the surface charge is zero is called the point of zero charge (pzc) and is typically used to quantify or define the electrokinetic properties of a surface; it describes the condition when the electrical charge density on a surface is zero. The value of pH is used to describe pzc only for systems in which  $\text{H}^+/\text{OH}^-$  are the potential determining ions. Many researchers studied the point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of adsorbents prepared from agricultural solid wastes in order to better understand the adsorption mechanism. Due to presence of functional group such as  $\text{OH}^-$ , cationic dye adsorption is favoured at  $\text{pH} > \text{pH}_{\text{pzc}}$ , whereas, anionic dye adsorption is favoured at  $\text{pH} < \text{pH}_{\text{pzc}}$  where the surface becomes positively charged (Tan et al., 2012). (Han et al., 2012) studied the adsorption of Methylene blue (MB) onto poplar leaf and they found that the zero point of charge ( $\text{pH}_{\text{pzc}}$ ) for the poplar leaf was around 5.6, while the maximum adsorption capacity of MB was at pH 9, in other word  $\text{pH} > \text{pH}_{\text{pzc}}$ . The adsorption of Blue Remazol onto babassu coconut mesocarp has been studied by (Vieira et al., 2009) and they found that the maximum adsorption capacity of Blue Remazol was at pH 1, while the point of zero charge ( $\text{pH}_{\text{pzc}}$ ) for the babassu coconut mesocarp was 6.7, in other word  $\text{pH} < \text{pH}_{\text{pzc}}$ .

**Table 2.7** The effect of solution pH on the adsorption of dyes using different adsorbents

<i>Adsorbents</i>	<i>Dyes name</i>	<i>pH</i>	<i>rang</i>	<i>% removal</i>	<i>References</i>
				<i>rang</i>	
<b>Modified Alumina</b>	Crystal violet	2.6-10.8		20-80	(Adak et al., 2005)
<b>Activated clay</b>	Methylene blue	2-9		60-95	(Weng and Pan, 2007)
<b>Activated Carbon</b>	Methylene blue	2-11		Increase	(Kannan and Sundaram, 2001)
<b>Kaolin</b>	Crystal violet		2-7	65-95	(Nandi et al., 2008)
<b>Activated Rice husk</b>	Acid yellow 36	2-9		80-45	(Imam Maarof et al., 2003)
<b>Bentonite</b>	Acid Blue 193	1.5-11		Decrease	(Özcan et al., 2005)
<b>Fly ash</b>	Methylene blue	2-8		36-45	(Kumar et al., 2005)
<b>Fe<sub>2</sub>O<sub>3</sub></b>	Acid red 27	1.5-10.5		98-27	(Nassar, 2010)
<b>Fe<sub>3</sub>O<sub>4</sub> nanoparticles</b>	Methylene blue	1-8		Decrease	(Zhang and Kong, 2011)
<b>Pine cone</b>	Congo red	3.55-10.95		60.5-5.75	(Dawood and Sen, 2012d)
<b>Pine cone</b>	Methylene blue	3.47-7.28		63.83-94.82	(Sen et al., 2011)
<b>Tobacco Stem Ash</b>	Methylene blue	2.08-7.93		60-81	(Ghosh and Reddy, 2013)
<b>Fish Bone</b>	Basic Yellow 28	2-11		25-85	(Ebrahimi et al., 2013)
<b>modified sawdust</b>	Methylene blue	2-11		Increase	(Zou et al., 2013)

### **2.5.2 Effect of Initial Dye Concentration**

The amount of adsorption for dye removal is highly dependent on the initial dye concentration. The effect of initial dye concentration depends on the immediate relation between the concentration of the dye and the available sites on an adsorbent surface. The effect of initial dye concentration can be studied by preparing adsorbent–adsorbate solution with fixed adsorbent dose and different initial dye concentration for different time intervals and shaken until equilibrium (Salleh et al., 2011).

In general, the percentage of dye removal decreases with an increase in the initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface. At a low concentration there will be vacant active sites on the adsorbent surface, and when the initial dye concentration increases, the active sites required for adsorption of the dye molecules will increase (Kannan and Sundaram, 2001). On the other hand the increase in initial dye concentration will cause an increase in the capacity of the adsorbent and this may be due to the higher driving force for mass transfer at a higher initial dye concentration (Bulut and Aydın, 2006).

(Zhang et al., 2012a) studied the adsorption of Methyl Orange by Chitosan/Alumina interface and it was found that when the Methyl Orange concentration increase from 20 mg/L to 400 mg/L, while the percentage of dye removal decreased from 99.53% to 83.55% with the same MB concentration range. (Senthamarai et al., 2012) studied the effect of initial dye concentration on the adsorption of methylene blue (MB) dye by Modified *Strychos potatorum* Seeds and they reported that at an initial dye concentration range from 50 mg/L to 250 mg/L, the percentage of dye removal was decreased from 99.95% to 93.5%. Table 2.8 presents the results of various reported studies on the of initial dye concentration effect on dye adsorption.

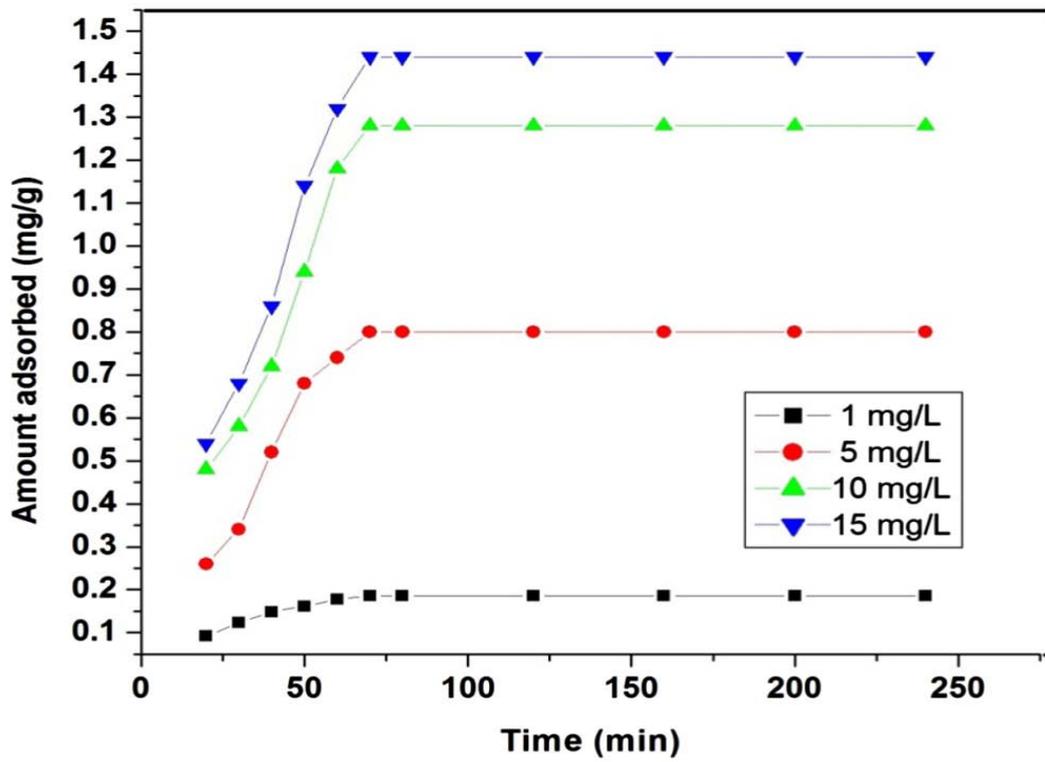


Figure 2.2 Effect of Initial MB Dye Concentration on the adsorption of Acid Yellow 23 onto saw dust (Banerjee and Chattopadhyaya, 2013)

**Table 2.8** The results of various reported studies on the effect of initial dye concentration on dye adsorption

<i>Adsorbents</i>	<i>Dyes name</i>	<i>Initial dye concentration range (mg/L)</i>	<i>percentage removal% range</i>	<i>References</i>
<b>Kaolin</b>	Methylene blue	10-40	90-62	(Tehrani-Bagha et al., 2011)
<b>Fly ash</b>	Congo red	5-30	99-84	(Mall et al., 2005b)
<b>Red mud</b>	Acid Violet	10-40	26.2-12.52	(Namasivayam et al., 2001)
<b>Bentonite</b>	Acid Blue 193	100-250	Decrease	(Özcan et al., 2005)
<b>Sawdust</b>	Direct brown 2	600-850	99.6-99.1	(Kannan and Sundaram, 2001)
<b>Pine leaves</b>	Methylene blue	10-90	96-41	(Yagub et al., 2012)
<b>Nanostructure TiO<sub>2</sub></b>	Reactive blue 21	32-56	10.93-8.28	(Srivastava et al., 2013)
<b>Saw dust</b>	Acid Yellow 23	1-15	97-71	(Banerjee and Chattopadhyaya, 2013)
<b>Sugarcane bagasse</b>	Rhodamine B	100-500	99.1-87.1	(Zhang et al., 2013)
<b>Sugarcane bagasse</b>	Basic Blue 9	250-500	94-55.5	(Zhang et al., 2013)
<b>Activated carbon</b>	Eriochrome Black T	30-150	45-10	(de Luna et al., 2013)
<b>ZnO</b>	Malachite Green	10-40	83-73	(Kumar et al., 2013)
<b>SnO<sub>2</sub></b>	Malachite Green	10-40	83-65	(Kumar et al., 2013)
<b>Modified Sawdust</b>	Methylene blue	25-500	91.2-66.3	(Zou et al., 2013)
<b>Rice husk</b>	malachite green	10-30	82.5-71	(Ramaraju et al., 2013)
<b>Raw Mango Seed</b>	Methylene blue	50-250	99.1-92.5	(Senthil Kumar et al., 2013)
<b>Modified Mango Seed</b>	Methylene blue	50-250	99.9-96.9	(Senthil Kumar et al., 2013)
<b>Apricot seed</b>	Astrazone Black	50-500	91-62	(Kahraman et al., 2012)

### 2.5.3 Effect of Temperature

Effect of temperature is another significant physical parameter because temperature will change the adsorption capacity of the adsorbent (Argun et al., 2008). To study the effect of temperature on the adsorption of dye process, it can be carried out by preparing adsorbent–adsorbate solution with fixed dye concentration and adsorbent dose but with different temperature. If the amount of adsorption increases with increasing temperature then the adsorption is an endothermic process. This may be due to increasing the mobility of the dye molecules and an increase in the number of active sites for the adsorption with increasing temperature. This effect depends mainly on the movement of dye molecules of each dye. Whereas the decrease of adsorption capacity with increasing temperature indicates that the adsorption is an exothermic process. This may be due to increasing temperature which decrease the adsorptive forces between the dye species and the active sites on the adsorbent surface as a result of decreasing the amount of adsorption (Salleh et al., 2011). (Wang et al., 2011) studied the adsorption of Methylene blue (MB) on chitosan-g-poly (acrylic acid)/attapulgate composite (CTS-g-PAA/APT), and they reported that the adsorption capacity increased with increase in temperature from 30 °C to 40 °C and with further increasing from 40°C to 60°C the amount of adsorption was decreased. (Auta and Hameed, 2012) studied the adsorption of Methylene blue (MB) by raw and modified Ball clay and they concluded that the adsorption uptake was increase with increased in temperature from 30°C to 50°C. Table 2.9 shows various studies on the effect of temperature on the adsorption process by each adsorbent.

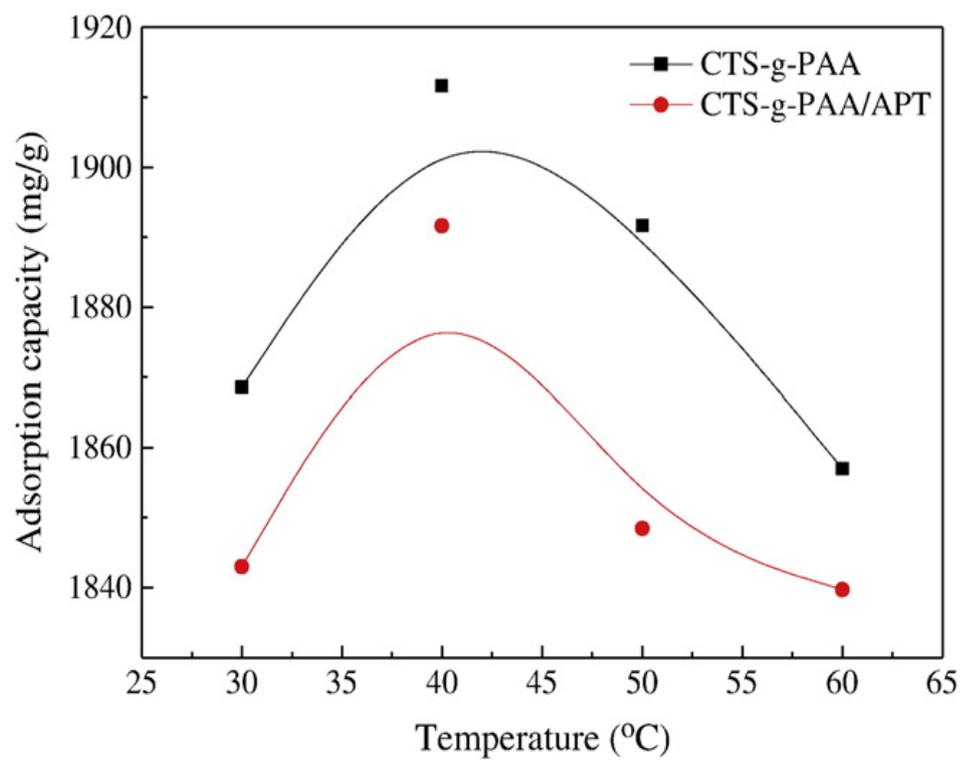


Figure 2.3 Effect of the temperature on the adsorption of MB onto CTS-g-PAA and CTS-g-PAA/APT (Wang et al., 2011)

**Table 2.9** The effect of temperature on the adsorption of dyes using adsorbents

<i>Adsorbents</i>	<i>Dyes name</i>	<i>Temperature range °K</i>	<i>Type of process</i>	<i>References</i>
<b>Kaolin</b>	Congo red	279-333	Exo-Therm	(Vimonses et al., 2009)
<b>NaBentonite</b>	Congo red	279-333	Exo-Therm	(Vimonses et al., 2009)
<b>Modified ball clay</b>	Methylene blue	303-313	Endo-Therm	(Auta and Hameed, 2012)
<b>Raw ball clay</b>	Methylene blue	303-313	Endo-Therm	(Auta and Hameed, 2012)
<b>Activated carbon</b>	Methylene blue	308-333	Endo-Therm	(Kavitha and Namasivayam, 2007)
<b>natural Sepiolite</b>	Acid Blue 25	293-323	Endo-Therm	(Han et al., 2013)
<b>Activated clay</b>	Methyl Orange	293-303	Endo-Therm	(Ma et al., 2013b)
<b>saw dust</b>	Acid Yellow 23	298-318	Endo-Therm	(Banerjee and Chattopadhyaya, 2013)
<b>light yellow</b>	Acid Blue 92	298-318	Endo-Therm	(Olya et al., 2013)
<b>Sugarcane bagasse</b>	Rhodamine B	303-323	Endo-Therm	(Zhang et al., 2013)
<b>Sugarcane bagasse</b>	Basic Blue 9	303-323	Endo-Therm	(Zhang et al., 2013)
<b>Treated Rice husks</b>	Methylene blue	293-313	Endo-Therm	(Lin et al., 2013)
<b>Bottom Ash</b>	Eosin Yellow	303-323	Endo-Therm	(Mittal et al., 2013b)
<b>Hen Feathers</b>	Amido Black	303-323	Endo-Therm	(Mittal et al., 2013a)
<b>residue sludge</b>	Congo Red	288-323	Endo-Therm	(Attallah et al., 2013)
<b>residue sludge</b>	Naphthol Green B	288-323	Endo-Therm	(Attallah et al., 2013)
<b>Peanut husk</b>	Indosol Black	303-333	Exo-Therm	(Sadaf and Bhatti, 2013)
<b>Activated Bamboo waste</b>	Reactive Black 5	303-323	Endo-Therm	(Ahmad et al., 2013)

### 2.5.4 Effect of Amount of Adsorbent

Adsorbent dosage is another important process parameter because this determines the capacity of an adsorbent for a given amount of the adsorbent at any operating condition (Sari et al. 2007). The effect of the amount of adsorbent on the adsorption process can be determined by preparing adsorbent–adsorbate solution with different amount of adsorbents added to fixed initial dye concentration and fixed initial solution pH then shaken together until equilibrium is achieved. Generally, the percentage of dye removal increases with increasing adsorbent dosage, where the quantity of sorption sites at the surface of adsorbent will increase by increasing the amount of the adsorbent. To study the effect of adsorbent dosage gives an idea of the ability of a dye to be adsorbed by the adsorbent (Salleh et al., 2011). (Feng et al., 2012b) studied the effect of adsorbent dose on the removal of Methylene blue dye by Swede rape straw and they observed increase of percentage of dye removal with decrease of adsorbent dose. (Ata et al., 2012) studied the adsorption of Coomassie Brilliant Blue on wheat bran at different amount of adsorbent and they concluded that the percentage of adsorption increased by increasing the amount of adsorbent from (0.1 to 1.0g). (Chowdhury et al., 2011a). Table 2.10 shows previous studies on the effect of adsorbent dosage on the percentage of dye removal.

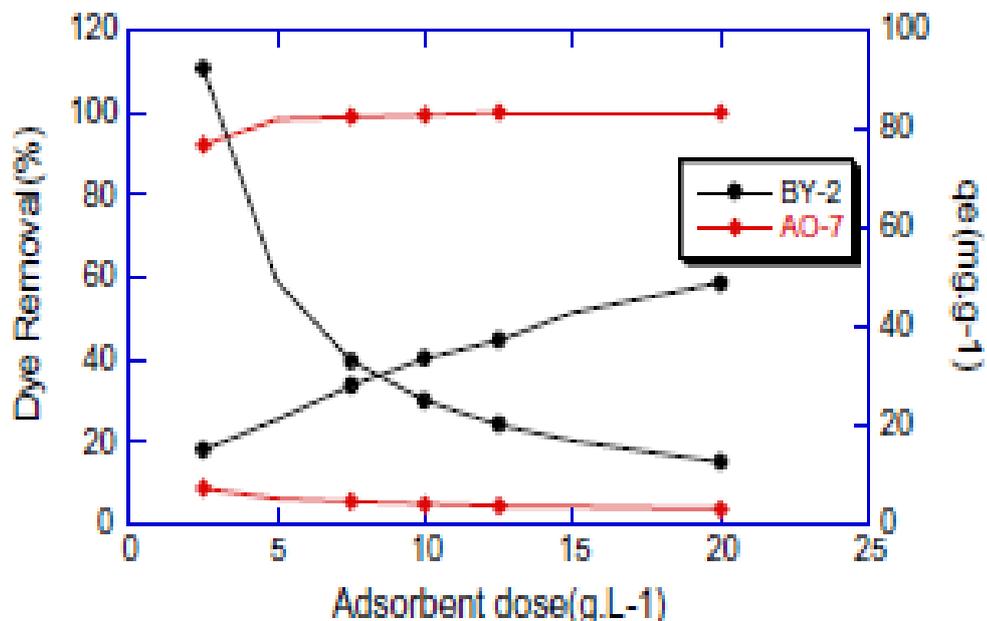


Figure 2.4 Effect of adsorbent dose on percentage removal of acidic and basic dye on tea waste (Khosla et al., 2013).

**Table 2.10** The effect of adsorbent dosage on the percentage of dye removal

<i>Adsorbents</i>	<i>Dye name</i>	<i>Adsorbent Dosage</i>	<i>Percentage removal (%)</i>	<i>References</i>
<b>Chitosan/Alumina Composite</b>	Methyl Orange	1-12 g.L <sup>-1</sup>	92.84-99.23	(Zhang et al., 2012a)
<b>Pine cone</b>	Congo red	0.01-0.03mg	13.45-18.96	(Dawood and Sen, 2012d)
<b>Modified Alumina</b>	Crystal violet	5-20 g.L <sup>-1</sup>	58-99	(Adak et al., 2005)
<b>Kaolin</b>	Crystal violet	0.25-4 g.L <sup>-1</sup>	75-97	(Nandi et al., 2008)
<b>Fly ash</b>	Methylene blue	8-20 g	45.16-96	(Kumar et al., 2005)
<b>modified sawdust</b>	Methylene blue	1.5-5 g	34.4-96.6	(Zou et al., 2013)
<b>Raw Mango Seed</b>	Methylene blue	0.1-1.2 g	99.5-68	(Senthil Kumar et al., 2013)
<b>Modified Mango Seed</b>	Methylene blue	0.1-1.2 g	99.8-79	(Senthil Kumar et al., 2013)
<b>Tea waste</b>	Basic yellow2	2-20 g.L-1	19-60	(Khosla et al., 2013)
<b>Tea waste</b>	Acid orange7	2-20 g.L-1	90-99	(Khosla et al., 2013)
<b>Spent tea bags</b>	Methylene blue	0.05-0.6 g	43.8-95.5	(Hameed, 2009b)
<b>Papaya Seeds</b>	Methylene blue	0.05-1.0 g	43.6-80	(Hameed, 2009a)
<b>Cashew nut shells</b>	Congo red	5-30 g.L-1	56.3-99.3	(Senthil Kumar et al., 2010)
<b>treated saw dust</b>	Brilliant Green	1-30 g.L-1	61-99.9	(Mane and Babu, 2011)
<b>Modified Sugarcane Bagasse</b>	Methyl red	0.2-1.0 g/100mL	67.8-83.2	(Saad et al., 2010)
<b>Orange Peel</b>	Acid Violet 17	50-600 mg/50mL	15-98	(Sivaraj et al., 2001)
<b>Coir Pith Carbon</b>	Congo Red	100-900 mg/50mL	50-97	(Namasivayam and Kavitha, 2002)
<b>Indian Rosewood Sawdust</b>	Methylene blue	0.2-1.0 g/100mL	45.1-97.1	(Garg et al., 2004)
<b>Bagasse fly ash</b>	Orange-G	0.05-0.2	23-89	(Mall et al., 2006)
<b>Rice hull</b>	Reactive Orange 16	0.02-0.08 g	21.7-56.2	(Ong et al., 2007)
<b>Treated Sawdust</b>	Malachite Green	0.2-1.0 g/100mL	18.6-86.9	(Garg et al., 2003)

## 2.6 Theory of Adsorption

### 2.6.1 Adsorption Kinetics

The controlling mechanisms of adsorption process such as chemical reaction or diffusion mass transfer controlling are used to determine kinetic models. The kinetics of dye adsorption onto adsorbent materials is a prerequisite for choosing the best operating conditions for the full-scale batch process. The study of adsorption kinetics illustrates the solute uptake rate and obviously this rate controls the residence time of the adsorbate at the solution interface. This rate is most important when designing the adsorption system and this rate can be calculated from kinetic study.

Thus, the kinetics of anionic and cationic dye onto various adsorbent materials was analysed using different kinetic models which are presented below:

#### 2.6.1.1 Adsorption kinetic Models

##### *Pseudo-first-order Model*

The Lagergren pseudo-first-order model for adsorption kinetic data which is the earliest known equation describing the adsorption rate based on the adsorption capacity. The differential equation is generally expressed as (Lagergren, 1898):

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (2.1)$$

Where;  $q_t$  and  $q_e$  ( $\text{mg g}^{-1}$ ) are the adsorption capacity at time  $t$  and at equilibrium, respectively,  $k_1$  is the rate constant of pseudo-first-order adsorption ( $\text{min}^{-1}$ ) and  $t$  is the contact time (min).

The linearized integral form of the Pseudo-first-order Model generally expressed as (Dogan et al., 2004, Nandi et al., 2009b, Santhi et al., 2009) :

$$\text{Log } (q_e - q_t) = \text{Log } q_e - \frac{k_1}{2.303} t \quad (2.2)$$

To plot  $\log (q_e - q_t)$  versus  $t$  give a linear relationship from which  $k_1$  and predicted  $q_e$  can be determined from the slope and intercept of the plot respectively.

### ***Pseudo-second-order Model***

The adsorption kinetics may also be described by the pseudo-second-order model. The differential equation is generally given as (Ho and McKay, 1999):

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (2.3)$$

Where;  $k_2$  ( $\text{g (mg min)}^{-1}$ ) is the second-order rate constant of adsorption. Integrating Eq. (2.3) is simplified and linearized to get

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2.4)$$

The plot of  $t/q_t$  versus  $t$  shows a linear relationship. Values of  $k_2$  and equilibrium adsorption capacity  $q_e$  were calculated from the intercept and slope of the plot of  $t/q_t$  versus  $t$  according to Eq. (2.4).

### 2.6.1.2 Adsorption Diffusion kinetic Models

#### *Intra-particle Diffusion Model*

The adsorption proceeds in several steps involving transport of solute molecules from the bulk aqueous phase to the surface of the adsorbent particles followed by integration of the molecules into the interior of the solids pores. According to Weber and Morris (1963) for most adsorption process, the amount of adsorption varies almost proportionally with  $t^{1/2}$  and can be expressed as (Weber and Morris, 1963):

$$q_t = K_{id} t^{0.5} \quad (2.6)$$

Where  $q_t$  is the adsorption capacity at time  $t$ ,  $t^{0.5}$  is the half-life time in seconds,  $K_{id}$  (mg/g min<sup>0.5</sup>) is the rate constant of intraparticle diffusion.

To find out the rate constants, a plot of  $q_t$  versus  $t^{0.5}$  gives a linear relationship,  $K_{id}$  can be determined from the slope of the plot.

#### *Liquid film diffusion model*

Through the transport of the adsorbate molecules from the liquid phase up to the solid phase, the boundary layer plays an important role in adsorption, the liquid film diffusion model equation may be used (Boyd et al., 1947):

$$\ln(1 - q_t/q_e) = -K_{fd} t \quad (2.7)$$

Where  $q_t/q_e$  is the fractional attainment of equilibrium, and  $K_{fd}$  is the film diffusion rate constant.

The film diffusion rate constant,  $K_{fd}$ , can be determined from the slope of the linear relationship between  $(1 - (q_t/q_e))$  vs  $t$ .

### **Kinetic model validations and literature review on dye adsorption kinetics:**

Generally the best-fit model can be chosen based on the values of the linear regression correlation coefficient  $R^2$ . Beside the value of  $R^2$  the applicability of various kinetic models are also verified through the sum of error squares (SES). The higher value of  $R^2$  and the lower value of SES, will be the goodness of fit. Usually the kinetic adsorption is better represented by Pseudo-second-order model for adsorption of dyes. (Rebitanim et al., 2012) studied the use of raw empty fruit bunch biomass for adsorption of Methylene blue. They found that the values of the regression correlation coefficient  $R^2$  values of the Pseudo-first-order model were between 0.83 and 0.86, while the values of  $R^2$  for the second order model were between 0.992 and 0.999 indicating applicability of second order model. (Dursun et al., 2012) evaluated the adsorption of Remazol Black B dye using sugar beet pulp and they found that the values of the constants for the Pseudo-second and Pseudo-first order models were increased with increasing temperature and the regression correlation coefficient  $R^2$  values for second order model were greater than 0.994 indicating applicability of the second-order nature of the adsorption process compared to the Pseudo-first order. (Zawani et al., 2009) studied the adsorption of Remazol Black 5 by Palm Kernel Shell based on Activated Carbon; and they found that the regression correlation coefficient  $R^2$  value of the Pseudo-first-order model was higher than the Pseudo-second-order kinetic. (Feng et al., 2012a) investigated the adsorption of Reactive Red 228 dye by Chitosan modified Flax shive, and they found that the data was best correlated by Pseudo-second-order kinetics. Table 2.11 shows that dye adsorption is predominantly Pseudo-second-order.

**Table 2.11** Various Kinetic studies for dye adsorption by various adsorbents

<i>Adsorbents</i>	<i>Dyes name</i>	<i>Kinetic Model</i>	<i>References</i>
<b>Activated Charcoal</b>	Brilliant Red HE-3B	Pseudo-second-order	(Suteu and Bilba, 2005)
<b>Beech wood sawdust</b>	Basic blue 86	Pseudo-second-order	(Dulman and Cucu-Man, 2009)
<b>Chitosan/Alumina</b>	Methyl Orange	Pseudo-second-order	(Zhang et al., 2012a)
<b>Jute fiber</b>	Malachite green	Pseudo-second-order	(Porkodi and Vasanth Kumar, 2007)
<b>Modified Clay</b>	Methylene blue	Pseudo-second-order	(Auta and Hameed, 2012)
<b>Pine cone</b>	Congo red	Pseudo-second-order	(Dawood and Sen, 2012c)
<b>Hazelnut shell</b>	Methylene blue	Pseudo-second-order	(Ferrero, 2007)
<b>Spent tea bags</b>	Methylene blue	Pseudo-second-order	(Hameed, 2009b)
<b>Cashew nut shells</b>	Congo red	Pseudo-second-order	(Senthil Kumar et al., 2010)
<b>treated saw dust</b>	Brilliant Green	Pseudo-second-order	(Mane and Babu, 2011)
<b>Modified Sugarcane Bagasse</b>	Methyl red	Pseudo-second-order	(Saad et al., 2010)
<b>Wood Apple Shell</b>	CrystalViolet	Pseudo-second-order	(Jain and Jayaram, 2010)
<b>Fe<sub>3</sub>O<sub>4</sub> nanospheres</b>	Neutral red	Pseudo-second-order	(Iram et al., 2010)
<b>Cashew nut shell</b>	Methylene blue	Pseudo-second-order	(Kumar et al., 2011)
<b>Treated Rice husk</b>	Malachite Green	Pseudo-second-order	(Chowdhury et al., 2011b)
<b>Almond Shell</b>	Methyl Violet	Pseudo-second-order	(Duran et al., 2011)
<b>Raw and Modified Mango Seed</b>	Methylene blue	Pseudo-second-order	(Senthil Kumar et al., 2013)
<b>Treated Onion Skins</b>	Methylene blue	Pseudo-second-order	(Saka et al., 2012)
<b>Bentonite</b>	Congo Red	Pseudo-second-order	(Bulut et al., 2008b)

## 2.6.2 Adsorption Isotherm

The adsorption isotherm is significant for the explanation of how the adsorbent will interact with the adsorbate and give an idea of adsorption capacity. They play an important role to understanding the mechanism of adsorption. The surface phase may be considered as a monolayer or multilayer. Several isotherm models are presented in the literature(Allen et al., 2004). Langmuir and Freundlich models are the most widely used to describe adsorption isotherms.

### *Langmuir Adsorption Isotherm*

The Langmuir adsorption isotherm model assumed that adsorption takes place at specific homogeneous sites within the adsorbent, and it has been used successfully for many adsorption processes of monolayer adsorption. The Langmuir equation is expressed by the following relation(Langmuir, 1918):

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (2.8)$$

Where,  $q_e$  is the amount of dye adsorbed at equilibrium time (mg/g),  $C_e$  is equilibrium concentration of dye in solution (mg L<sup>-1</sup>),  $q_m$  is maximum adsorption capacity (mg/g) and  $K_a$  is isotherm constants for Langmuir (L mg<sup>-1</sup>).

The linearized form of Langmuir can be written as two different forms;

#### **a/ Langmuir-1**

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_a q_m} \quad (2.9a)$$

The slope and intercept of plot between  $C_e/q_e$  vs.  $C_e$  will give  $q_m$  and  $K_a$  respectively.

#### **b/ Langmuir-2**

$$\frac{1}{q_e} = \frac{1}{K_a q_m} \frac{1}{C_e} + \frac{1}{q_m} \quad (2.9b)$$

In this form  $q_m$  and  $K_a$  are determined from plots of  $1/q_e$  vs.  $1/C_e$ .

The separation factor,  $R_L$  can be determined from Langmuir plot as per the following relation

$$R_L = \frac{1}{1 + K_a C_0} \quad (2.9c)$$

Where  $R_L$  values indicate the type of adsorption to be irreversible ( $R_L = 0$ ), favourable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) or unfavourable ( $R_L > 1$ ),  $K_a$  is the Langmuir constant and  $C_0$  is the initial MB dye concentration (ppm).

### ***Freundlich Adsorption Isotherm***

The Freundlich adsorption isotherm model considers a heterogeneous adsorption surface that has unequal available sites with different energies of adsorption. The Freundlich adsorption isotherm model is represented as follows (Freundlich, 1906):

$$q_e = K_f C_e^{\frac{1}{n}} \quad (2.10)$$

The linearized form of Freundlich can be expressed as;

$$\ln q_e = \ln K_f + \frac{1}{n} (\ln C_e) \quad (2.11)$$

Where  $q_e$  is the amount of metal ion adsorbed at equilibrium time (mg/g),  $C_e$  is equilibrium concentration of dye in solution ( $\text{mg L}^{-1}$ ).  $K_f$  is the capacity of the adsorbent and  $n$  is the intensity of adsorption constant for Freundlich. The plot of  $\ln q_e$  versus  $\ln C_e$  is employed to determine the  $K_f$  and  $n$  from intercept and slope respectively.

Generally, the value of the linear regression correlation coefficient  $R^2$  gives an indication of which model can be chosen to give best-fit. (Senthamarai et al., 2012) used the surface modified *Strychnos potatorum* seeds for adsorption of Methylene blue, and they have found that the maximum monolayer adsorption capacity was 78.84 mg/g and the Freundlich adsorption isotherm model has a best-fit compare to the other isotherm models according to the values of the regression correlation coefficient  $R^2$ . (Ozer et al., 2012) reported that the results were best correlated by

Langmuir model according to the values of the regression correlation coefficient  $R^2$ . (Theydan and Ahmed, 2012) investigated the adsorption of Methylene blue dye by Date pits activated carbon, and they reported that the data were fit with the Sips isotherms model and it had the best correlation coefficient  $R^2$ . Table 2.11 shows various isotherm studies of dye adsorption by various agricultural adsorbents.

**Table 2.12** Various isotherm studies of dyes adsorption by various agricultural adsorbents

<i>Adsorbents</i>	<i>Dyes name</i>	<i>Isotherm Model</i>	<i>References</i>
<b>Chitosan</b>	Congo Red	Langmuir	(Wang and Wang, 2007)
<b>Poplar leaf</b>	Methylene blue	Langmuir	(Han et al., 2012)
<b>Chitosan</b>	Methylene blue	Freundlich	(Chang and Juang, 2004)
<b>Chitosan</b>	Reactive Blue 19	Redlich–Peterson	(Hasan et al., 2008)
<b>Sugar beet pulp</b>	Remazol black B	Langmuir	(Dursun et al., 2012)
<b>Pine leaves</b>	Basic red 46	Langmuir	(Deniz and Karaman, 2011)
<b>Pine cone</b>	Methylene blue	Langmuir	(Sen, 2012)
<b>Activated pine cone</b>	Congo Red	Freundlich	(Dawood and Sen, 2012a)
<b>Activated clay</b>	Methyl orange	Langmuir	(Ma et al., 2013b)
<b>Modified barley straw</b>	Acid Blue	Langmuir	(Ibrahim et al., 2010)
<b>Zeolite synthesized</b>	Methylene blue	Freundlich	(Fungaro et al., 2009)
<b>Marine green alga</b>	Methylene blue	Langmuir and Freundlich	(El Sikaily et al., 2006)
<b>Green alga Chlorella vulgaris</b>	Remazol Black	Langmuir	(Aksu and Tezer, 2005)

## **2.7 Various Adsorbents for the Removal of Dyes**

### **2.7.1 Activated carbon**

Activated carbon is the most popular for the removal of pollutants from wastewater amongst all the sorbent materials proposed (Ramakrishna and Viraraghavan, 1997, Babel and Kurniawan, 2003). In particular, the effectiveness of adsorption on activated carbons for removal of a large variety of dyes from wastewaters has made it an ideal alternative to other expensive treatment options (Ramakrishna and Viraraghavan, 1997). However, activated carbon presents several disadvantages, it is quite expensive, and ineffective against disperse and vat dyes (Babel and Kurniawan, 2003). The use of carbons based on relatively expensive starting materials is also unjustified for most pollution control applications (Banat et al., 1996). This has led many workers to search for alternative low cost adsorbents which are given below:

### **2.7.2 Low Cost Adsorbents for Dyes Removal**

Selection of the precursor for the development of low cost adsorbents depends on many factors. The precursor should be freely available, in-expensive and non-hazardous in nature. In recent times, attention has been focused on different natural solids, which are able to remove pollutants from contaminated water at low cost. Cost is an important parameter for comparing the sorbent materials. In general, a sorbent can be assumed to be “low cost” if it requires little processing and is abundant in nature, or is a waste material from another industry, or is a by product in an industry. There are many low cost adsorbents that have been used for the removal of dye contaminates. Certain waste products from industrial and agricultural operations, natural materials and biosorbents represent potentially economical alternative sorbents. Many of them have been tested and proposed for dye removal.

### 2.7.2.1 Agricultural Solid Wastes

Waste materials and raw agricultural solid wastes from forest industries such as bark and sawdust have been applied as adsorbents. Agricultural by-products are available in large quantities around the world, therefore large amount of wastes rejected. These materials may have potential as sorbents due to inexpensive and their physio-chemical characteristics. Recently many researchers indicated the effective removal capabilities of various agricultural solid wastes as adsorbents to remove inorganic/organic pollutants including dyes. Salleh et al (2012) reported a review article on the use of agricultural solid wastes to remove cationic and anionic dyes. The waste material and raw agricultural solid wastes adsorption capacities are reported in Table 2.12.

**Table 2.13** Adsorption capacities  $q_m$  (mg/g) for waste materials from raw agriculture

<i>Material</i>	<i>Dye</i>	<i>Maximum adsorption capacity <math>q_m</math> (mg/g)</i>	<i>References</i>
<b>Tree fern</b>	Basic red 13	408	(Ho et al., 2005)
<b>Pine sawdust</b>	Acid yellow 132	398.8	(Ozacar and Sengil, 2005)
<b>Pine sawdust</b>	Acid blue 256	280.3	(Ozacar and Sengil, 2005)
<b>Egyptian bagasse pith</b>	Basic blue 69	168	(Ho and McKay, 2003)
<b>Coffee residues</b>	Basic Blue 3G	179	(Kyzas et al., 2012)
<b>Poplar leaf</b>	Methylene Blue	135.35	(Han et al., 2012)
<b>Oil palm fiber</b>	Methylene Blue	382.32	(Foo and Hameed, 2012)
<b>Swede rape straw</b>	Methylene Blue	246.4	(Feng et al., 2012b)
<b>Grapefruit peel</b>	Crystal violet	254.16	(Saeed et al., 2010)
<b>Skin almond waste</b>	Crystal violet	85.47	(Atmani et al., 2009)
<b>Wheat bran</b>	Crystal violet	80.37	(Wang et al., 2008c)
<b>Japonica</b>	Crystal violet	82.83	(Wang et al., 2008c)
<b>Tomato plant root</b>	Crystal violet	94.7	(Kannan et al., 2009)
<b>Coniferous pinus bark</b>	Crystal violet	32.78	(Ahmad, 2009)

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<b>Citrus sinensis</b>	Methylene Blue	96.4	(Bhatti et al., 2012)
<b>Bagasse</b>			
<b>Papaya seeds</b>	Methylene Blue	99.3	(Hameed, 2009a)
<b>Peanut hull</b>	Methylene Blue	68.06	(Gong et al., 2005)
<b>Banana peel</b>	Methylene Blue	20.8	(Annadurai et al., 2002)
<b>Pineapple stem</b>	Methylene Blue	119.05	(Hameed et al., 2009)
<b>Garlic peel</b>	Methylene Blue	82.64	(Hameed and Ahmad, 2009)
<b>Coconut bunch waste</b>	Methylene Blue	70.92	(Hameed et al., 2008)
<b>Hen feathers</b>	Methylene Blue	134.76	(Chowdhury and Saha, 2012)
<b>Meranti sawdust</b>	Methylene Blue	120.48	(Ahmad et al., 2009)
<b>Coffee husk</b>	Methylene Blue	90.1	(Oliveira et al., 2008)
<b>Rubber seed shell</b>	Methylene Blue	82.64	(Oladoja et al., 2008)
<b>Fallen phoenix tree's leaves</b>	Methylene Blue	80.9	(Han et al., 2007)
<b>Ground hazelnut shells</b>	Methylene Blue	76.9	(Ferrero, 2007)
<b>Luffa cylindrical fibers</b>	Methylene Blue	47	(Demir et al., 2008)
<b>Walnut sawdust</b>	Methylene Blue	59.17	(Ferrero, 2007)
<b>Yellow passion fruit waste</b>	Methylene Blue	44.7	(Pavan et al., 2008)
<b>Olive pomace</b>	Methylene Blue	42.3	(Banat et al., 2007)
<b>Rice husk</b>	Methylene Blue	40.59	(Vadivelan and Kumar, 2005)
<b>Cherry sawdust</b>	Methylene Blue	39.84	(Ferrero, 2007)
<b>Coconut coir</b>	Methylene Blue	15.59	(Sharma and Upadhyay, 2009)
<b>Egg shell</b>	Methylene Blue	16.43	(Tsai et al., 2006)
<b>Indian rosewood sawdust</b>	Methylene Blue	11.8	(Garg et al., 2004)

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<b>Neem leaf powder</b>	Methylene Blue	3.67	(Bhattacharyya and Sharma, 2005)
<b>pineapple leaf powder</b>	Crystal violet	78.22	(Chakraborty et al., 2012)
<b>Calotropis procera leaf</b>	Crystal violet	4.14	(Ali and Muhammad, 2008)
<b>Sawdust</b>	Crystal violet	37.83	(Parab et al., 2009)
<b>Eggshells</b>	Congo Red	69.45	(Saha et al., 2012)
<b>Rice husk</b>	Crystal violet	44.87	(Chakraborty et al., 2011)
<b>Empty Fruit Bunch</b>	Methylene Blue	50.76	(Rebitanim et al., 2012)
<b>Orange Peel</b>	Methylene Blue	18.6	(Annadurai et al., 2002)
<b>Mango seed kernel</b>	Methylene Blue	142.86	(Kumar and Kumaran, 2005)
<b>Jute processing waste</b>	Methylene Blue	16.6	(Banerjee and Dastidar, 2005)
<b>Rambutan peel</b>	Remazol Brilliant Blue R	112.69	(Alrozi et al., 2012)
<b>Loofa sponge-immobilized fungal biomass</b>	Remazol Brilliant Blue R	101.06	(Iqbal and Saeed, 2007)
<b>Free fungal biomass</b>	Remazol Brilliant Blue R	85.21	(Iqbal and Saeed, 2007)
<b>Pine Tree Leaves</b>	Basic Red 46	71.94	(Deniz and Karaman, 2011)
<b>Pine cone</b>	Basic Red 46	73.53	(Deniz et al., 2011)
<b>Canola hull</b>	Basic Red 46	49.00	(Mahmoodi et al., 2010)
<b>Princess tree leaf</b>	Basic Red 46	43.1	(Deniz and Saygideger, 2011)
<b>Rice husk</b>	Direct Red 23	4.35	(Abdelwahab et al., 2005)
<b>Rhizophora apiculata bark</b>	Direct Red 23	21.55	(Tan et al., 2010)
<b>De-oiled soya</b>	Methyl Orange	16.7	(Mittal et al., 2007)
<b>Peanut hull</b>	Reactive Black 5	55.55	(Tanyildizi, 2011)

<b>Natural rice husk</b>	Methylene Blue	19.77	(Zou et al., 2011)
<b>Spent rice</b>	Methylene Blue	8.3	(Rehman et al., 2012)
<b>Biomass</b>			
<b>Pine cone</b>	Methylene Blue	109.89	(Sen et al., 2011)
<b>Modified sawdust</b>	Methylene Blue	111.46	(Zou et al., 2013)
<b>Bagasse</b>	Indosol Turquoise FBL	65.09	(Sadaf et al., 2013)

### 2.7.2.2 Modified Agriculture Solid Waste

Literature also demonstrates that modification of agricultural adsorbents for better removal of dye and is a good method to improve the surface properties of agricultural wastes. Chemical treatment of agricultural adsorbent has been demonstrated to improve adsorption properties. Chemical treatment removes natural fats, waxes and low-molecular weight lignin compounds from agricultural adsorbent surface, thus revealing chemically reactive functional groups. The removal of the surface impurities also develops the surface roughness of the particles, thus opening more reactive functional groups on the surface (Auta and Hameed, 2012, Dawood and Sen, 2012b, Zhang et al., 2012b).

The main reason for the modification of raw agricultural waste is that it has net negative surface charge, thus it has little ability to remove negatively charged anionic dye particles (Banerjee et al., 2013). Some work reported that the modification of adsorbents with chemical solution successfully reversed the surface properties of the adsorbents from negative charge to positive that is beneficial for removal of dye contaminants (Namasivayam and Sureshkumar, 2006, Su et al., 2013). Moreover, chemical modification also introduced alkyl chain hydrophobic medium, which may be soluble low polarity pollutants into its layer (Kumar and Ahmad, 2011). Due to this, modification with a chemical solution was considered as suitable for the raw adsorbent to be used for remediation of dye pollutant contaminated wastewater (Bestani et al., 2008).

Another important consideration is the cost of the agricultural adsorbent and the chemicals used in the synthesis of the adsorbent material. For new modified

adsorbent materials to be considered attractive alternatives to those currently available, they should offer the advantage of low cost of production and maximum efficiency for the removal of a variety of contaminants from wastewaters. In addition, the recent concept of green chemistry requires that agricultural adsorbent can be recycled (Mohamed, 2004, Benkli et al., 2005, Kumar and Ahmad, 2011).

Work on applicability of chemically modified adsorbents for remediation of wastewater contaminated with dyes was actively done, and some are reported in Table 2.13.

**Table 2.14** Adsorption capacities  $q_m$  (mg/g) for modified agriculture waste materials

<i>Modified waste material</i>	<i>Dye</i>	<i>Maximum adsorption capacity <math>q_m</math> (mg/g)</i>	<i>References</i>
<b>Shorea dasyphylla sawdust</b>	Acid blue 25	24.39	(Hanafiah et al., 2012)
<b>Rice Husk</b>	Safranin Dye	37.97	(Chowdhury et al., 2012)
<b>Pine Cone</b>	Congo Red	40.19	(Dawood and Sen, 2012a)
<b>Coconut Coir</b>	Methylen blue	121	(Ong et al., 2013)
<b>Rice Straw</b>	Crystal Violet	80.917	(Chowdhury et al., 2013)
<b>Clam Shell</b>	Orange II	1017.13	(Ma et al., 2013a)
<b>Sugarcane Bagasse</b>	Methylen blue	202.43	(Gusmão et al., 2013)
<b>Sugarcane Bagasse</b>	Gentian violet	327.83	(Gusmão et al., 2013)
<b>Swede Rape Straw</b>	Methylen blue	432	(Feng et al., 2013)
<b>Bangalora Mango Seed</b>	Methylen blue	58.08	(Senthil Kumar et al., 2013)
<b>Rice Husk</b>	Crystal Violet	44.87	(Chakraborty et al., 2011)
<b>Kenaf Fibre Char</b>	Methylen blue	18.181	(Mahmoud et al., 2012)
<b>Sugarcane Bagasse</b>	Brilliant Red 2BE	73.6	(Da Silva et al., 2011)
<b>Rice Husk</b>	Malachite Green	19.98	(Chowdhury et al., 2011b)
<b>Rice Straw</b>	Malachite Green	256.41	(Gong et al., 2006)
<b>Rejected Tea</b>	Methylen blue	242.11	(Nasuha and Hameed, 2011)
<b>Wheat Straw</b>	Methylen blue	396.9	(Han et al., 2010)

### 2.7.2.3 Activated Carbons Biomass Based Adsorbents

Activated carbon (AC) has been proven to be an effective adsorbent for the removal of a wide variety of organic and inorganic pollutants dissolved in aqueous media or from gaseous environment. AC obtained from agricultural by-product has the advantage of offering an effective low cost replacement for non-renewable coal based granular activated carbon (CACs) provided that they have similar or better adsorption efficiency. The abundant availability of agricultural by-product are good sources of raw materials for activated carbon (AC) production. Table 2.14 lists the compilation of various biomass based activated carbon and its maximum adsorption capacity towards dye removal. Ali et al. (2012) reviewed biomass based activated carbon in the removal of organics.

**Table 2.15** Adsorption capacities  $q_m$  (mg/g) for activated carbon materials made from agricultural solid wastes

<i>AC from waste material</i>	<i>Dye</i>	<i>Maximum adsorption capacity <math>q_m</math> (mg/g)</i>	<i>References</i>
<b>Pink Guava</b>	Methylen blue	333.00	(Amri et al., 2012)
<b>Coconut Shell</b>	Malachite Green	214.63	(Bello and Ahmad, 2012)
<b>Hazelnut husks</b>	Methylen blue	204.00	(Ozer et al., 2012)
<b>Pine fruit shell-carbon</b>	Methylen blue	529.00	(Royer et al., 2009)
<b>Walnut shell-carbon</b>	Methylen blue	315.00	(Yang and Qiu, 2010)
<b>Piassava fibbers-carbon</b>	Methylen blue	276.40	(Avelar et al., 2010)
<b>Oil palm shell-carbon</b>	Methylen blue	243.90	(Tan et al., 2008)
<b>Wood apple rind-carbon</b>	Methylen blue	40.00	(Malarvizhi and Ho, 2010)
<b>Citrus fruit peel-</b>	Methylen	25.51	(Dutta et al., 2011)

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<b>carbon</b>	blue		
<b>Coal-based mesoporous</b>	Congo red	189	(Lorenc-Grabowska and Gryglewicz, 2007)
<b>Rice husk</b>	Methylen blue	9.73	(Sharma and Upadhyay, 2011)
<b>Pinewood</b>	Acid blue 264	1176	(Tseng et al., 2003)
<b>Pinewood</b>	Basic blue 69	1119	(Tseng et al., 2003)
<b>Pinewood</b>	Basic blue 9	556	(Tseng et al., 2003)
<b>Rice husk</b>	Basic green 4	511	(Guo et al., 2003)
<b>Waste newspaper</b>	Basic blue 9	390	(Okada et al., 2003)
<b>Waste carbon slurries</b>	Acid blue 113	219	(Jain et al., 2003)
<b>Waste carbon slurries</b>	Acid yellow 36	211	(Jain et al., 2003)
<b>Waste carbon slurries</b>	Ethyl orange	198	(Jain et al., 2003)
<b>sugar beet pulp</b>	Black B	80.00	(Dursun et al., 2012)
<b>bagasse fly ash</b>	Malachite green	42.18	(Mall et al., 2005a)
<b>Bagasse</b>	Acid blue 80	391	(Valix et al., 2004)
<b>Rice husk</b>	Acid blue	50	(Mohamed, 2004)
<b>Plant Leaf Powder</b>	Methylen blue	61.22	(Gunasekar and Ponnusami, 2012)
<b>Attapulgit/Rice Hull</b>	Yellow X-GL	213	(Liu et al., 2012)
<b>Bottom ash</b>	Methyl Orange	3.6	(Mittal et al., 2007)

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#### 2.7.2.4 Industrial By-Products

Industrial by-products such as metal hydroxide sludge, fly ash, red mud and waste slurry are classified as low-cost and locally available materials, and can be used as adsorbents for dye removal (Netpradit et al., 2003, Acemioğlu, 2004, Namasivayam and Sumithra, 2005, Weng and Pan, 2006, Ahmad et al., 2007). The application of low cost adsorbents obtained from industrial waste is a replacement of costly conventional methods.

**a) Metal hydroxide sludge:** Metal hydroxide sludge is one industrial by-product to remove azo dyes. The sludge is a dried waste from the electroplating industry, which is produced by precipitation of metal ions in wastewater with calcium hydroxide. It contains insoluble metal hydroxides and other salts. (Netpradit et al., 2003) studied reactive dyes removal by electroplating industry hydroxide sludge and they found that the maximum adsorption capacities of 45.87 and 61.73 mg/g for Reactive Red 120 and Reactive Red 2 respectively at 30 °C and at pH 8–9. The researchers also found out that the pH played an important effect on the adsorption and formation of dye–metal complexes. (Golder et al., 2006) investigated the adsorption of Congo red dye by metal hydroxide sludge as adsorbent and they reported the maximum adsorption capacities of 270.8 mg/g, at 30 °C and initial pH of 10.4, and 512.7 mg/g, for initial pH of 3.0. (Santos et al., 2008) studied the metal hydroxides as a low-cost adsorbent for removing a reactive dye Remazol Brilliant Blue in solution, and they found that at 25 °C and pH 7, a maximum mono layer adsorption capacity of 91.0 mg/g.

**b) Fly ash:** Fly ash is another industrial solid waste to adsorb dyes (Mohan et al., 2002, Acemioğlu, 2004, Weng and Pan, 2006). The estimated global production of fly ash was 67.5 million tons per year in 2010 (Ali et al., 2012). Fly ash is a waste material originating in large amounts in the burning processes. Although it may contain some hazardous materials, such as heavy metals, it is generally utilized in industry in many countries (Janos et al., 2003). However, bagasse fly ash generated in the sugar industry does not contain large amounts of toxic metals and has been commonly used for adsorption of dyes (Mohan et al., 2002, Kumar et al., 2005). Its properties are very different and depend on its origin (Janos et al., 2003, Weng and Pan, 2006). (Basava Rao and Ram Mohan Rao, 2006) presented the adsorption studies for treating the dye solutions of Congo red (CR) and methylene blue (MB)

textile dyes by using fly ash, and they found that the monolayer formation on the adsorbent surface and process is exothermic in nature. They have also reported that the fly ash from power generation units can be effectively used as adsorbent for the colour removal from dyeing industrial effluents. They found that at 30 °C the maximum adsorption capacities of 3.1 mg/g, for methylene blue MB and for Congo red CR the maximum adsorption capacities of 4.1 mg/g at the same conditions. (Rastogi et al., 2008) studied the removal of methylene blue by using fly ash as an adsorbent, and the maximum removal of 58.24% was observed at pH 6.75 and at adsorbent dosage of 900 mg/l for an initial methylene blue dye concentration of 65 mg/l. (Saha and Datta, 2009) reported that almost 95–99% of dye could be removed from the solution using fly ash at different initial conditions, and it is observed that the Langmuir constants  $q_m$  is 1.91 mg g<sup>-1</sup> and  $K_a$  is 48.94 L mg<sup>-1</sup> with a linear regression coefficient of 0.999.

**c) Red mud:** Another industrial by-product is red mud (Namasivayam and Kanchana, 1992, Namasivayam and Arasi, 1997, Weng and Pan, 2006). Waste red mud is a bauxite processing residue discarded in alumina production. (Namasivayam et al., 2002) studied the ability of waste red mud as an adsorbent in the remove of dye from its solution, and they found that the red mud can be effectively used as an adsorbent for the removal of dye from wastewaters. They also reported that the maximum adsorption for dye removal occurred at pH 2 and it is followed by Freundlich isotherm. Red mud has also been employed as adsorbents for the removal of a basic dye, methylene blue, from its aqueous solution (Wang et al., 2005). They found that the adsorption capacity of red mud was  $7.8 \times 10^{-6}$  mol/g, the results also indicate that the Redlich–Peterson model provides the best correlation of the experimental data. (Namasivayam and Arasi, 1997) presented the waste red mud as adsorbent to remove Congo red from aqueous solution. They found that the adsorption capacity of the red mud for the dye was 4.05 mg/g. (Tor and Cengeloglu, 2006) investigated the adsorption of Congo red (CR) from wastewater by using the acid activated red mud. The Langmuir isotherm was the best-fit adsorption isotherm model for the experimental data obtained. (Gupta et al., 2004) studied the removal of methylene blue, fast green, and rhodamine B from wastewater using red mud. The percentage removal of methylene blue, fast green, and rhodamine B on red mud were 75.0, 94.0, and 92.5, respectively. and the adsorption process followed both the Langmuir and Freundlich models and was exothermic in nature. (Magdy and

Daifullah, 1998) studied the ability of sugar industry mud to remove the Basic Red-22 dye from its solutions, and they found that the capacity was 519 mg dye per gram mud. Table 2.15 presented the maximum adsorption capacities of various biomass based on industrial by-products.

**Table 2.16** Adsorption capacities  $q_m$  (mg/g) for industrial by-products

<i>Material</i>	<i>Dye</i>	<i>Maximum adsorption capacity <math>q_m</math> (mg/g)</i>	<i>References</i>
<b>Metal hydroxide sludge</b>	Remazol Brilliant Blue	91.0	(Santos et al., 2008)
<b>Metal hydroxide sludge</b>	Congo Red	271	(Golder et al., 2006)
<b>Activated sludge</b>	Basic Red 18	285.71	(Gulnaz et al., 2004)
<b>Activated sludge</b>	Basic Blue 9	256.41	(Gulnaz et al., 2004)
<b>Sewage sludge</b>	Methylene blue	114.9	(Otero et al., 2003)
<b>Sewage sludge</b>	Vat red 10	73.1	(Dhaouadi and M'Henni, 2009)
<b>Sewage sludge</b>	Vat orange 11	58.7	(Dhaouadi and M'Henni, 2009)
<b>Coal fly ash</b>	Methylene blue	16.6	(Wang et al., 2008b)
<b>Fly ash</b>	Methylene blue	7.99	(Weng and Pan, 2006)
<b>bagasse fly ash</b>	Methylene blue	6.46	(VINOD et al., 2000)
<b>Fly ash</b>	Methylene blue	6.04	(Janos et al., 2003)
<b>Fly ash</b>	Methylene blue	5.57	(Kumar et al., 2005)
<b>Red mud</b>	Methylene blue	2.49	(Wang et al., 2005)
<b>Red mud</b>	Congo Red	4.05	(Namasivayam and Arasi, 1997)
<b>Red mud</b>	Rhodamine B	92.5	(Gupta et al., 2004)
<b>Red mud</b>	Fast Green	94.0	(Gupta et al., 2004)
<b>Red mud</b>	Methylene Blue	75.0	(Gupta et al., 2004)
<b>Red mud</b>	Remazol Brilliant Blue	27.8	(Ratnamala et al., 2012)

### 2.7.2.5 Inorganic Materials for Dye Removal

**a) Clays:** The clays are generally defined as those minerals that make up the colloid fraction ( $<2\mu\text{m}$ ) of soils, sediments, rocks and water and may be created as mixtures of fine grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonate and metal oxides. The clays always contain exchangeable ions on their surface and give important role in the environment by acting as a natural scavenger of contaminants by taking up cations and/or anions either through ion exchange or adsorption (Babel and Kurniawan, 2003).

Natural clay minerals are familiar and well known to mankind for a long time. As clay has some properties such as abundance in most continents of the world, high sorption properties and potential for ion exchange, clay materials are strong adsorbents and low cost. They possess layered structure and are considered as host materials for the adsorbates and counter ions (Babel and Kurniawan, 2003). They are classified by the differences in their layered structures. There are some classes of clays such as smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pyrophyllite (talc), vermiculite and sepiolite. The natural clay materials have a high surface area and high porosity (Shichi and Takagi, 2000).

In recent years, there has been an increasing interest in utilizing clay raw materials such as kaolinite, bentonite, diatomite and Fuller's earth for their capacity to adsorb inorganic ions and organic molecules. The interactions between dyes and clay elements have been extensively studied (Lee et al., 1997, Bagane and Guiza, 2000, Ghosh and Bhattacharyya, 2002, Al-Ghouti et al., 2003, Atun and Hisarli, 2003, Espantaleon et al., 2003, Özacar, 2003, Shawabkeh and Tutunji, 2003, Gürses et al., 2004, Safa Özcan et al., 2004). The clay minerals show a strong affinity for both cationic and anionic dyes and good removal capabilities of clays to uptake dyes has been demonstrated by many researchers (Table 2.16). However, the adsorption of dyes on clay minerals is mainly dominated by ion-exchange processes. This means that the sorption capacity can vary strongly with pH.

**b) Siliceous materials:** The natural siliceous sorbents such as silica beads, alunite, dolomite and perlite is increasingly used for wastewater treatment because of their low cost, abundance and high sorption properties and availability. Among inorganic materials, silica beads deserve particular attention (Phan et al., 2000, Krysztalkiewicz et al., 2002, Woolard et al., 2002), considering chemical reactivity of their hydrophilic surface. Their porous texture, mechanical stability and high surface area make them attractive as sorbents for pollution applications (Ahmed and Ram, 1992). Moreover, among other surface groups the surface of siliceous materials contains acidic silanol which causes a strong and often irreversible non-specific adsorption. For that reason, it is necessary to eliminate the negative features of these sorbents (Phan et al., 2000). In order to promote their interaction with dyes, the silica surface can be modified using silane coupling agents with the amino functional group (Krysztalkiewicz et al., 2002).

Alunite is another sorbent from siliceous minerals to adsorb dye and it is one of the materials of the jarosite group. However, untreated alunite does not have good adsorbent properties (Özacar, 2003). After treated, alunite-type layered compounds are useful as adsorbents for removing dyes. Regeneration is not necessary because alunite is so cheap.

Other siliceous materials such as dolomite, perlite and glass have been proposed for dye removal (Table 2.16). Dolomite is both a mineral and a rock. Burnt dolomite has a higher equilibrium capacity for reactive dye removal than activated carbon. Perlite is a glassy volcanic rock and has high silica content, generally more than 70%. It is inexpensive and simply available in several countries. Perlite is a good adsorbent for decontamination uses. However, because of the differences in composition, perlites of different origins have different properties and of different types expanded and unexpanded.

Natural siliceous materials have good quality removal capabilities for dyes and it has been established by several researchers (Table 2.16).

**c). Zeolites:** Zeolites have different cavity structures, this means it is highly porous. Their structures consist of a three dimensional framework and having negative charges. The negative charge is balanced by cations which are exchangeable with certain cations in solutions. Zeolites consist of more than 40 natural types. However, the most abundant and commonly studied zeolite is clinoptilolite, a mineral of the heulandite group. Relatively high specific surface areas, high ion-exchange capacity and more importantly their relatively low-cost, make zeolites attractive adsorbents (Babel and Kurniawan, 2003).

Zeolites are becoming generally used as optional materials in areas where sorption applications are required. They have been extensively studied recently because of their applicability in removing trace quantities of contaminants such as heavy metal ions and phenols. Several studies have been conducted on the sorbent behaviour of zeolites (El-Geundi, 1997, Ghobarkar et al., 1999, Calzaferri et al., 2000, Meshko et al., 2001, Armağan and Turan, 2004, Ozdemir et al., 2004). However, raw clinoptilolite was not suitable for the up-take of dyes due to extremely low sorption capacities (Karcher et al., 2001, Armağan and Turan, 2004, Ozdemir et al., 2004, Benkli et al., 2005). Zeolites also come into view as suitable sorbents for dyes (Table 2.16). The sorption mechanism on zeolite particles is complex because of their porous structure (Altın et al., 1998, Calzaferri et al., 2000). However, it is recognized that, like clay, the adsorption properties of zeolites result mainly from their ion-exchange capabilities. Although the removal efficiency of zeolites for dyes may not be better than that of clay materials, their easy availability and low cost may compensate for the associated drawbacks.

**d). Kaolin:** Kaolin is a common low-cost natural clay adsorbent. Kaolin has been studied as an adsorbent for the removal of dyes. (Nandi et al., 2008) reported that kaolin has high potential for the adsorption of crystal violet dye from its aqueous solution. They found that the adsorption experimental data are best fitted by the Langmuir isotherm and maximum adsorption capacity of 45 mg/g, and the percentage adsorption decreased from about 95% to 65% when the pH is slowly decreased from 7 to 3 for an initial dye concentrations of 20 mg/L. (Ghosh and Bhattacharyya, 2002) investigated the removal of methylene blue on kaolin. They found that the raw kaolin itself was a relatively good adsorbent, and they also found that the adsorption capacity was improved by purification and treated with NaOH

solution. The adsorption experimental data was best fitted by the Freundlich and Langmuir isotherm models. Kaolin was effectively used in the removal of brilliant green dye from aqueous solution and the maximum monolayer adsorption capacity is 65.42 mg/g and the adsorption experimental data was best fitted by the Langmuir adsorption isotherm model, and the rate of dye adsorption follows pseudo-second-order model for the dye concentration range studied (Nandi et al., 2009a). (Tehrani-Bagha et al., 2011) studied the potential use of kaolin for removal of Basic Yellow 28 (BY28), Methylene Blue (MB) and Malachite Green (MG) in aqueous solution. They found that the isotherm data of dyes were fitted by the Langmuir adsorption isotherm and the adsorption capacity of kaolin were 16 mg/g, 29.85 and 52 mg/g for Basic Yellow 28 (BY28), Methylene Blue (MB) and Malachite Green (MG) respectively. The adsorption of cationic and anionic industrial dyes by kaolin as a low-cost adsorbent was studied by (Ziółkowska et al., 2009) and they found that the experimental isotherms for the adsorption of the dyes could all be described by the Langmuir equation as the maximum mono layer adsorption capacity ranged from 4 mg/g to 29 mg/g.

**e). Bentonite:** The adsorption of Congo Red onto bentonite in a batch adsorber has been investigated by (Bulut et al., 2008b). They found that the experimental isotherm data fitted the Langmuir isotherm model and the maximum adsorption capacity of 158.7 mg/g, and they also found that the system followed pseudo second-order kinetic model. (Bulut et al., 2008a) also studied the adsorption of malachite green onto bentonite in a batch adsorber. They reported that the adsorption of malachite green onto bentonite followed pseudo second-order kinetic adsorption model with adsorption capacity of 178.6 mg/g. The removal of anionic dyes Direct Fast Scarlet, Eosin Y and Reactive Violet K-3R on modified bentonite was reported by (Kang et al., 2009). The total amounts of dyes adsorbed were 148.6, 88.4, and 106.7 mg/g for Direct Fast Scarlet, Eosin Y and Reactive Violet K-3R respectively, and followed pseudo-second-order kinetic model. (Hu et al., 2006) reported the ability of bentonite as a low-cost adsorbent for the removal of a Basic Red dye from its aqueous solution under various experimental conditions. They found that the adsorption equilibrium data described by the Langmuir adsorption isotherm model, and the adsorption capacity of approximately 274 mg/g at 30 °C. (Hong et al., 2009) studied the effect of temperature on the equilibrium adsorption for removal of methylene blue dye

from its aqueous solution by bentonite. They found the data best fitted by Redlich-Peterson isotherm model, and the maximum mono layer adsorption capacities were 151, 172, 173, 175mg/g at 283, 293, 303, 308 K respectively, and they suggested that the methylene blue adsorption on to bentonite was a spontaneous and endothermic process.

**f). Metal Oxides:** (Nassar, 2010) reported the adsorption of acid red 27 dye from aqueous solutions by  $\text{Fe}_2\text{O}_3$  nanoadsorbents. The experiments were carried out at different conditions and it was found that the adsorption equilibrium data fitted very well by using Langmuir and Freundlich adsorption isotherm models, and the adsorption process was found to be spontaneous, exothermic and physical in nature. The results show that  $\text{Fe}_2\text{O}_3$  nanoadsorbents could be employed for the removal of dyes from wastewater.  $\text{Fe}_3\text{O}_4$  hollow nanospheres used for application as an adsorbent for the removal of neutral red dye contaminants from water and the maximum mono layer adsorption capacity at 25°C and pH 6 of  $105 \text{ mg g}^{-1}$  (Iram et al., 2010). They also found that Langmuir and Freundlich adsorption isotherms models were selected to explicate the interaction of the dye and magnetic adsorbent, and adsorption kinetic followed pseudo-second-order kinetic model. (Zhang and Kong, 2011) studied the adsorption of organic dyes from its aqueous solutions by magnetic  $\text{Fe}_3\text{O}_4$  core-shell nanoparticles as adsorbent. They reported that the adsorption capacities for Methylene blue (MB) and Congo Red (CR) in the concentration range studied were  $44.38 \text{ mg/g}^{-1}$  and  $11.22 \text{ mg/g}^{-1}$  respectively. Metal oxide nanoparticles ZnO and  $\text{SnO}_2$  was effectively used in the removal of Malachite Green Oxalate dye from its aqueous solution (Kumar et al., 2013). They reported that the equilibrium data was best fitted with the Langmuir and Freundlich isotherm models with the maximum adsorption capacity of 310.5 and  $216.9 \text{ mg/g}^{-1}$  for ZnO and  $\text{SnO}_2$  respectively. They found that the kinetic studies indicated the adsorption process followed second order kinetic model. (Srivastava et al., 2013) studied the adsorption of reactive blue (RB) 21 dye using  $\text{TiO}_2$ . They reported that the Langmuir and pseudo-second order kinetic models give better explanation of the adsorption processes and the maximum mono layer adsorption capacity of  $22.79 \text{ mg/g}^{-1}$ . The effectiveness of modified Manganese oxides -diatomite (MOMD) in the removal of basic and reactive dyes methylene blue (MB), hydrolysed reactive black (RB) and hydrolysed reactive yellow (RY) from aqueous solution were reported by (Al-Ghouti

et al., 2009). The adsorption capacity of MOMD for methylene blue (MB), hydrolysed reactive black (RB) and hydrolysed reactive yellow (RY) were 320, 419, and 204 mg/g<sup>-1</sup> respectively. The adsorption capacities of various natural materials are also reported in Table 2.16.

**Table 2.17** Adsorption capacities  $q_m$  (mg/g) for natural inorganic materials

<i>Material</i>	<i>Dye</i>	<i>Maximum adsorption capacity <math>q_m</math> (mg/g)</i>	<i>References</i>
<b>Raw Ball clay</b>	Methylene blue	34.65	(Auta and Hameed, 2012)
<b>Modified Ball clay</b>	Methylene blue	100	(Auta and Hameed, 2012)
<b>Montmorillonite</b>	Methylene blue	556	(Nogueira et al., 2009)
<b>Heated montmorillonite</b>	Methylene blue	62	(Nogueira et al., 2009)
<b>Modified montmorillonite</b>	Methylene blue	322.6	(Wibulswas, 2004)
<b>Clay</b>	Methylene blue	58.2	(Gürses et al., 2006)
<b>Modified montmorillonite</b>	Methyl orange	24	(Chen et al., 2011)
<b>Clay/carbons mixture</b>	Acid blue	64.7	(Ho and Chiang, 2001)
<b>Gypsum</b>	Basic Red 46	39.17	(Deniz and Saygideger, 2010)
<b>Kaolin</b>	Congo red	1.98	(Vimonses et al., 2009)
<b>NaBentonite</b>	Congo red	35.84	(Vimonses et al., 2009)
<b>Clay</b>	Basic blue 9	300	(Bagane and Guiza, 2000)
<b>Bentonite</b>	Methylene blue	151/175	(Hong et al., 2009)
<b>Diatomite</b>	Methylene blue	198	(Al-Ghouti et al., 2003)
<b>Spent activated clay</b>	Methylene blue	127.5	(Weng and Pan, 2007)

<b>Fibrous clay minerals</b>	Methylene blue	85	(Hajjaji et al., 2006)
<b>Pyrophyllite</b>	Methylene blue	70.42	(Gücek et al., 2005)
<b>Palygorskite</b>	Methylene blue	44	(Al-Futaisi et al., 2007)
<b>Palygorskite treated pure kaolin</b>	crystal violet	47	(Al-Futaisi et al., 2007)
<b>Raw kaolin</b>	Methylene blue	20.45	(Ghosh and Bhattacharyya, 2002)
<b>glass fibers</b>	Methylene blue	13.99	(Ghosh and Bhattacharyya, 2002)
<b>Charred dolomite</b>	dye E-4BA	2.24	(Chakrabarti and Dutta, 2005)
<b>Activated bentonite</b>	Acid blue 193	950	(Walker et al., 2003)
<b>Activated bentonite</b>	fast brown H	740.5	(Safa Özcan et al., 2004)
<b>Calcined alunite</b>	R. yellow 64	360.5	(Espantaleon et al., 2003)
<b>Activated clay</b>	Basic red 18	236	(Özacar, 2003)
<b>Diatomite</b>	Basic blue 9	157	(Ho et al., 2001)
<b>Zeolite</b>	Basic dye	156.6	(Shawabkeh and Tutunji, 2003)
<b>Modified silica</b>	Acid blue 25	55.86	(Meshko et al., 2001)
<b>Glass powder</b>	Acid red 4	45.8	(Phan et al., 2000)
<b>Modified Mg<sub>2</sub>O<sub>2</sub></b>	Methylene blue	5	(Atun and Hisarli, 2003)
<b>TiO<sub>2</sub></b>	Reactive blue 21	320	(Al-Ghouti et al., 2009)
<b>Magnetic Fe<sub>3</sub>O<sub>4</sub></b>	Methylene blue	22.79	(Srivastava et al., 2013)
<b>Magnetic Fe<sub>3</sub>O<sub>4</sub></b>	Congo Red	44.38	(Zhang and Kong, 2011)

### 2.7.2.6 Biosorbents

Biosorption is the concentration and accumulation of contaminants from aqueous solutions by the use of biological matters. In this case, biological materials, such as chitin, chitosan, peat, yeasts, fungi or bacterial biomass, are used as sorbents in order to remove dyes from solutions. The biosorbents are often much more selective than traditional ion-exchange resins and commercial activated carbons, and can reduce dye to lower concentrations. Biosorption is a new approach, competitive, effective and low-priced. A significant number of biosorption studies for the removal of dyes and heavy metal from aqueous solutions have been conducted worldwide. Nearly all of them reported effective use of different biomaterials and optimization of biosorption process parameters. Diverse functional groups such as carboxyl, hydroxyl, sulfate, and amino groups which are originally present on the biosorbent are responsible for possible binding mechanism. Biosorption is an alternative technology for the removal of inorganic and organic pollutants from dilute solution by employing biomass as adsorbents e.g. agricultural and fermentation wastes and various types of microorganism (Arief et al., 2008). Following are various biomaterials used as biosorbent:

**a) Chitin and chitosan:** The sorption of dyes using chitin and chitosan is one of the new biosorption methods for the removal of dyes, even at low concentrations. Chitin and chitosan are plentiful, renewable resources and able to biodegrade. Chitin has been found in a wide range of natural sources such as crustaceans, fungi, insects, annelids and molluscs. However, chitin and chitosan are only commercially taken out from crustaceans primarily because of a large amount of the exoskeleton for crustacean is available as a by-product of the food industry (Wu et al., 2000). Various studies on chitin and chitosan have been conducted in recent years (Wu et al., 2000, Chiou and Li, 2003, Chiou et al., 2004, Wong et al., 2004, Wang et al., 2008c, Dotto et al., 2012). These studies showed that chitin and chitosan biosorbents are efficient materials and used to remove many classes of dyes which are presented in Table 2.17.

**b) Peat:** Peat is quite a complex soil material with organic substance in various steps of decomposition and it is porous. Peat is classified into four groups based on the nature of original materials, herbaceous peat, woody peat, moss peat and sedimentary peat. These natural materials are widely available and plentiful, relatively inexpensive which has adsorption capabilities for different contaminants (Sun and

Yang, 2003). Major constituents in peat are lignin, cellulose, fulvic and humic acid. These components, especially lignin and humic acid have polar functional groups that can be involved in chemical bonding such as alcohols, aldehydes, ketones, carboxylic acids, phenolic hydroxides and ethers. Due to their polar nature, peat can efficiently remove dyes from its solution (Ho and McKay, 1998, Aksu and Tezer, 2000b, Ho and McKay, 2003, Sun and Yang, 2003). Many studies investigated the use of peat to remove dyes. It was observed that peat is an effective sorbent for the removal of dyes, and tends to have a high cation exchange capacity.

However, natural peat has small mechanical strength, a high affinity for water, poor chemical stability, and therefore it is chemically activated. Chemical pre-treatment and the improvement of immobilized biomass beads can make a further robust medium. Chemical processes are also used for developing sorption properties and selectivity. Peat adsorption capacities are also reported in Table 2.17.

**c). Microbial Biomass:** The removal of dye from wastewater by dead or living biomass was the subject of several studies (Robinson et al., 2001, Stolz, 2001, Fu and Viraraghavan, 2002c, Aksu and Tezer, 2005). These studies investigated that biosorbents derived from suitable biomass can be used for the effective removal of dyes from solutions. The increasing use of biomass for wastewater treatment is because it is inexpensive and available in large quantities. A large amount of microbial biomass by-products is generated from fermentation processes which can be used in biosorption of contaminants. Biomass has a high potential as a sorbent due to its physio-chemical characteristics. A large range of microorganisms including algae, yeasts, bacteria and fungi are able to remove dyes with a high efficiency (Fu and Viraraghavan, 2001, Fu and Viraraghavan, 2002b, O'Mahony et al., 2002, Aksu and Dönmez, 2003, El Sikaily et al., 2006, Caparkaya and Cavas, 2008). In fungal decolorization, fungi can be classified into two types according to their life state: living cells, and dead cells to adsorb dye (Fu and Viraraghavan, 2001). Most of the studies concentrated on living fungi for biosorption of the dyes. Table (2.17) shows some of the adsorption capacities reported in the literature. The biosorption capacity of fungal biomass could be increased by some pretreatment (Fu and Viraraghavan, 2001). Other types of biomass such as yeasts have been studied for dye removal. Yeasts are extensively used in a variety of large-scale industrial fermentation processes and waste biomass from these processes is a potential source of low-priced adsorbent material.

**Table 2.18** Adsorption capacities  $q_m$  (mg/g) for various natural inorganic materials

<i>Material</i>	<i>Dye</i>	<i>Maximum adsorption capacity <math>q_m</math> (mg/g)</i>	<i>Reference</i>
<b>Chitin</b>	FD&C yellow 5	30	(Dotto et al., 2012)
<b>Chitosan</b>	FD&C yellow 5	350	(Dotto et al., 2012)
<b>Chitosan/Alumina</b>	Methyl Orange	32.7	(Zhang et al., 2012a)
<b>Chitosan</b>	Remazol Black 13	130	(Dursun et al., 2012)
<b>CTS-g-PAA</b>	Methylene blue	1873	(Wang et al., 2011)
<b>CTS-g-PAA/APT</b>	Methylene blue	1848	(Wang et al., 2011)
<b>CTS-g-PAA/MMT</b>	Methylene blue	1859	(Wang et al., 2008a)
<b>Chitosan Modified</b>	Reactive Red 228	14.34	(Feng et al., 2012a)
<b>Chitosan bead</b>	Reactive blue 2	2498	(Chiou et al., 2004)
<b>Chitosan bead</b>	Reactive red 2	2422	(Chiou et al., 2004)
<b>Chitosan bead</b>	Direct red 81	2383	(Chiou et al., 2004)
<b>Chitosan bead</b>	Reactive yellow 86	1911	(Chiou et al., 2004)
<b>Chitosan bead</b>	Reactive red 189	1936	(Chiou and Li, 2003)
<b>Chitosan (bead, crab)</b>	Reactive red 222	1106	(Wu et al., 2000)
<b>Chitosan (bead, lobster)</b>	Reactive red 222	1037	(Wu et al., 2000)
<b>Chitosan (flake, lobster)</b>	Reactive red 222	398	(Wu et al., 2000)
<b>Chitosan (flake, crab)</b>	Reactive red 222	293	(Wu et al., 2000)
<b>Chitosan</b>	Acid orange 12	973.3	(Wong et al., 2004)
<b>Chitosan</b>	Acid orange	922.9	(Wong et al., 2004)

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<b>Chitosan</b>	Acid red 73	728.2	(Wong et al., 2004)
<b>Chitosan</b>	Acid red 18	693.2	(Wong et al., 2004)
<b>Chitosan</b>	Acid green 25	645.1	(Wong et al., 2004)
<b>Peat</b>	Acid Blue 25	14.4	(Ho and McKay, 2003)
<b>Peat</b>	Acid Blue 25	12.7	(Ho and McKay, 1998)
<b>Peat</b>	Basic blue 69	195	(Ho and McKay, 1998)
<b>Modified peat</b>	Basic violet 14	400	(Sun and Yang, 2003)
<b>Modified peat</b>	Basic green 4	350	(Sun and Yang, 2003)
<b>Rhizopus arrhizus</b>	Reactive black 5	588.2	(Aksu and Tezer, 2000a)
<b>Green alga</b>	Reactive red 5	555.6	(Aksu and Tezer, 2005)
<b>Dead rimosus</b>	Methylene blue	34.34	(Nacèra and Aicha, 2006)
<b>Caulerpa lentillifera</b>	Methylene blue	417	(Marungrueng and Pavasant, 2007)
<b>Sargassum muticum</b>	Methylene blue	279.2	(Rubin et al., 2005)
<b>Dead macro fungi (F)</b>	Methylene blue	232.73	(Maurya et al., 2006)
<b>Dead macro fungi (P)</b>	Methylene blue	204.38	(Maurya et al., 2006)
<b>Algae Gelidium</b>	Methylene blue	171	(Vilar et al., 2007)
<b>Duckweed</b>	Methylene blue	144.93	(Waranusantigul et al., 2003)
<b>Algal waste</b>	Methylene blue	104	(Vilar et al., 2007)
<b>Composite material</b>	Methylene blue	74	(Vilar et al., 2007)
<b>Green alga</b>	Methylene blue	40.2	(El Sikaily et al., 2006)
<b>The brown alga</b>	Methylene blue	38.61	(Caparkaya and Cavas, 2008)
<b>Rhizopus arrhizus</b>	Reactive orange 16	190	(O'Mahony et al., 2002)
<b>Rhizopus arrhizus</b>	Reactive red 4	150	(O'Mahony et al., 2002)
<b>Rhizopus arrhizus</b>	Reactive blue 19	90	(O'Mahony et al., 2002)
<b>Yeasts</b>	Remazol blue	173.1	(Aksu and Dönmez, 2003)
<b>Yeasts</b>	Reactive black 5	88.5	(Aksu and Dönmez,

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			2003)
<b>Spirodela polyrrhiza</b>	Basic blue 9	144.93	(Waranusantigul et al., 2003)
<b>Aspergillus niger</b>	Direct red 28	14.72	(Fu and Viraraghavan, 2002a)
<b>Aspergillus niger</b>	Disperse red 1	5.59	(Fu and Viraraghavan, 2002b)
<b>Aspergillus niger</b>	Acid blue 29	13.82	(Fu and Viraraghavan, 2001)
<b>Living fungus</b>	Acid blue 29	6.63	(Fu and Viraraghavan, 2001)
<b>Dead fungus</b>	Methylene blue	18.54	(Fu and Viraraghavan, 2000)
<b>Living fungus</b>	Methylene blue	1.17	(Fu and Viraraghavan, 2000)

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#### 2.7.2.7 Miscellaneous Sorbents

Various other materials have also been reported as low-cost alternative sorbents such as starch, cellulose, lignin etc. (Delval et al., 2001, Delval et al., 2002, Delval et al., 2003). Starch is widely available as carbohydrate in the world and is present in living plants as an energy storage material. Starch is used generally in food applications. Other materials studied as inexpensive choice sorbents include cyclic derivative, cyclodextrin (Shao et al., 1996, Crini and Morcellet, 2002, Crini et al., 2002, Crini, 2003). It contains six to twelve glucose units. The cyclic derivative, cyclodextrin molecules are natural macrocyclic polymers, formed by the action of an enzyme on starch (Szejtli, 1998). The most characteristic feature of cyclic derivative, cyclodextrins is the ability to remove dye contaminants. Materials used to adsorb dyes are cotton waste and alumina (Desai et al., 1997, McKay et al., 1999, Harris et al., 2001, Bouzaida and Rammah, 2002). Cotton is widely used and is the most abundant of all naturally occurring organic substrates. The characteristic of this material is good physical and chemical properties in terms of stability, water absorbency and ability to remove dyes (McKay et al., 1999, Bouzaida and Rammah, 2002). Adsorption capacities by miscellaneous sorbents are also reported in Table (2.18).

Besides these various materials, there are also some materials that have been studied less widely as inexpensive adsorbents, such as melamine–formaldehyde–urea resin (Ozdemir et al., 2009), eggshell (Tsai et al., 2006), hair (McKay et al., 1986), crushed brick (Hameed et al., 2007), and spent tea leaves (Hameed, 2009b).

**Table 2.19** Adsorption capacities  $q_m$  (mg/g) for miscellaneous sorbents

<i>Material</i>	<i>Dye</i>	<i>Maximum adsorption capacity <math>q_m</math> (mg/g)</i>	<i>Reference</i>
<b>Spent tea leaves</b>	Methylene blue	300.05	(Hameed, 2009b)
<b>Hair</b>	Methylene blue	120	(McKay et al., 1986)
<b>Crushed brick</b>	Methylene blue	96.61	(Hamdaoui, 2006)
<b>MFUR</b>	Methylene blue	15	(Ozdemir et al., 2009)
<b>Eggshell</b>	Methylene blue	0.8	(Tsai et al., 2006)
<b>Cotton waste</b>	Basic red 2	875	(McKay et al., 1999)
<b>Cotton waste</b>	Basic blue 9	277	(McKay et al., 1999)
<b>Treated cotton</b>	Acid blue 25	589	(Bouzaida and Rammah, 2002)
<b>Treated cotton</b>	Acid yellow 99	448	(Bouzaida and Rammah, 2002)
<b>Treated cotton</b>	Reactive yellow 23	302	(Bouzaida and Rammah, 2002)
<b>Starch-based material</b>	Acid blue 25	249	(Delval et al., 2002)
<b>cyclodextrin</b>	Acid blue 25	88	(Crini, 2003)
<b>Chitosan/cyclodextrin</b>	Acid blue 25	77.4	(Martel et al., 2000)

## 2.8 Column Adsorption Study

Column adsorption experiments are for the study of adsorption dynamics. The fixed bed column operation permits more efficient utilization of the adsorption capacity than the batch operation. The most important condition in the design of fixed bed adsorption systems is judged through its service time, known as column breakthrough or the shape of the adsorption wave front, which verify the operation lifetime of the bed. To determine the operation and dynamic response of an adsorption column, it is very important to know the breakthrough curve shape and the breakthrough time appearance characteristics at various column parameters such as sorbent bed height, flow rate and initial dye concentration (Sarin et al., 2006).

The performance and the capacity of small-scale column, containing coarse particles of metal hydroxide sludge, were studied by (Netpradit et al., 2004) using 30 mgL<sup>-1</sup> dye solutions of C.I. Reactive Red 141. The bed depths were 2.5–20 cm and the flow rates were 1.1, 2.2 and 3.3 ml min<sup>-1</sup> cm<sup>-2</sup> and the breakthrough volume was increased with increasing bed depth or decreasing flow rate, due to an increase in empty bed contact time (EBCT). They found that the data followed the bed depth service time model. Gupta et al. (Gupta et al., 2004) found that the successful removal of methylene blue, rhodamine B, and fast green from wastewater using red mud through column study. The percentage removals of dyes on this adsorbent were achieved 95-97% removal in column experiments at a flow rate of 0.5 mL min<sup>-1</sup>, compared with 71.1-94% in a batch experiments, and they found that the developed system is very useful, rapid, and reproducible for the removal of these three dyes.

Tsai et al. (Tsai et al., 2008) investigated the possibility of activated carbon prepared from oil palm shell to remove methylene blue from its aqueous solutions through batch and column studies. The equilibrium data were fitted by the Langmuir isotherm model, and the effects of the bed height, initial dye concentration, and flow rate on methylene blue adsorption were studied in column experiments.

Continuous fixed-bed studies to evaluate the efficiency of jackfruit leaf powder as an adsorbent for the removal of methylene blue from its aqueous solution under various conditions such as bed depth, flow rate and initial methylene blue concentrations was studied by (Tamez Uddin et al., 2009). The results showed that the maximum

methylene blue adsorption and the longest breakthrough time were obtained at pH 10. The equilibrium removal decreased with increasing flow rate and increased with increasing initial methylene blue concentration, and the results showed that the column performed well at low flow rate. Also, breakthrough time and exhaustion time increased with increasing bed depth.

Ahmad and Hameed (Ahmad and Hameed, 2010) investigated the adsorption potential of bamboo waste based granular activated carbon to remove Reactive Black 5 from aqueous solution using fixed-bed adsorption column. The effects of inlet RB5 concentration, feed flow rate and adsorbent bed height on the breakthrough characteristics of the adsorption system were studied. The maximum bed capacity of  $39.02 \text{ mg g}^{-1}$  was obtained using  $100 \text{ mg L}^{-1}$  inlet dye concentration, 80 mm bed height and  $10 \text{ mL min}^{-1}$  flow rate. The adsorption data were fitted well to the Thomas and Yoon–Nelson models at different conditions.

A continuous fixed bed study was studied by using rice husk as the adsorbent for the removal of Congo red from its aqueous solution by Han et al. (Han et al., 2008). The effects of initial pH, existing salt, flow rate, influent concentration of Congo red and bed depth, were studied. The results showed that the breakthrough curves were dependent on flow rate, initial dye concentration and bed depth, and Thomas model was found suitable for the describe the breakthrough curve at the experimental condition, they were concluded that the rice husk column can remove Congo red from its solution.

### **2.8.1 Modelling of Fixed Bed Column Breakthrough**

The breakthrough curve is defined as a column effluent concentration over time. The time appearance and the curve shape of breakthrough are important characteristics for determining the dynamic response and operation of the adsorption column. Further, the breakthrough curve shape indicates the performance of the column system (Al Hawari, 2004). Generally, there are three kinds of breakthrough curves: (a) poor adsorption, (b) normal adsorption and (c) strong adsorption as shown in Fig. 2.5. In adsorption studies, the breakthrough curve often observed is the normal adsorption curve or the ‘S’ shape. In Fig. 2.5,  $t_b$  and  $V_b$  represent the breakthrough time and breakthrough volume respectively, and  $C_{\text{eff}}$  is referred to as the effluent concentration, respectively; column exhaustion time and column exhaustion volume

are denoted by  $t_{exh}$  or  $V_{exh}$  where  $C_{ex}$  is representing as corresponding column exhaustion concentration and  $C_i$  is the initial concentration.

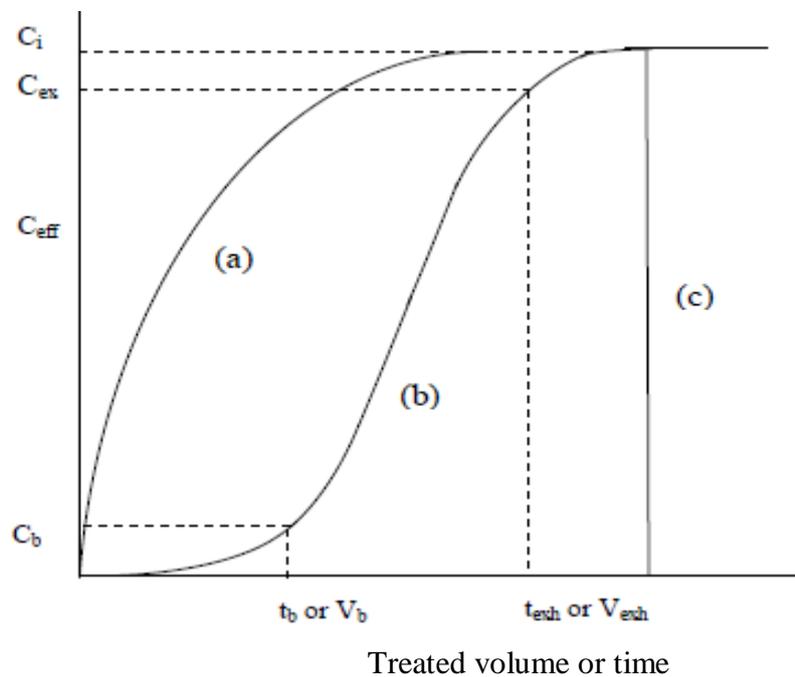


Figure 2.5 Breakthrough curves: (a) poor adsorption (b) normal adsorption and (c) strong adsorption. (Al Hawari, 2004).

To understand the behaviour of adsorption of dyes under column operation, the experimental data obtained were mathematically analyzed by using widely used column models. Following several mathematical models have been developed to describe pollutant sorption over different adsorbents.

***Thomas model:***

One of the most generally and widely used kinetic models in the column performance theory is the Thomas model. The assumption of this model is that the process follows Langmuir kinetics of adsorption-desorption with no axial dispersion, and the rate driving force obeys 2<sup>nd</sup> order reversible reaction kinetics. Thomas model also assumes that the constant separation factor is applicable to either favourable or unfavourable isotherm (Thomas, 1944).

The adsorption rate constant for a continuous adsorption process in column and the maximum solid phase concentration of the solute on the sorbent are developed by the expression of Thomas. The model has the following form (Thomas, 1944):

$$\frac{C}{C_0} = \frac{1}{1 + \exp \left[ K_T \left( \frac{q_0 m - C_0 V}{Q} \right) \right]} \quad (2.12)$$

where  $K_T$  is the Thomas rate constant (mL/mg min),  $q_0$  is the equilibrium adsorbate uptake (mg/g),  $m$  is the amount of adsorbent in the column (g),  $C_0$  inlet or initial concentration (mg L<sup>-1</sup>),  $C$  effluent phenol concentration (mg L<sup>-1</sup>),  $Q$  is the flow rate (ml min<sup>-1</sup>), and  $V$  is effluent volume (ml). The linearized form of Eq. 2.12 is given as:

$$\ln \left( \frac{C_0}{C} - 1 \right) = \left( \frac{K_T q_0 m}{Q} \right) - \left( \frac{K_T C_0 V}{Q} \right) \quad (2.13)$$

The kinetic coefficient  $K_T$  and the adsorption capacity of the bed  $q_0$  can be determined from a plot of  $\ln[(C_0/C) - 1]$  vs.  $t$  at a given flow rate.

***Yoon–Nelson model:***

The Yoon and Nelson model (Yoon and Nelson, 1984) is judged the less complicated column model as it requires no detailed data concerning the characteristics of adsorbate, the type of adsorbent, and the physical properties of adsorption bed. The assumption of this model is based on the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent. For a single component system the Yoon and Nelson equation is expressed as (Yoon and Nelson, 1984):

$$\frac{C}{C_0} = \frac{1}{1 + \exp [K_{YN} (\tau - t)]} \quad (2.14)$$

where  $K_{YN}$  is the Yoon and Nelson rate constant (min<sup>-1</sup>),  $C_0$  inlet or initial concentration (mg L<sup>-1</sup>),  $C$  effluent phenol concentration (mg L<sup>-1</sup>),  $t$  is the breakthrough (sampling) time (min), and  $\tau$  the time required for 50% adsorbate breakthrough (min). The linearized form of Eq. 2.14 is given as:

$$\ln\left(\frac{C}{C_0 - C}\right) = K_{YN} t - K_{YN} \tau \quad (2.15)$$

The plot of  $\ln(C/(C_0 - C))$  versus sampling time ( $t$ ) according to Eq. (2.15), will result in a straight line with slope of  $K_{YN}$  and intercept  $K_{YN} \tau$ .

## 2.9 Summary

This chapter highlights the environmental concerns of dye wastewater. Several treatment methods currently used including physical, chemical and biological treatment techniques provide good results but each of them has disadvantages and there is always room for improvement. The adsorption technique has been found the best option available especially for dye wastewater treatment without resulting in the formation of harmful substances. Activated carbon is a well known material that is used for dye wastewater treatment, but the cost of activated carbon is relatively expensive which limits its application. Agricultural by-product wastes have been chosen as an adsorbent to remove dye from its solutions. Modification of low cost adsorbent materials based on agricultural by-product wastes seems logical for dye removal. It is clear from the present literature survey that non-conventional adsorbents may have potential as readily available, inexpensive and effective sorbents for dyes. They also possess some other advantages that make them excellent materials for environmental purposes, such as high capacity and rate of adsorption, high selectivity for different concentrations, and also rapid kinetics.

This chapter present up to-date development on the application of adsorption in the removal of dyes from aqueous solution and this review include the following:

- This review provides extensive literature information about dyes, its classification and toxicity, various treatment methods dye adsorption and characteristics by various adsorbents.
- This review is to organize the scattered available information on various aspects on a wide range of potentially effective adsorbents in the removal of dyes.
- An extensive list of various adsorbents such as natural materials, waste materials from industry, agricultural by-products, and biomass based activated carbon in the removal of various dyes has been compiled
- The effectiveness of various adsorbents under different physio-chemical process parameters and their comparative adsorption capacity towards dye adsorption has also been presented.
- This review also includes some factors affecting adsorption of dye such as solution pH, initial dye concentration, adsorbent dosage, and temperature.

- The applicability of various adsorption kinetic models and isotherm models for dye removal by various adsorbents are also reported in this review.
- This review also includes column adsorption study and the application of various column models.

Literature to date has reported the successful results of using raw and modified agricultural by-products adsorbents for dye removal. Many types of adsorbents ranging from inorganic material to synthetic material have been modified with various conditions. Nevertheless, the use of agricultural waste as a material was not widely pursued. As far as the author is concerned, to date only a few modified agricultural by-products waste materials were used. Agricultural waste are known mostly consisting of charged surface sites and it has the ability to remove dye from its solutions. A few modified agricultural waste materials were used to remove dye. This study was undertaken to utilize raw and treated agricultural wastes pine cone and pine leaves in the removal of cationic dye Methylene Blue in a more economical way.

## **CHAPTER 3**

# **STUDIES ON CHARACTERIZATION OF RAW AND MODIFIED PINE CONE AND PINE LEAVES BIOMASS**

### **3.1 Introduction**

This chapter describes the characterization of raw and modified pine cone and pine leaves materials. The spectroscopic and various physicochemical properties of raw and modified pine cone and pine leaves materials were determined to establish the characteristics of the adsorbent and more important to study the influence of the modification to the pine materials properties for the sorption. The characterization of the structure and surface chemistry of pine materials biomass is of considerable interest for the development of adsorption and separation processes. The ability of adsorption of pine materials and treated pine materials depend upon chemical reactivity as well as porosity of functional groups at the surface. In this study the raw and modified pine materials surfaces were investigated by scanning electron microscopy (SEM) as it provides the information of surface morphology. The samples of six adsorbents used in the present study were analyzed by Fourier transform infrared spectroscopy (FTIR) which gives function groups information of adsorbents. Surface area, zeta potential, and bulk density were also discussed in this chapter.

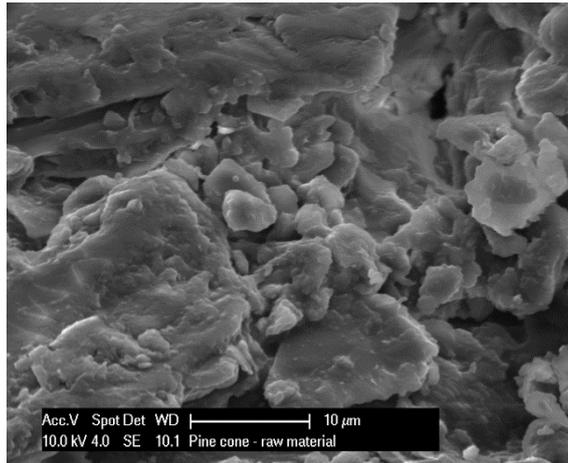
### **3.2 Characterization of Raw and Modified Pine Cone**

#### **3.2.1 Morphology Study of Raw and Modified Pine Cone Biomass**

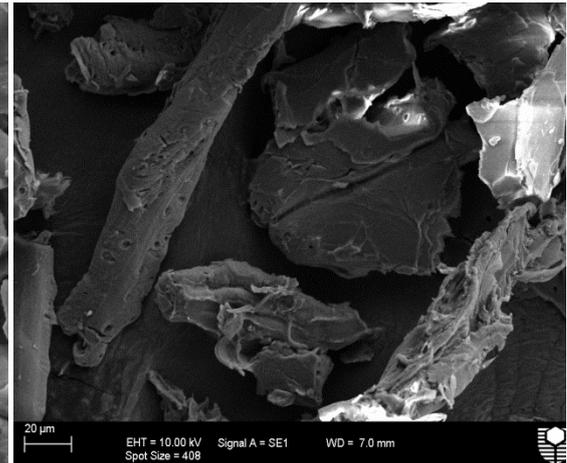
Raw and modified pine materials surface was examined by scanning electron microscopy

(SEM) as it gives the information of surface morphology. The SEM of all the prepared adsorbents illustrated the highly irregular size and shapes Figs. (3.1a-c). The surface morphology of untreated pine materials is different from the treated ones as the treatment may significantly alter the physicochemical properties and porosity of the materials. The treatment with alkaline was expected to partially remove protective thin wax on pine cone surface as what can be observed in Figure (3.1 b) and (3.1c). Figure (3.1 b) and (3.1c) also shows the appearance of perforation probably due to the leaching of structural materials that might have exposed the active sites on PC1 and PC2. This conclusion was also shared by (Rocha et al., 2009) in the modification of rice straw.

Comparing the modified pine cone Figure (3.1 b) and (3.1c) with the unmodified one (Fig. 3.1 a), it can be seen that the modified surface appears to be rough, indicating that the surface had been covered with organic molecular layer.



a/ Raw pine cone ( PC )



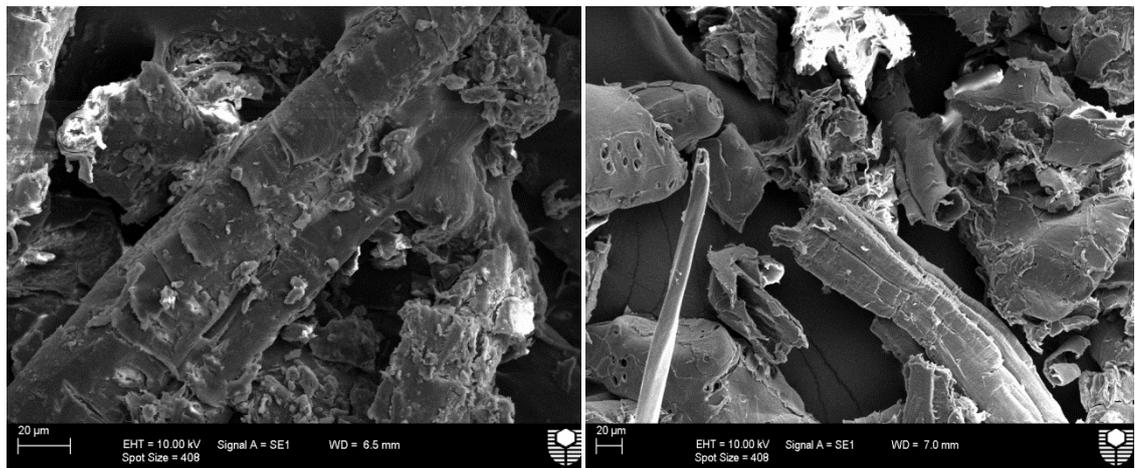
b/ Treated pine cone ( PC1 )



c/ Treated pine cone ( PC2 )

Figure 3.1 SEM micrographs of pine cone (a) before treated, (b) and (c) pine cone after treated.

Scanning electron micrographs (SEM) of pine cone biomass after adsorption is shown in (Figures 3.2a-c), The availability of pores and internal surface is evidently presented in the SEM picture of the pine cone biomass before and after adsorption and the pores by the adsorbed methylene blue MB is shown in Fig. 3.2. Essentially, the porous structure that was evident in Fig. 3.1 gets unclear in Fig. 3.2 because of adsorption.



a/ Raw pine cone ( PC )

b/ Treated pine cone ( PC1 )



c/ Treated pine cone (PC2)

Figure 3.2 SEM micrograph of pine cone materials after adsorption (a) (PC), (b) PC1, (c) PC2.

### 3.2.2 FTIR Study for Raw and Modified Pine Cone Biomass

One important characteristic of pine cone biomass is surface function groups present that are largely characterized by the FTIR spectroscopy method. The FTIR spectrum of pine cone and modified pine cone are shown in Fig (3.3a, b). FTIR provides information of the interaction of light and vibrational motion of the covalent chemical bonding of the molecules and lattice vibrations of ionic crystals (Ofomaja et al., 2009). As each substance is a unique grouping of atoms, no two compounds produce the same infrared spectrum. Therefore, infrared spectroscopy can result in a positive classification of different kinds of functional groups present in materials.

Fig. (3.3a) shows the spectra of pine cone biomass. The spectra for treated pine cone did not show any radical change indicating that treatment with a mild base solution did not significantly alter the chemical properties of the pine cone. Several peaks were observed from the spectra. Fig. (3.3a) indicating that pine cone is composed of various functional groups which are responsible for binding of cationic dye MB. The peaks at  $3,335.89\text{ cm}^{-1}$  represent vibrations, spectra bands observed at  $2,929.34\text{ cm}^{-1}$  indicate vibration of  $\text{CH}_n$  particularly due to  $\text{C-CH}_2$  and  $\text{C-CH}$  bonds. The peak at  $1,606.49\text{ cm}^{-1}$  indicate to  $\text{C=O}$  and vibration of  $\text{C=C}$ . The peak at  $1,263.48\text{ cm}^{-1}$  corresponds to  $\text{C-N}$  stretching with amine or  $\text{C-O}$  vibration of carboxylic acid (Ofomaja et al., 2009). The peaks  $1,027.97\text{ cm}^{-1}$  possibly assigned to the  $\text{-C-C-}$  stretching. Similar types of FTIR spectra of pine cone have been reported by few other investigators (Argun et al., 2008, Ofomaja et al., 2009). These function groups are responsible for adsorption.

The infrared spectrum of basic-modified pine cone sample showed similar characteristics as that of raw pine cone with minor changes. The FTIR spectra showed similar peaks but with small variation in the intensity in the band at  $3,333.98$  and  $3,331.15\text{ cm}^{-1}$ , the peak at  $2879.56$  and  $2,901.40\text{ cm}^{-1}$  and  $1,602.12$  and  $1601.06\text{ cm}^{-1}$ , indicating unbounded  $\text{-OH}$ , aliphatic  $\text{C-H}$  group and  $\text{C=O}$  stretch (Blázquez et al., 2011, Ofomaja and Naidoo, 2011, Akar et al., 2012, Deniz, 2013).

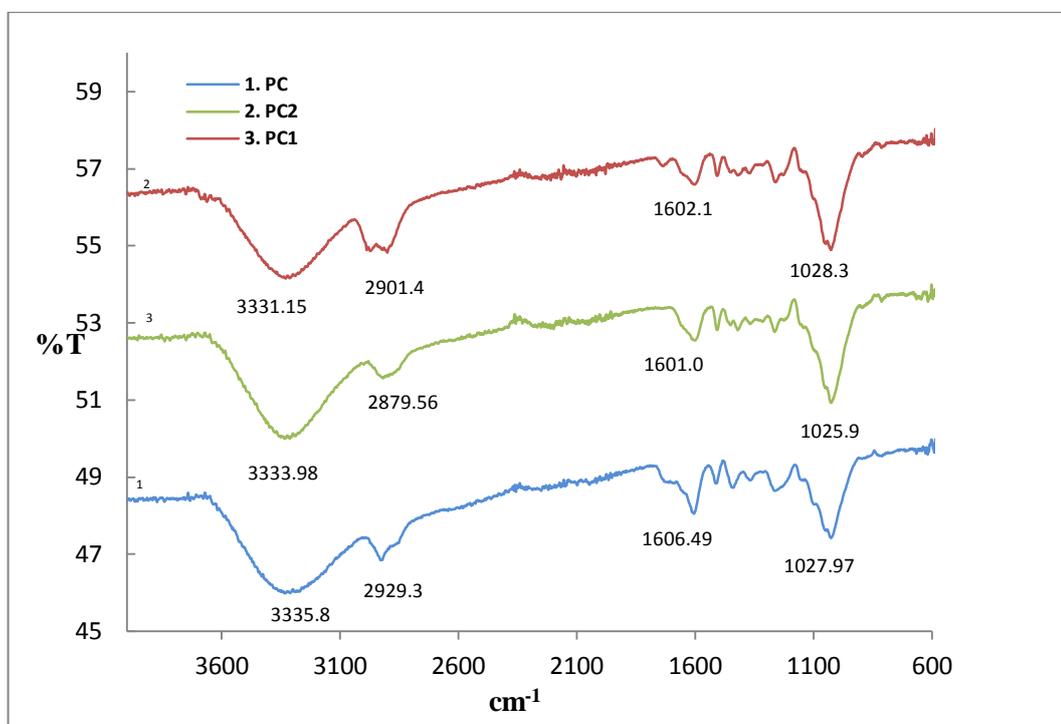


Figure (3.3a) FTIR spectra of raw pine cone (PC) and base-treated pine cone (PC1) & (PC2) before adsorption

The participation of raw and treated pine cone on MB dye removal was confirmed by the FTIR spectra of MB dye loaded adsorbents Fig (3.3b). The comparison of the spectra before and after MB dye adsorption of raw and modified pine cone (PC, PC1 and PC2) are shown in Figs. 3.3a and 3.3b. As shown in Fig. 3.3b, after adsorption the peaks of O–H stretching are shifted from (3335.89, 3331.15, and 3333.98  $\text{cm}^{-1}$ ) to (3332.16, 3329.56, and 3331.55  $\text{cm}^{-1}$ ) and the also the peaks of  $\text{CH}_n$  are shifted from (2929.34, 2901.40, and 2879.56  $\text{cm}^{-1}$ ) to (2927.21, 2899.34, and 2877.81  $\text{cm}^{-1}$ ) and the peaks of C=O are also shifted from (1606.49, 1602.12, and 1601.06  $\text{cm}^{-1}$ ) to (1604.65, 1601.32, and 1600.01  $\text{cm}^{-1}$ ) for PC, PC1, and PC2 respectively.

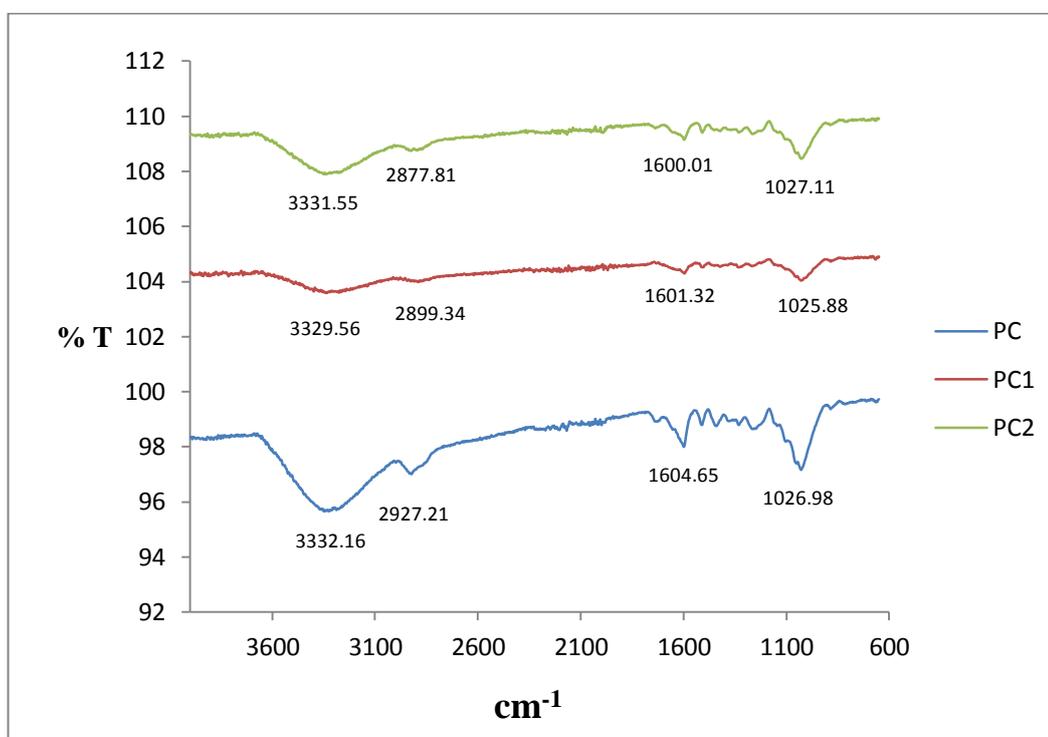


Figure (3.3b) FTIR spectra of raw pine cone (PC) and base-treated pine cone (PC1) & (PC2) after adsorption

### 3.2.3 Determination of Size and Surface Area of Raw and Modified Pine Cone

Surface area is also important as the larger surface area can raise the contact between the dye and the surface of pine cone materials. Table 3.1 compares the values of BET surface areas ( $\text{m}^2/\text{gm}$ ) for the raw pine cone (PC) and base treated pine cone (PC1 & PC2).

The results in Table 3.1 reveal that the raw pine cone had the least BET surface area ( $1.54 \text{ m}^2/\text{gm}$ ). Treatment of pine cone with NaOH produced an increase in surface area. Increasing surface area with base treatment has been attributed to extraction of plant components such as sugars, cementing materials and lignin which usually block pores on biomass materials and may dissolve some of the low molecular weight organic substances thus creating more pores and leading to further exposure of the biomass surface. The BET surface areas for treated pine cone were (2.5 and  $1.9 \text{ m}^2/\text{gm}$ ) for PC1 and PC2 respectively.

**Table 3.1** BET surface area for raw and treated pine cone

<i>Biomass</i>	<i>Surface area (<math>\text{m}^2/\text{gm}</math>)</i>
PC	1.54
PC1	2.5
PC2	1.9

### 3.2.4 Zeta Potential Study for Raw and Modified Pine Cone

Zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. The magnitude of the zeta potential of the particles is a measure of this particle interaction. The Zeta potential is a useful parameter for determining electrokinetic chemical properties of both raw and modified surfaces. One of the most important parameters that determine zeta potential is solution pH. The pH at which the surface charge is zero is called the point of zero charge (pzc) and is typically used to quantify or define the electrokinetic properties of a surface. Point of zero charge is of fundamental importance in surface science. The point of zero charge (pzc), in physical chemistry, is a concept relating to the phenomenon of adsorption, and it describes the condition when the electrical charge density on a surface is zero. The value of pH is used to describe pzc only for systems in which  $H^+/OH^-$  are the potential-determining ions. In the field of environmental science, it determines how easily a substrate is able to adsorb contaminated ions. The  $pH_{PZC}$  of pine cone materials were obtained from the plot of  $\Delta pH$  (the difference between initial pH and final pH at equilibrium) versus initial pH. The results shown in Fig (3.4a-c) indicate that the  $pH_{pzc}$  of raw pine cone was around 4.7. Surface modification reduced  $pH_{pzc}$  and therefore points of zero charge,  $pH_{pzc}$  of activated pine cone are 4.0 and 4.2 for PC1 and PC2 respectively. Due to presence of functional group, cationic dye adsorption is favoured at  $pH > pH_{pzc}$ . Negative surface of pine cone material increases with alkaline range.

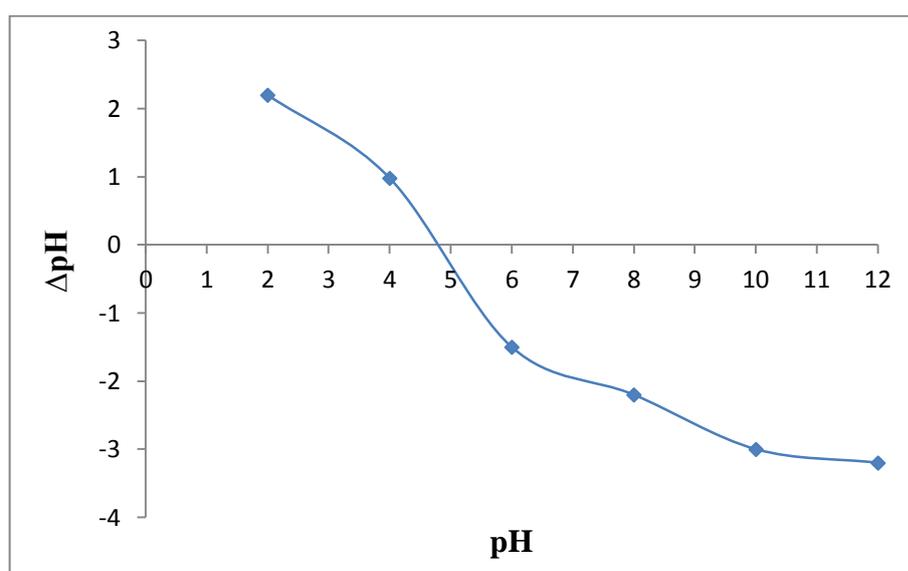


Figure 3.4a The point of zero charge of raw pine cone

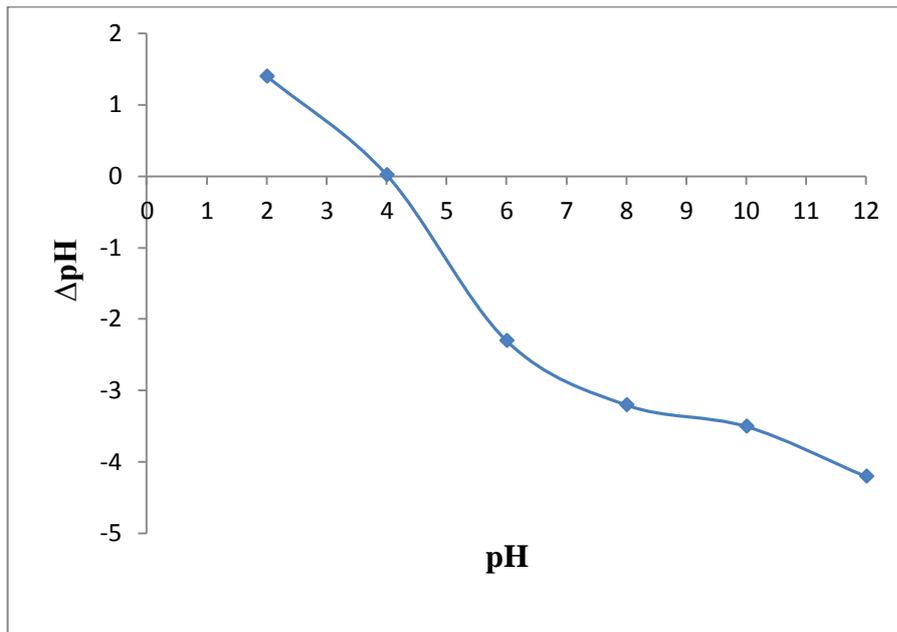


Figure 3.4b The point of zero charge of treated pine cone PC1

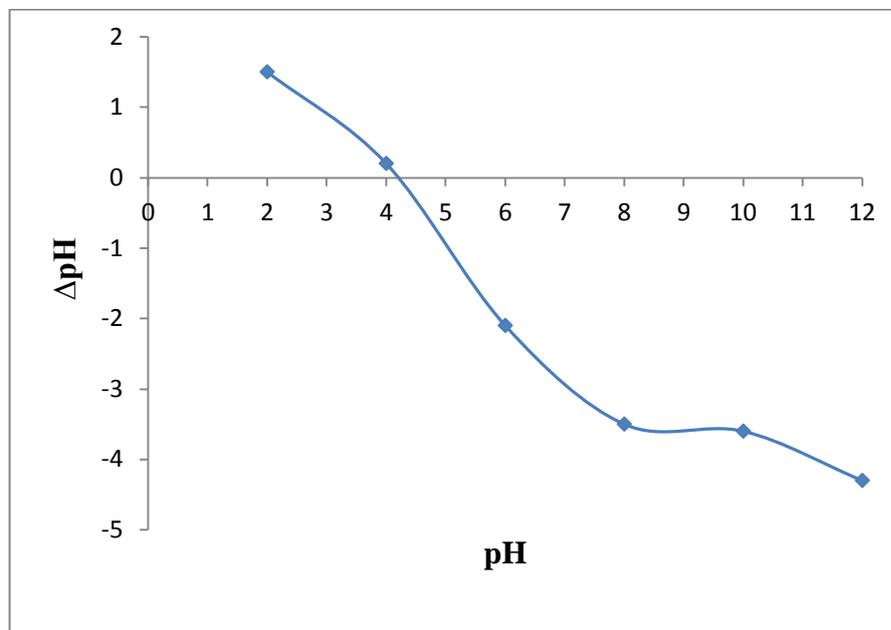


Figure 3.4c The point of zero charge of treated pine cone PC2

### 3.2.5 Bulk Density for Raw and Modified Pine Cone

Bulk density is an important parameter for consideration in the design of adsorption towers for use either in pilot plant or large commercial applications. It affects the overall performance of adsorption process. Bulk density proportional to the particle size.

Bulk density is defined as the mass of particles of the material divided by the total volume they occupy. It is a property that characterises powders, granules and other solids, and is used in reference to mineral components, chemical substances, ingredients, foodstuff or any other masses of corpuscular or particulate matter (Ahmedna et al., 1997).

The apparent (bulk) density was determined by the procedure described by Ahmedna et al. (Ahmedna et al., 1997). A 10 ml measuring tube was filled up with dry adsorbent sample and capped to a constant (minimum) volume by tapping on a table and weighed. The experiments were repeated under the same conditions. The bulk density was estimated by:

$$\text{Bulk Density} = \frac{\text{weight of dry sample (g)}}{\text{volume of packed dry material (cm}^3\text{)}} \quad (3.1)$$

A higher bulk density resulted for treated pine cone compared to raw pine cone as shown in Table 3.2. Higher bulk density in this case is favourable as it reflects the higher degree of compaction with less porosity which is fine for holding aqueous solution.

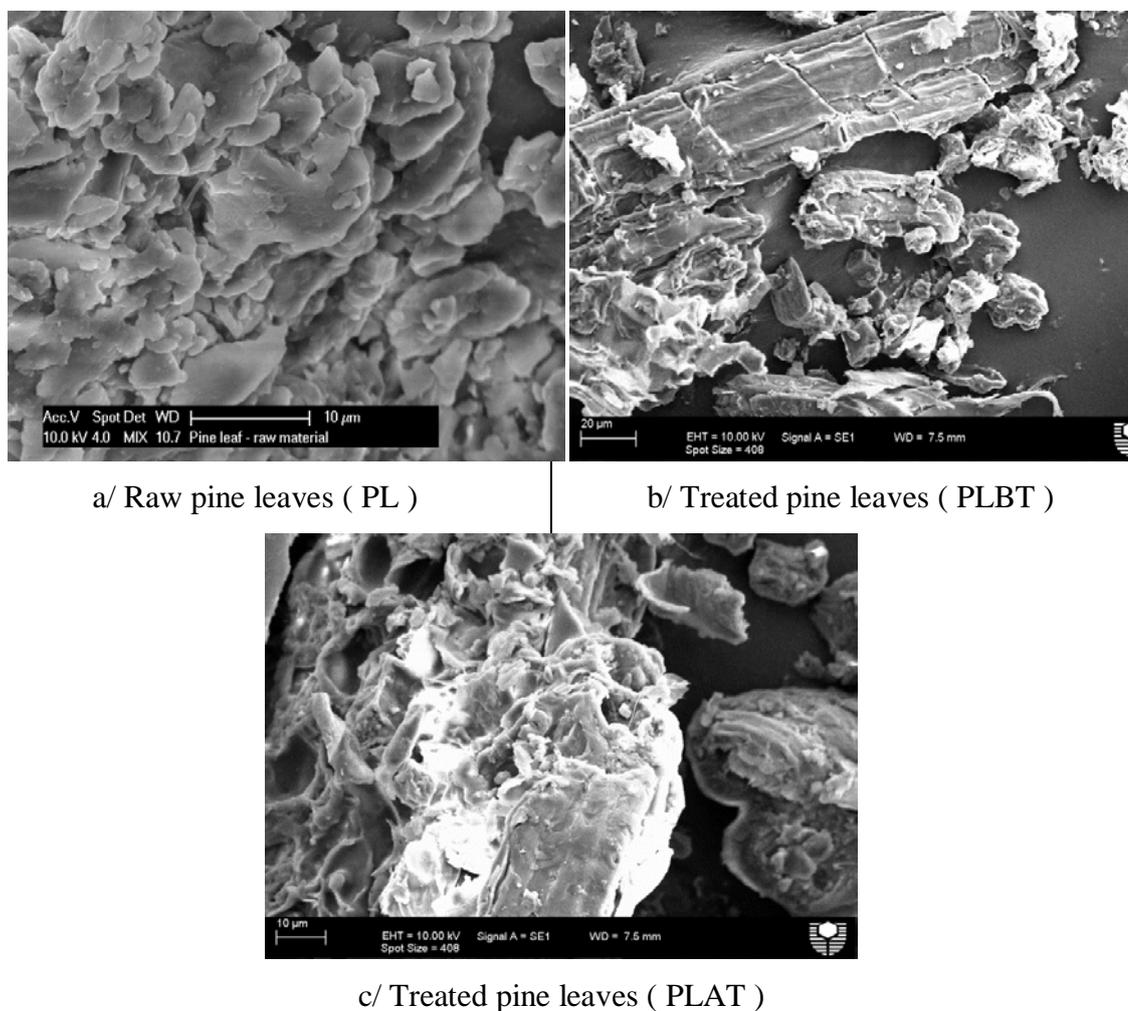
**Table 3.2** Bulk density for raw and treated pine cone

<i>Biomass</i>	<i>Bulk density (gm/cm<sup>3</sup>)</i>
PC	0.272
PC1	0.315
PC2	0.294

### 3.3 Characterization of Raw and Modified Pine Leaves

#### 3.3.1 Morphology Study for Raw and Modified Pine Leaves

The scanning electron microscope (SEM) was used to characterise raw and modified pine leaves surfaces. The SEM micro photos of raw and modified pine leaves adsorbents showed highly unequal size and shapes (Figs. 3.5a-c). Figures (3.5a-c) showed the surface morphology of treated pine leaves materials which is different from that of untreated pine materials. It can be seen that treated surface appears to be rougher than untreated pine leaves surface. The modification for pine leaves was supposed to partially remove protective thin wax on the surface of the pine leaves materials as can be seen in Fig. 3.5 a. The appearance of punctures maybe due to the leaching of structural materials and could result in more active sites on treated pine leaves.



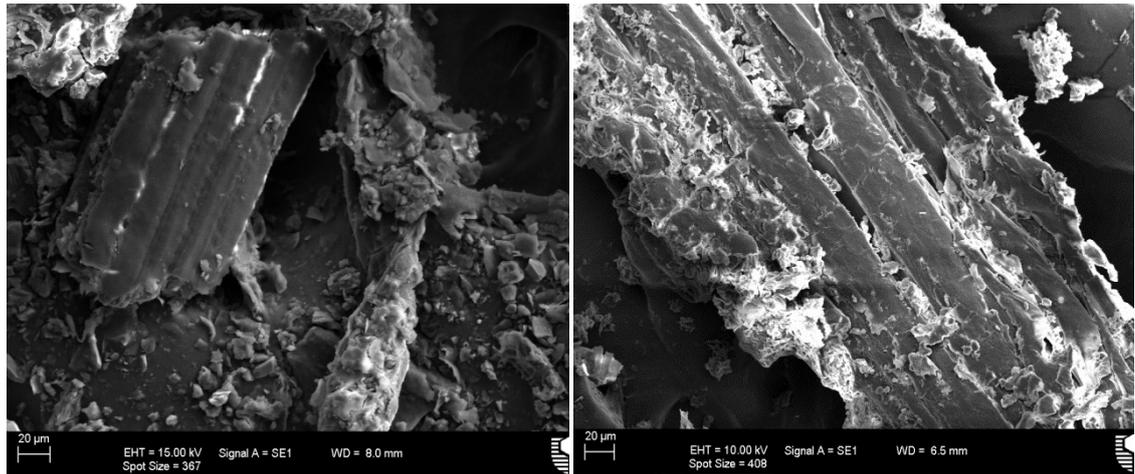
a/ Raw pine leaves ( PL )

b/ Treated pine leaves ( PLBT )

c/ Treated pine leaves ( PLAT )

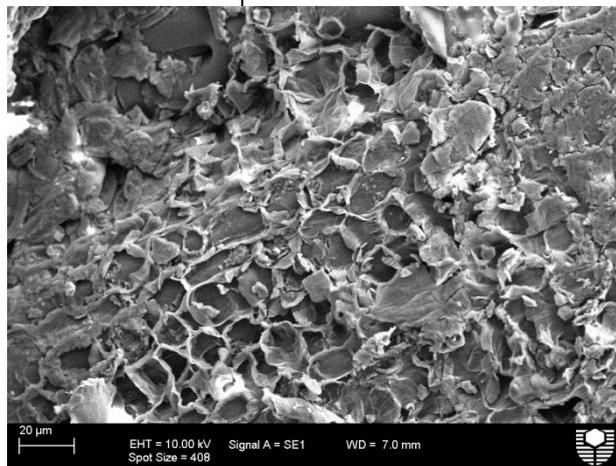
Figure 3.5 SEM micrograph of pine leaves (a) before treatment, (b) and (c) pine leaves after treatment

The scanning electron micrographs (SEM) of raw and modified pine leaves after adsorption are shown in Figures 3.6a-c.



a/ Raw pine leaves ( PL )

b/ Treated pine leaves ( PLBT )



c/ Treated pine leaves (PLAT)

Figure 3.6 SEM micrograph of raw and treated pine leaves materials after adsorption (a) (PL), (b) PLBT, (c) PLAT

### 3.3.2 FTIR Study for Raw and Modified Pine Leaves

The adsorption capacity of pine leaves biomass depends upon the chemical reactivity of functional groups at the surface. Pine leaves is composed of epidermal and sclerenchyma cells which contain cellulose, hemicellulose, lignin, rosin and tannins in their cell walls which contain polar functional groups such as alcohols, aldehydes, ketones, carboxylic, phenolic and other groups (Ofomaja et al., 2009). These groups will form active sites for sorption on the material surface. Therefore, knowledge of surface functional groups would give insight to the adsorption capacity of the pine cone biomass. These function groups are determined by the FTIR spectroscopy method.

The FTIR spectrum of raw and treated pine leaves are shown in Fig (3.7a, b). Fig. (3.7a) shows the spectra of pine leaves biomass. The spectra for modified pine leaves did not show any major changes indicating that treatment with either a mild acid or base solution did not significantly alter the chemical properties of the pine leaves. Several peaks were observed from the spectra. Fig. (3.7a) indicates that pine leaves are composed of different functional groups which are responsible for adsorption of the cationic dye MB.

The peaks at  $3,350.79\text{ cm}^{-1}$  represent O–H stretching vibrations, and spectra bands observed at  $2,919.13\text{ cm}^{-1}$  indicate vibration of CHn particularly due to C–CH<sub>2</sub> and C–CH bonds. The peak at  $1,622.79\text{ cm}^{-1}$  indicate C=O bond and vibration of C=C. The peak  $1,030.6\text{ cm}^{-1}$  is possibly assigned to the–C–C– stretching.

The FTIR spectrum for basic and acid modified pine leaves sample showed a similar characteristics as that of raw pine leaves biomass fig (3.7a). The FTIR spectra fig (3.7a) showed similar peaks but with small variation in the intensity in the band at  $3,339.4, 3,348.5\text{ cm}^{-1}$ , the peak at  $2,921.7, 2922.6\text{ cm}^{-1}$ , the peak at  $1,622.9, 1728.5\text{ cm}^{-1}$ , and the peak at  $1,030.6, 1,028.2\text{ cm}^{-1}$  for base and acid treated pine leaves respectively.

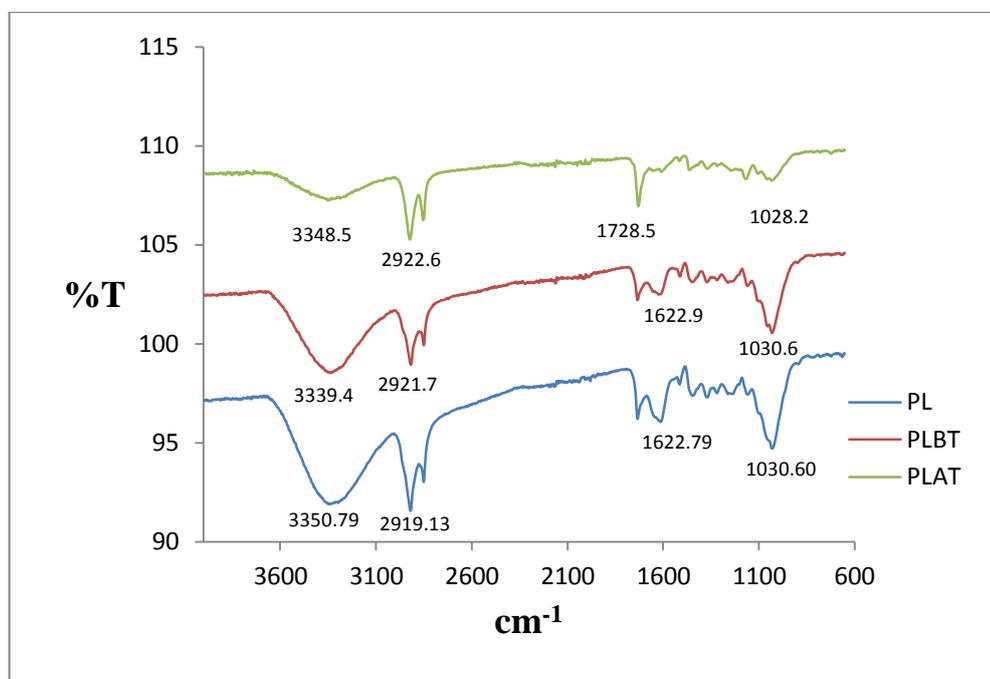


Figure 3.7a FTIR spectra of raw pine leaves (PL) and base (PLBT) & acid (PLAT) modified pine leaves before adsorption

The FTIR spectra of MB dye loaded raw and treated pine leaves are shown in fig. (3.7b).

The comparison between raw and treated pine leaves (PL, PLBT, PLAT) before and after MB dye adsorption are shown in Figs.(3.7a & 3.7b).

The FTIR spectra after MB dye loaded raw and treated pine leaves showed the peaks of O–H stretching are shifted from (3,350.79, 3,339.4, and 3,348.5  $\text{cm}^{-1}$ ) to (3,347.98, 3,335.2, and 3,335.3  $\text{cm}^{-1}$ ) and the also the peaks of  $\text{CH}_n$  are shifted from (2,919.13, 2,921.7, and 2,922.6  $\text{cm}^{-1}$ ) to (2,917.21, 2,919.0, and 2,921.2  $\text{cm}^{-1}$ ) and the peaks of C=O are also shifted from (1,622.79, 1,622.9, and 1,728.5  $\text{cm}^{-1}$ ) to (1,619.97, 1,599.0, and 1,728.7  $\text{cm}^{-1}$ ) for PL, PLBT, and PLAT respectively.

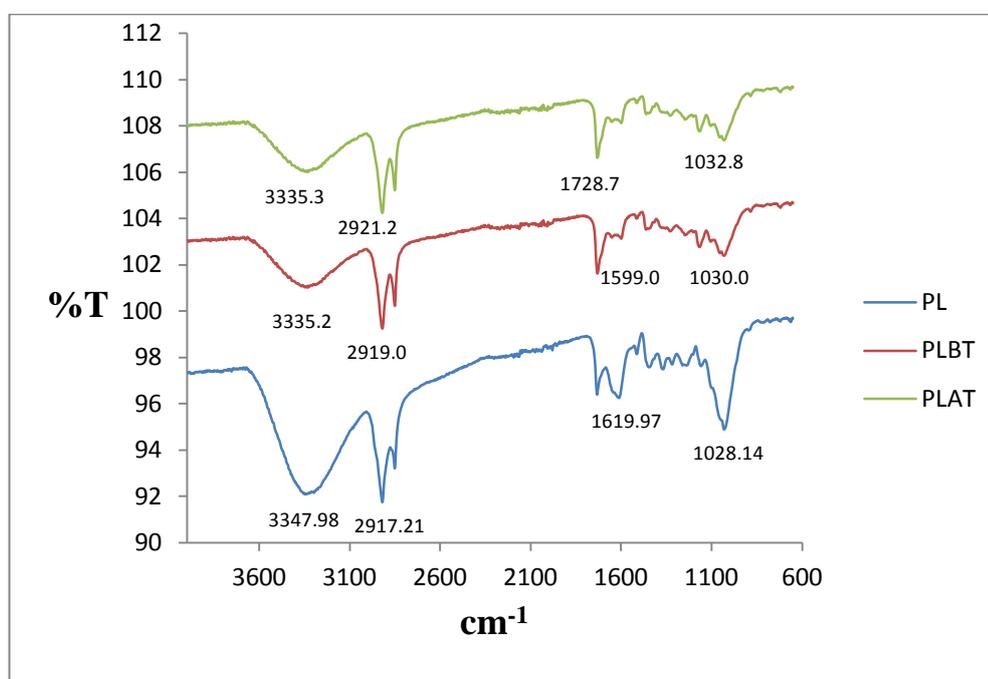


Figure 3.7b FTIR spectra of raw pine leaves (PL) and base & acid modified pine leaves (PPLBT) & (PLAT) after adsorption

### 3.3.3 Determination of Size and Surface Area of Raw and Modified Pine Leaves

Table 3.3 shows the values of BET surface areas ( $\text{m}^2/\text{gm}$ ) for the raw pine leaves (PL), base treated pine leaves (PLBT), and acid treated pine leaves (PLAT).

The results reveal that the treatment of pine leaves with NaOH and HCl produced an increase in surface area especially for acid treated pine leaves ( $1.53 \text{ m}^2/\text{gm}$ ).

The increasing surface area with chemical treatment has been attributed to loading of pine leaves biomass components such as sugars, cementing materials and lignin which generally dissolve some of the low molecular weight organic substance and may block pores on biomass materials thus creating more pores and leading to further exposure of the adsorbent surface.

**Table 3.3** BET surface area for raw and treated pine leaves

<i>Biomass</i>	<i>Surface area (<math>\text{m}^2/\text{gm}</math>)</i>
PL	1.17
PLBT	1.21
PLAT	1.53

### 3.3.4 Zeta potential Study for Raw and Modified Pine Leaves

The results were shown in Fig (3.8a-c) and the  $pH_{pzc}$  of raw pine leaves was (5.1), whereas the surface treatment decreases the points of zero charge  $pH_{pzc}$ . The points of zero charge  $pH_{pzc}$  for treated pine leaves are 4.5 and 4.3 for PLBT and PLAT respectively. From these results, cationic MB dye adsorption is favoured at  $pH > pH_{pzc}$ .

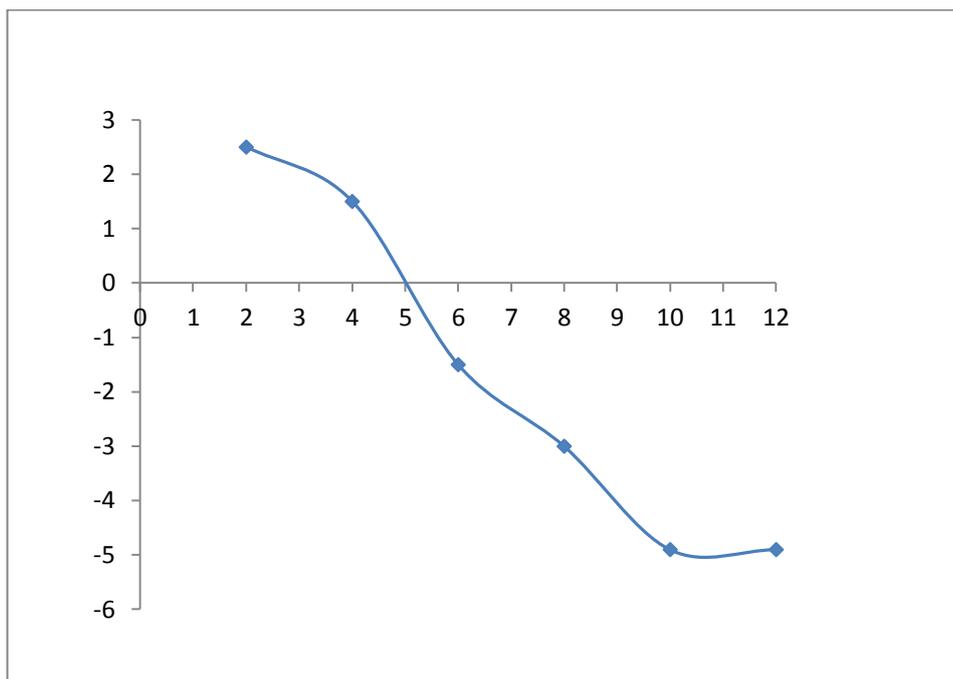


Figure 3.8a The point of zero charge of raw pine leaves

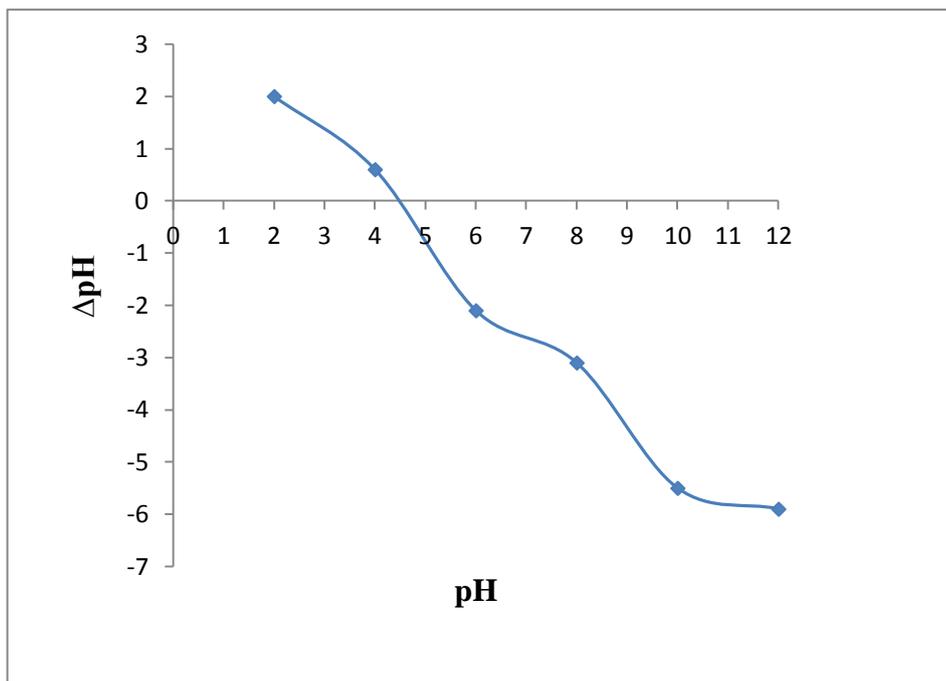


Figure 3.8b The point of zero charge of treated pine leaves PLBT

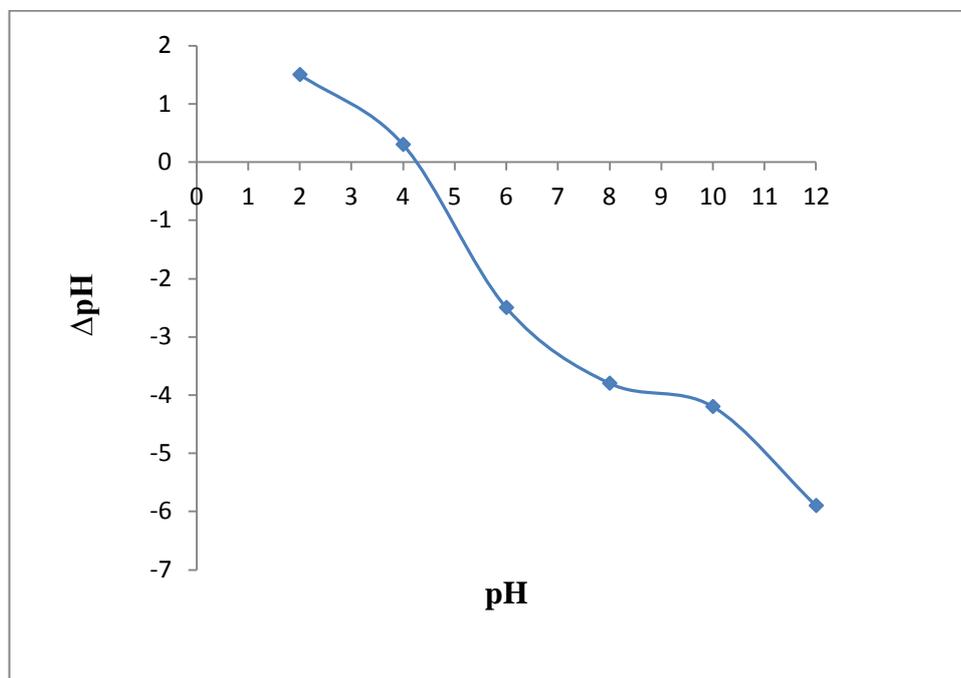


Figure 3.8c The point of zero charge of treated pine leaves PLAT

### 3.3.5 Bulk density for Raw and Modified pine leaves

The tests were conducted as per the method reported in section 3.2.5, and the results are shown in Table (3.4)

Table (3.4) shows higher bulk density for treated pine leaves than raw pine leaves. This is because the chemical treatment of pine leaves may dissolve some of the soluble compounds in the biomass. The bulk density for raw pine leaves was 0.216 (gm/cm<sup>3</sup>), whereas the bulk density for treated pine leaves were 0.244 and 0.267 (gm/cm<sup>3</sup>) for PLBT and PLAT respectively.

**Table 3.4** Bulk density for raw and treated pine cone

<b>Biomass</b>	<b>Bulk density (gm/cm<sup>3</sup>)</b>
PL	0.216
PLBT	0.244
PLAT	0.267

### 3.4 Summary

The characterizations of pine cone and pine leaves were presented in detail in this chapter. The study of characterization helps in understanding adsorption behaviour and mechanisms combined with the biomass and the summary is based on the results of the characterization of prepared raw and treated pine cone and leaves the and outcomes of this chapter are as follows

- The scanning electron microscopy (SEM) of prepared raw materials (pine cone and pine leaves) and modified materials (pine cone and pine leaves) showed the surface morphology of untreated pine materials is different from that of treated pine materials with chemicals was expected to partially remove protective thin wax on pine material surface.
- The FTIR of raw and modified pine materials showed that the two new peaks matching with peaks at about 2901.4 and 2879.56  $\text{cm}^{-1}$  on both PC1 and PC2, and 2921.7 and 2922.6  $\text{cm}^{-1}$  on both PLBT and PLAT, confirmed that the chemical treated was successfully retained on the pine cone surface.
- Surface area was higher for chemically treated pine materials (PC1, PC2, PLBT and PLAT) compared to untreated pine materials (PC and PL), this is due to dissolution of some substances. The increased percentage of surface area for PC1 and PC2 are 62.3% and 23.4%, respectively and those for PLAT and PLBT are 30.7% and 3.4%, respectively.
- The study of zeta potential for raw and modified pine materials showed a decrease of the point of zero charge for modified pine materials compared to unmodified ones. The point of zero charge for activated pine cone PC1 and PC2 are 4.0 and 4.2 respectively, whereas for raw pine cone was 4.7, and the point of zero charge for raw pine leaves was 5.1, whereas for modified pine leaves PLAT and PLBT are 4.3 and 4.5 respectively.
- The study of bulk density for raw and modified pine materials showed that higher bulk densities for treated pine materials. The bulk density for pine cone was 0.272  $\text{gm/cm}^3$ , whereas those for modified pine cone PC1 and PC2 are 0.315 and 0.294  $\text{gm/cm}^3$  respectively, and the bulk density for activated pine leaves PLAT and PLBT are 0.267 and 0.244  $\text{gm/cm}^3$  respectively, whereas for raw pine leaves is 0.216  $\text{gm/cm}^3$ .

## **CHAPTER 4**

# **REMOVAL OF METHYLENE BLUE DYE (MB) FROM AQUEOUS SOLUTION BY RAW AND MODIFIED PINE CONE BIOMASS**

## 4.0 Abstract of Article Published from this Chapter

The adsorption capacity of raw and sodium hydroxide-treated pine cone powder in the removal of methylene blue (MB) from aqueous solution was investigated in a batch system. It was found that the base modified pine cone exhibits large adsorption capacity compared with raw pine cone. The extent of adsorption capacity was increased with the increase in NaOH concentration. Overall, the extent of MB dye adsorption increased with increase in initial dye concentration, contact time, and solution pH but decreased with increase in salt concentration and temperature for both the systems. Surface characteristics of pine cone and base modified pine cone were investigated using Fourier transform infrared spectrophotometer and scanning electron microscope. Equilibrium data were best described by both Langmuir isotherm and Freundlich adsorption isotherm. The maximum monolayer adsorption capacity was found to be 129.87 mg g<sup>-1</sup> at solution pH of 9.02 for an initial dye concentration of 10 ppm by raw pine cone. The base modified pine cone showed the higher monolayer adsorption capacity of

142.25 mg g<sup>-1</sup> compared with raw pine cone biomass. The value of separation factor, RL, from Langmuir equation and Freundlich constant, n, both give an indication of favourable adsorption. The various kinetic models, such as pseudo-first-order model, pseudo-second-order model, intraparticle diffusion model, double-exponential model, and liquid film diffusion model, were used to describe the kinetic and mechanism of adsorption process. Overall, kinetic studies showed that the dye adsorption process followed pseudo-second-order kinetics based on other models. The different kinetic parameters, including rate constant, half-adsorption time and diffusion coefficient, were determined at different physicochemical conditions. A single-stage bath adsorber design for the MB adsorption onto pine cone and modified pine cone has been presented based on the Langmuir isotherm model equation. Thermodynamic parameters, such as standard Gibbs free energy ( $\Delta G^{\circ}$ ), standard enthalpy ( $\Delta H^{\circ}$ ) and standard entropy ( $\Delta S^{\circ}$ ), were also calculated.

YAGUB, M. T., SEN, T. K. & ANG, M. 2013. Removal of cationic dye methylene blue (MB) from aqueous solution by ground raw and base modified pine cone powder. *Environmental Earth Sciences*, 13, 1-13. (DOI: 10.1007/s12665-013-2555-0)

## 4.1 Introduction

This chapter deals with the investigation of effectiveness of raw and chemically modified pine cone as adsorbents for the removal of methylene blue (MB) dye from its aqueous solution. Batch adsorption studies were conducted to determine the effectiveness of the prepared adsorbents, pine cone (PC), and chemically treated pine cone (PC1&PC2) in removing methylene blue (MB) dye from its aqueous solution. The influence of various physiochemical parameters conditions such as contact time, initial dye concentration, pH, amount of adsorbent, agitation speed, salt concentration and system temperature on the removal of dye were investigated and discussed. To provide better understanding of the adsorption process and mechanism, batch experimental data were analyzed with commonly used kinetic models; pseudo first-order model and pseudo- second- order model, intrapartical diffusion model, and liquid film diffusion model. To simulate the adsorption isotherm, two commonly used models, the Langmuir and Freundlich were selected to explore dye–pine cone interaction and adsorption mechanism. Thermodynamic parameters such as standard Gibbs free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ), and entropy change ( $\Delta S^\circ$ ) were calculated. Finally the effectiveness of raw and treated pine cone adsorbent under various conditions tested here were compared with other published biomass based adsorbents.

## 4.2 System Identification

Raw and chemically treated pine cone biomass adsorbents were selected as agricultural by-product. Methylene blue (MB), the typical cationic dye was selected as the adsorbat.

## 4.3 Materials and Methods

### a) Pine cone of adsorbent and its characterization

Pine tree cones were collected locally from Curtin University campus, Perth, Western Australia, between April and May 2010. The cones were washed several times with distilled water to remove impurities, such as dirt and sand, and then dried in an oven at 65 °C for a day time period. Dried pine cones were then ground using a crusher. The resultant powders were passed through British standard sieves and particles measuring less than 100 µm were collected in a plastic container and used as adsorbent for adsorption experiments.

Base modified pine cone powder adsorbent was prepared by mixing 10 g of raw pine cone powder with 100 mL of 0.1 and 0.05 M NaOH solution. The whole reaction mixture was stirred in a magnetic stirrer for a period of 24 h and then the mixtures were filtered and washed with distilled water many times. The washed powder was then oven dried overnight at 50 °C and used for adsorption experiment and characterisation. The characterizations of raw and modified pine materials before and after experiment were characterized described in chapter -3.

### b) Adsorbate and other chemicals

MB (supplied by Sigma-Aldrich Pty. Ltd., NSW, Australia) was taken as the model adsorbate in this study. It was of analytical grade and used without further purification. The molecular weight of MB is 319.85 g and the formula of MB is  $C_{16}H_{18}N_3SCl \cdot 3H_2O$ . The stock dye solution was prepared by dissolving 1 g of MB in one litre distilled water. The pH of the experimental solutions was adjusted by addition of either dilute 0.1 M HCl or 0.1 M NaOH solutions. The pH measurements were performed using an Orien pH meter. The experimental solutions were obtained by diluting the stock dye solution with deionised water to give the appropriate concentration range of experimental solutions. The concentration of the residual dye was measured using UV/visible spectrometer at a  $\lambda_{max}$  corresponding to the maximum adsorption for the dye solution ( $\lambda_{max}=668$  nm) by withdrawing samples

at fixed time intervals, centrifuged and the supernatant was analysed for residual MB. Calibration curve was plotted between absorbance and concentration of the dye solution to obtain absorbance–concentration profile as shown in fig (4.1).

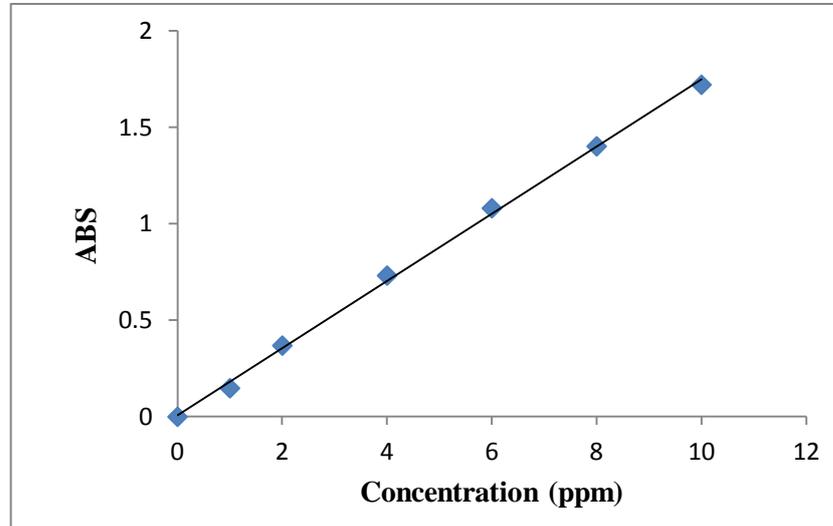


Figure 4.1 UV Calibration curve plot for MB adsorption

### c) Adsorption experiment

Adsorption measurement was determined by batch experiments of known amount of the adsorbent with 50 ml of aqueous methylene blue MB solutions of known concentration in a series of 250 ml conical flasks. The mixture was shaken at a constant temperature of 30 °C using Thermoline Scientific Orbital Shaker Incubator at 120 rpm for a period of 240 min. At pre-selected time interval, the bottles were withdrawn from the shaker, and centrifuged. The residual dye concentration in the reaction mixture was analyzed by UV spectrophotometer using calibration curve. Adsorption experiments were conducted by varying initial solution pH, contact time, adsorbent dose, initial methylene blue dye concentration, temperature, and salt concentration under the aspect of adsorption kinetics, adsorption isotherm, and thermodynamic study. The amount of dye adsorbed onto pine cone powder at time  $t$  is  $q_t$  (mg/g) which was calculated by the following mass balance equation:

$$q_t = \frac{(C_0 - C_t)}{m} V \quad (4.1)$$

where  $C_0$  is the initial dye concentration ( $\text{mg L}^{-1}$ ),  $C_t$  is the concentration of dye at any time  $t$ ,  $V$  is the volume of solution (L) and  $m$  is the mass of pine cone powder in (g)

The percentage dye removal was calculated as:

$$\% \text{ Removal} = \frac{(C_0 - C_t)}{C_0} * 100 \quad (4.2)$$

All measurements are in general reproducible within  $\pm 10\%$ .

The same experiments were repeated by using treated pine cone to compare the amount of adsorption  $q_t$  (mg/g) and extent of adsorption% between raw and treated pine cone.

## 4.4 Results and Discussion

Some of the experimental data used to obtain the results of the study of the effect of pine cones are listed in Appendix A1-23.

### 4.4.1 Effect of Initial Solution pH on MB Dye Adsorption

The pH of the adsorbate solution has been reported to be one of the most important variables for dye adsorption (Quintelas et al., 2009). This is partly due to the fact that hydrogen ions themselves are physically powerful competing ions and partly that the solution pH influences the dye as well as the ionization of the functional groups of the adsorbent surfaces (Quintelas et al., 2009, Saueprasearsit et al., 2010, Yu et al., 2009).

The results of MB solution studies indicate that change of initial pH (2.01 to 9.20) of dye solution has negligible effect on the  $\lambda_{\text{max}}$  of MB. This observation proves that no chemical structure charge of MB molecules occurs at that pH range.

The effect of pH on adsorption was studied in the range of 2.01 to 9.20 in both cases of raw and treated pine cone powder which is presented in Figures 4.2a, 4.2b, 4.2c. From Figure (4.2a) it was found that the amount of dye adsorbed ( $q_t$  mg) increased with increased pH for both the systems. From Figures (4.2a, 4.2b) it was also found that the amount of dye adsorbed increased from 14.08 mg/g (43.65% removal efficiency) to 30.37 mg/g (95.32% removal efficiency), for raw pine cone (PC) for a

fixed initial dye concentration of 10 ppm at equilibrium. Similarly from Fig (4.2a, 4.2b), it was found that the uptake of dye increased from 14.45 mg/g (46.35% removal efficiency) to 33.72 mg/g (96.96% removal efficiency), and from 14.21 mg/g (44.63% removal efficiency) to 32.07 mg/g (96.22% removal efficiency) for treated pine cone (PC1&PC2) respectively, due to change in pH from 2.01 to 9.2 for a fixed initial dye concentration of 10 ppm at equilibrium. Basically, here the amount of adsorbed mass of MB dye,  $q_t$  (mg/g) consistently increased with increasing solution pH (Fig. 4.2a). However the base-treated pine cone gives higher dye sorption capacity than the untreated (Fig. 4.2a) one. This is because of increase of the internal surface of treated sample (2.5 & 1.9  $m^2/g$ ) for (PC1 & PC2) than the raw pine cone powder (1.54  $m^2/g$ ). Maximum adsorption of MB occurs at basic pH (Fig 4.2a, b). Pine cone comprises of various functional groups such as amino, hydroxyl and carbonyl groups which are affected by the pH of the solution. The point of zero charge,  $pH_{PZC}$  of raw pine cone particles in aqueous solution is 4.7 and the negative zeta potential increased with increasing alkaline solution pH (Nuhoglu and Oguz, 2003; Blazque et al., 2011). Surface charge reduced  $pH_{PZC}$  and therefore points of zero charge,  $pH_{PZC}$  of treated pine cone were 4.01 and 4.20 for PC1 and PC2 respectively. In other words, the predominant charges on the pine cone at acidic pH are positive (Nuhoglu and Oguz, 2003). The dominant mechanism of the adsorption is electrostatic attraction (Mahmoode et al., 2011). The negative charge on cone biomass increased with increasing pH, which was also reported by Uzun et al. (Uzun et al., 2003) and therefore more cationic dye MB adsorption takes place due to electrostatic force of attraction.

The observed pH trend for both raw and modified pine cone clearly indicates that the maximum adsorption of methylene blue takes place at 7.01. This can be explained by the electrostatic interaction of cationic dye methylene blue with negatively charged surface of the pine cone. At acidic pH, the electrostatic repulsion gives poor adsorption between MB dye and positively charged adsorbent surface. In addition, lower adsorption of methylene blue at acidic pH might be due to the presence of excess  $H^+$  ions competing with dye cations for the available adsorption sites (Bestani et al., 2008, Vadivelan and Kumar, 2005).

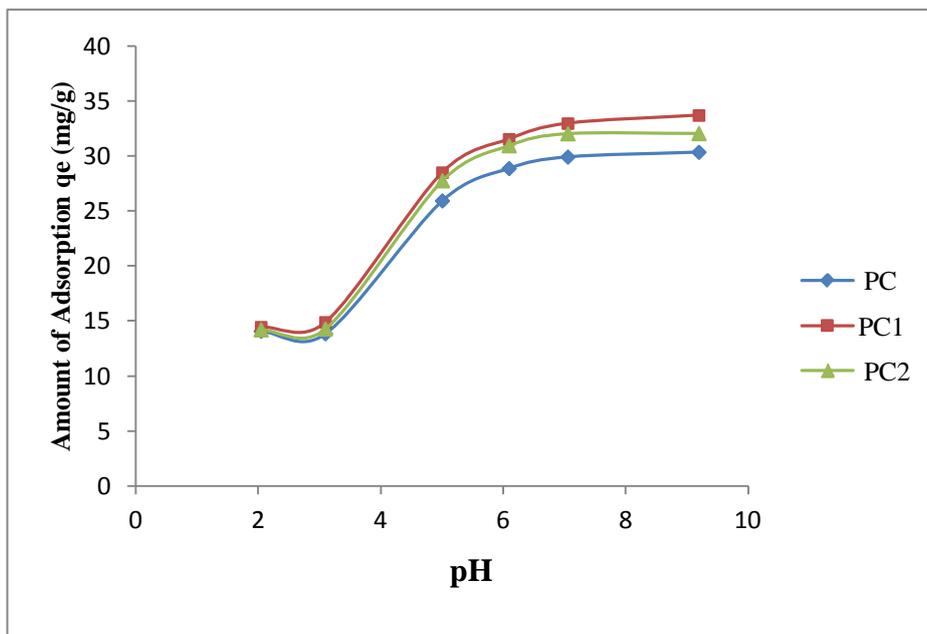


Figure 4.2a Effect of initial solution pH on the amount of adsorption of MB onto raw and treated pine cone

(Adsorbent=15mg; volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= 30°C; shaker speed=150 rpm; time 240 min)

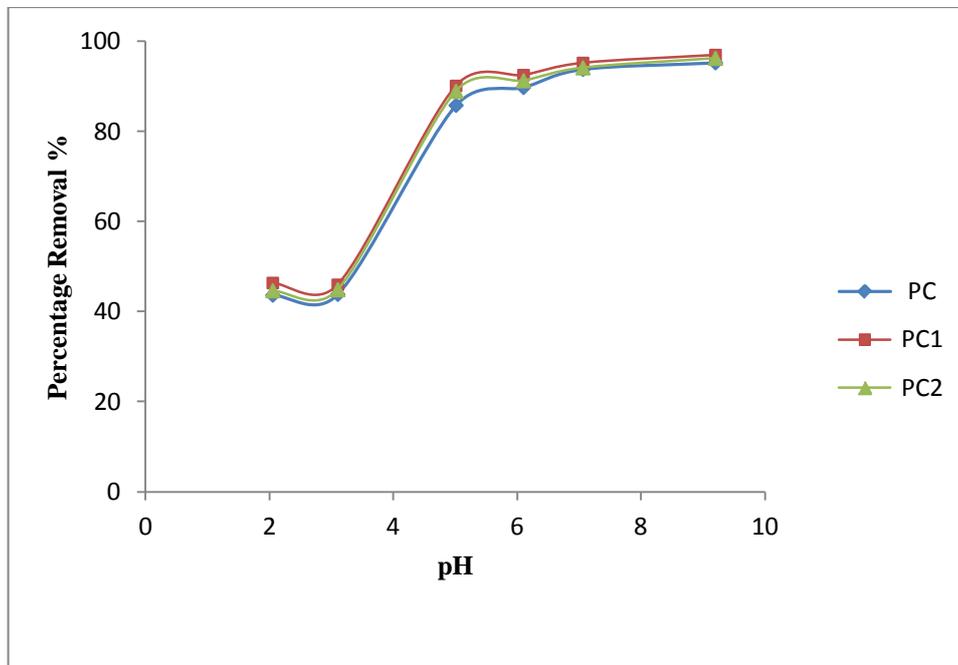


Figure 4.2b Effect of initial solution pH on percentage removal of MB onto raw and treated pine cone

(Adsorbent=15mg; volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= 30°C; shaker speed=150 rpm; time 240 min)

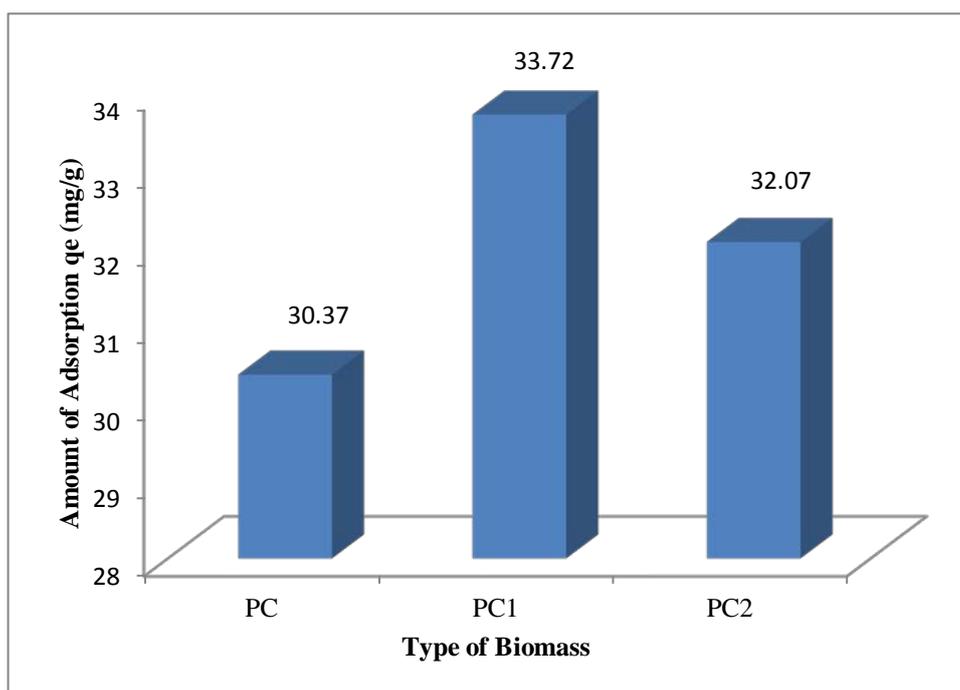


Figure 4.2c Effect of initial solution pH on maximum amount of adsorption of MB onto raw and treated pine cone

(Adsorbent=15mg; volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= 30°C; shaker speed=150 rpm; time 240 min)

#### 4.4.2 Effect of Contact Time on MB Dye Adsorption Kinetics

Contact time is one of the physical parameters for cost-effective wastewater treatment plant application (Saeprasearsit et al., 2010). Fig (4.3) shows that the removal of MB dye solutions was very fast at the initial period and decrease slightly until the equilibrium is reached for both raw and modified pine cone. Maximum adsorption of the MB takes place within 10min and thereafter the gradual increase in adsorption occurs with increasing contact time up to 120 min. This kinetic experiment clearly indicated that the adsorption of MB on raw and treated pine cone followed two step processes: a rapid initial adsorption followed by a period of slower uptake of MB. The first step is attributed to the instantaneous utilisation of the most readily available active sites on the adsorbent surface. Second step, exhibiting additional adsorption is attributed to the intra-particle diffusion in the interior of the adsorbent stimulating further movement of MB molecules from the liquid phase onto adsorbent pine cone surface. The rapid kinetics has significant practical importance, as it facilitates smaller reactor volumes, ensuring high efficiency and economy.

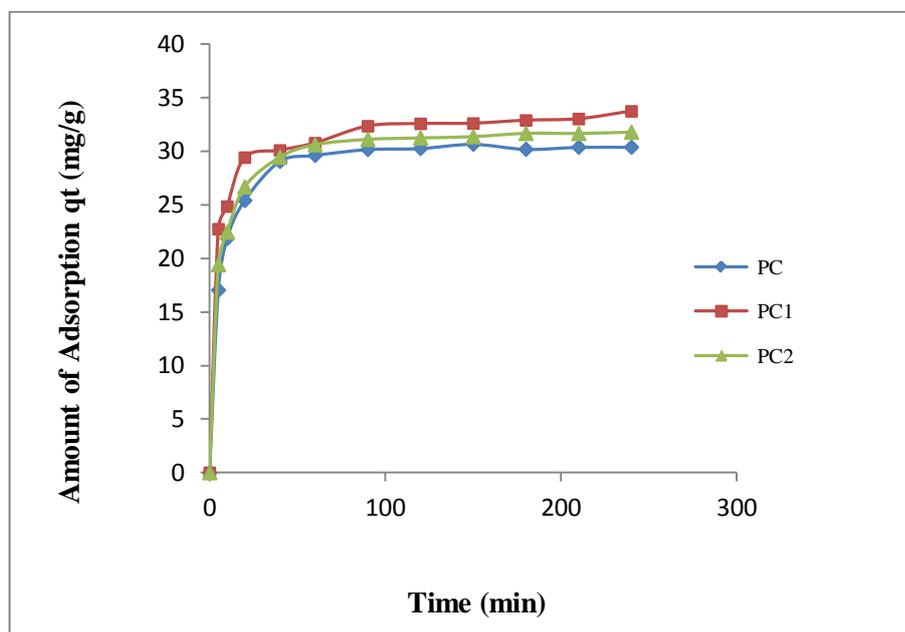


Figure 4.3 Effect of contact time on the adsorption of MB onto raw and treated pine cone

(Volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= 30°C; shaker speed=150 rpm; pine cone dosage 15mg; pH=9.20)

#### 4.4.3 Effect of Initial MB Dye Concentration on Adsorption

Figures (4.4a- c) show that the amount of adsorption increases with increase in initial dye concentration for both the systems. As the initial dye concentration increased from 10 to 90 mg/L, the adsorption capacity of dye onto raw and treated pine cone increased from 30.37 to 122.82 mg/g. Further, the adsorption capacity also increased with concentration of base modified pine cone. This indicates that the initial dye concentration plays a significant role in the adsorption characteristics of MB. However, the percentage removal of dye decreased from 95.5 to 40.9% for raw pine cone (PC), from 97.1 to 44.2%, and from 96.7 to 42.7% for modified pine cone (PC1&PC2) respectively, with increase in initial dye concentration from 10 to 90 mg/L after 240 minutes Fig (4.4b). Further, it was observed that the amount of methylene blue dye uptake,  $q_e$  mg/g, is increased with increase in initial dye concentration. Basically, from the figures (4.4b), the adsorption percentage decreases and the extent of adsorption increases with increasing initial dye concentration for

both raw and modified pine cone. This is because of the initial dye concentration provides the driving force to overcome the resistance to the mass transfer of dye between the aqueous and the solid phase. For constant dosage of adsorbent, at higher initial dye concentration, the available adsorption sites of adsorbent become fewer, and hence, the removal of methylene blue depends upon the initial concentration (Shahryari et al., 2010). The increase in initial concentration also enhances the interaction between adsorbent and dye. Therefore, an increase in initial dye concentration leads to increase in the adsorption uptake of dye. Similar types of results are reported by various researchers for methylene blue adsorption on activated carbon (Sharma, 2009), on carbon nanotube (Shahryari et al., 2010), on oak sawdust (Abd EI-Latif et al., 2010), on rice husk and rice husk ash (Sharma et al., 2010b), on water weeds biomass (Tarawou and Horsfall, 2007) and on cashew nut shell (Kumar et al., 2010).

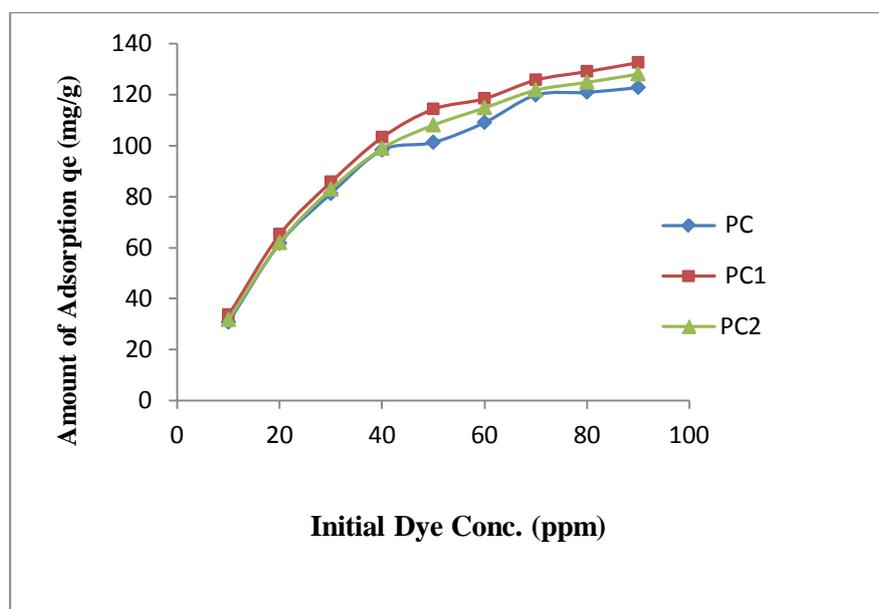


Figure 4.4a Effect of initial MB dye concentration on the amount of adsorption of MB onto raw and treated pine cone

(Volume of dye solution=50 ml; temperature= 30°C; pine cone dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

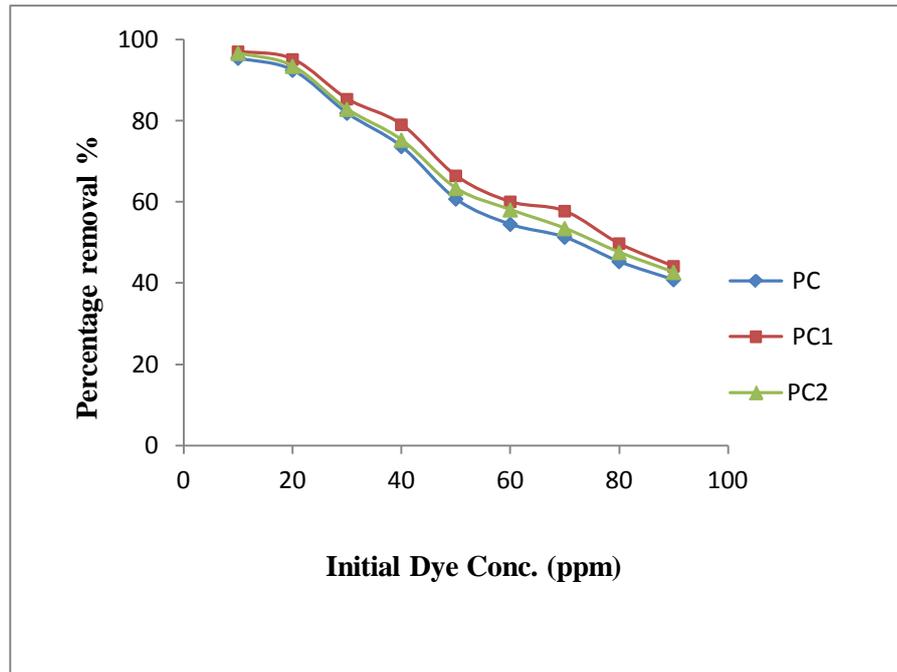


Figure 4.4b Effect of initial MB dye concentration on the percentage removal of MB onto raw and treated pine cone

(Volume of dye solution=50 ml; temperature= 30°C; pine cone dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

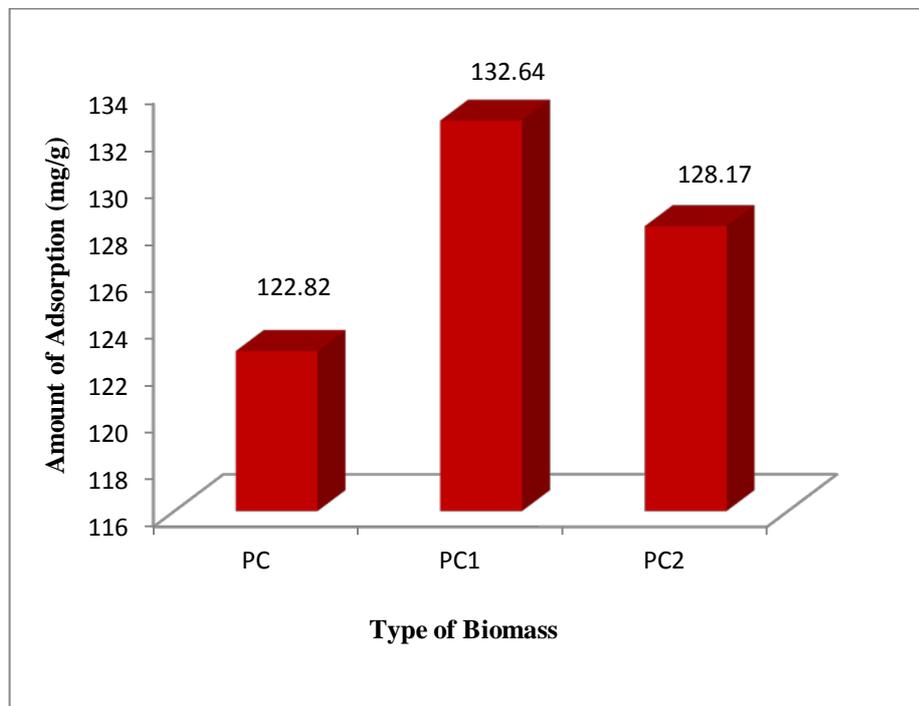


Figure 4.4c Effect of Initial MB Dye Concentration on the maximum amount of adsorption of MB onto raw and treated pine cone

(Volume of dye solution=50 ml; temperature= 30°C; pine cone dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

#### 4.4.4 Effect of Inorganic Monovalent Salt Concentration on MB Dye

The effect of salt concentration (NaCl) on removal of methylene blue MB was considered at different NaCl concentrations of 50, 100, 150, 200 mg L<sup>-1</sup> at fixed adsorbent dose of 15 mg. Figure (4.5) shows that the dye adsorption by raw and treated pine cone decreased with increase of inorganic salt. This result may be due to competition for adsorption sites between Na<sup>+</sup> ions and MB. Similar results for different system has been reported by different investigators (Mahmoode et al., 2011, Sen et al., 2011).

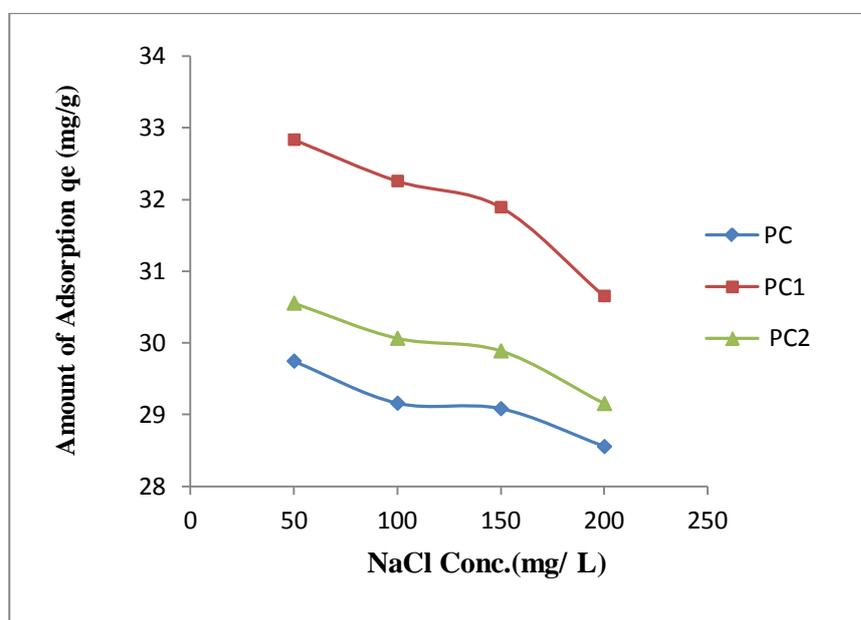


Figure 4.5 Effect of salt concentration on the adsorption of MB onto raw and treated pine cone

(Volume of dye solution=50 ml; temperature= 30°C; pine cone dosage 15mg; pH=9.2; agitation speed 150 rpm. and initial dye concentration 10 mgL<sup>-1</sup>; time 240 min)

#### 4.4.5 Effect of Temperature on MB Dye Adsorption

Effect of temperature is another major physical parameter because temperature may change the adsorption uptake of the adsorbent (Argun et al., 2008). To study the effect of temperature on the adsorption of MB dye adsorption by raw and treated pine cone, the experiments were carried out at temperatures of 30, 40, 50, and 60 °C. Figure (4.6), shows the influence of temperature on the adsorption of MB dye onto raw and modified pine cone. As it was observed, the equilibrium adsorption capacities of MB onto raw (PC) and modified pine cone (PC1 and PC2) decreased with increasing temperature. This is because of decreased surface activity suggesting that adsorption between MB and pine cone biomass was an exothermic process. With increasing temperature, the attractive forces between the pine cone biomass surface and MB are weakened and then sorption decreases. This may be due to a tendency for MB molecules to escape from the solid phase of pine cone to the liquid phase with an increase in temperature of the solution. Therefore the lower temperature is in favour of adsorption. Similar type of results for the methylene blue adsorption at various temperatures in (Kumar et al., 2010, Nandi et al., 2009b, Tarawou and Horsfall, 2007) have been reported for different system.

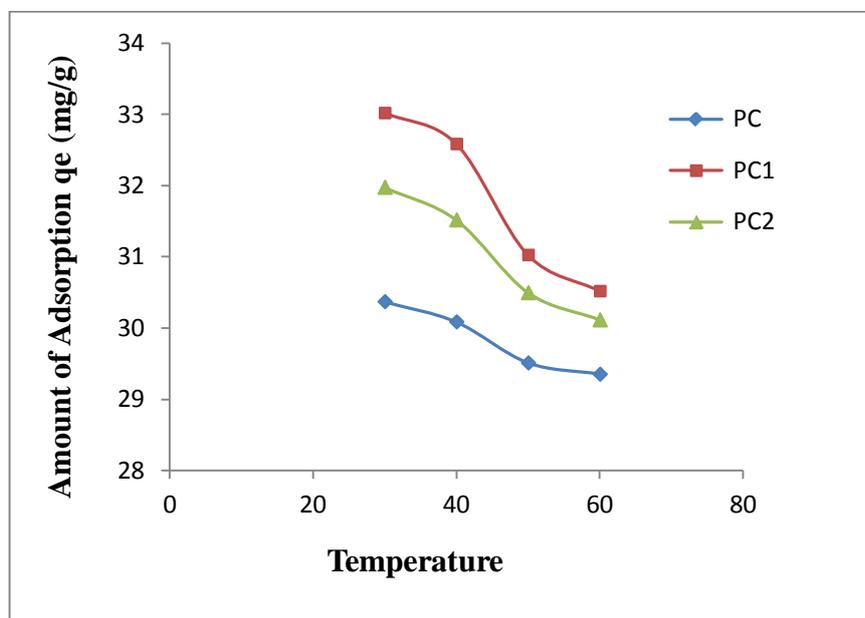


Figure 4.6 Effect of temperature on the adsorption of MB onto raw and treated pine cone

(Adsorbent=15mg; volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= (30, 40, 50, 60) °C; shaker speed=150 rpm; pH=9.17; time 240 min)

#### 4.4.5.1 Calculation of thermodynamic Parameters for MB Adsorption Process

Thermodynamic properties of an adsorption process are needed to conclude whether the process is favourable or not. The thermodynamic parameters, such as free energy change ( $\Delta G^{\circ}$ ), enthalpy change ( $\Delta H^{\circ}$ ), and entropy change ( $\Delta S^{\circ}$ ) are to be determined from temperature effect adsorption data. Assuming that the activity coefficients are unity at low concentrations (the Henry's law sense), the relationship of these thermodynamic parameters with sorption equilibrium constant  $K_e$  is given by the equation (Karagöz et al., 2008, Pehlivan and Arslan, 2007) as follows :

$$K_e = 1000 \frac{q_e}{C_e} \quad (4.3)$$

$$\ln K_e = \frac{\Delta S^{\circ}}{R} + \frac{-\Delta H^{\circ}}{RT} \quad (4.4)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \quad (4.5)$$

Where;  $K_e$  is the distribution coefficient of the adsorbate,  $q_e$  and  $C_e$  are the equilibrium concentration of methylene blue on the pine cone materials ( $\text{mg L}^{-1}$ ) and in the solution ( $\text{mg L}^{-1}$ ), respectively.  $R$  is the universal gas constant ( $8.314 \text{ J/mol K}$ ) and  $T$  is the temperature (K).  $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$  parameters can be calculated from the slope and intercept of the plot  $\ln K_e$  vs.  $1/T$ , respectively which is showed in Fig (4.7).

Thermodynamic parameters of an adsorption process such as Gibb's free energy change ( $\Delta G^{\circ}$ ), enthalpy change ( $\Delta H^{\circ}$ ), and entropy change ( $\Delta S^{\circ}$ ) for this system (methylene blue pine cone) were determined by the application of Eqs. (4.4) and (4.5) and also with the Van't Hoff plot fig (4.7). All three thermodynamic parameters are tabulated in Table 4.1. In general, the overall ( $\Delta G^{\circ}$ ) (Table 4.1) is negative with values ranging from  $-58.3$  to  $-62.7 \text{ kJ/mol}$  at the temperature range studies. This result corresponds to a spontaneous physical adsorption of MB indicating that this system does not gain energy from external resource. The increase in ( $\Delta G^{\circ}$ ) with increase in temperature indicates the adsorption becomes more favourable with increasing temperature. The negative value of enthalpy change ( $\Delta H^{\circ}$ ) (Table 4.1) indicates the exothermic nature of adsorption. The negative values of ( $\Delta S^{\circ}$ ) of pine

cone (Table 4.1) suggest a decrease in randomness at their solid/liquid interface, and no significant changes occur in the internal structure of the adsorbents through the adsorption (Sen et al., 2011).

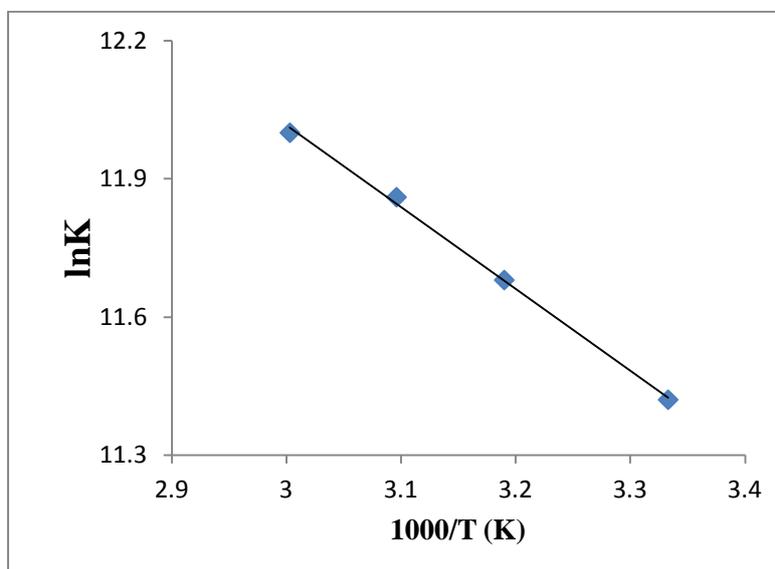


Figure 4.7 Van't Hoff plot for adsorption of MB into pine cine

**Table 4.1** Thermodynamic parameters for adsorption of MB onto raw pine cone at different temperatures

Temperature (K)	$\Delta G^\circ$ (kJ/mol <sup>-1</sup> )	$\Delta H^\circ$ (kJ/mol <sup>-1</sup> )	$\Delta S^\circ$ (kJ/mol <sup>-1</sup> K <sup>-1</sup> )
303	-58.3	-14.75	-0.144
313	-59.8	-14.75	-0.144
323	-61.2	-14.75	-0.144
333	-62.7	-14.75	-0.144

#### **4.4.6 Effect of Adsorbent Dosage on MB Dye Kinetic Adsorption**

The amount of adsorbent represents an important parameter due to its strong effect on the capacity of an adsorbent at given initial dye concentration (Sari et al., 2007). Figure (4.8a,b) shows that at equilibrium, the increase in adsorbent dosage from 10 to 30 mg resulted in decrease of amount of adsorbed dye for both the systems. A fixed mass of pine cone materials can only adsorb a fixed amount of dye. At higher pine cone to methylene blue concentration ratios, there is a very fast superficial sorption onto the biomass surface that gives a lower dye concentration in the solution compared to the lower biomass to dye concentration ratio. This is because a fixed mass of biomass can only adsorb a fixed amount of dye. Therefore, the more the adsorbent dosages, the bigger the volume of effluent that a fixed mass of biomass can purify (Kumar et al., 2005, Senthil Kumar et al., 2010b). In general, pH of final solution increases gradually with the increase in adsorbent dosages (Wang et al., 2008a, Arias and Sen, 2009). It may be attributed to evident increase of the amount of negatively charged sites which can induce more H<sup>+</sup> ions adsorb on pine cone surface and result in an increase in pH of the final solution. A similar behaviour was observed for methylene blue adsorption on rice husk (Vadivelan and Kumar, 2005, Sharma et al., 2010a), on cashew nut shell (Senthil Kumar et al., 2010b).

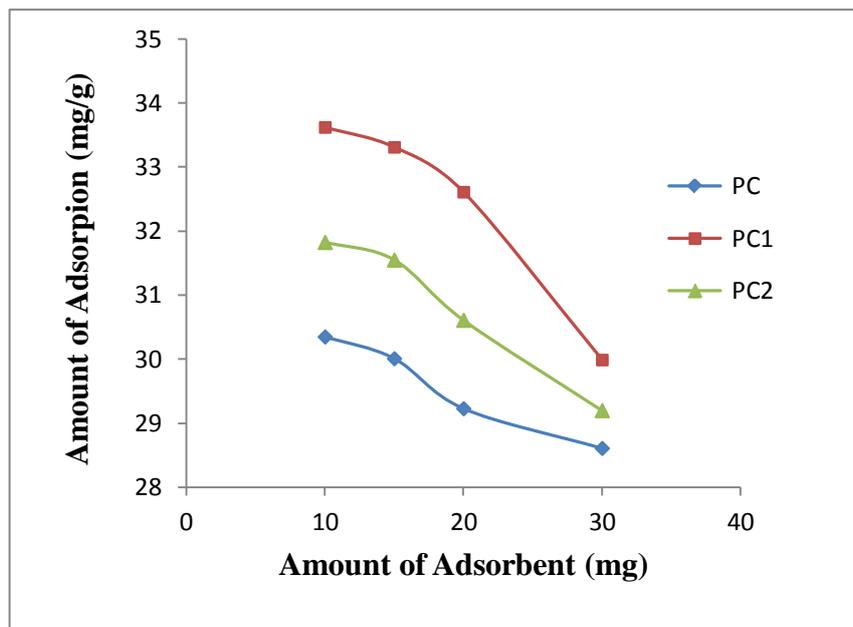


Figure 4.8a Effect of adsorbent pine cone materials dosage on the percentage removal of MB

(Volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= 30°C; shaker speed=150 rpm; pH=9.2; time 240 min)

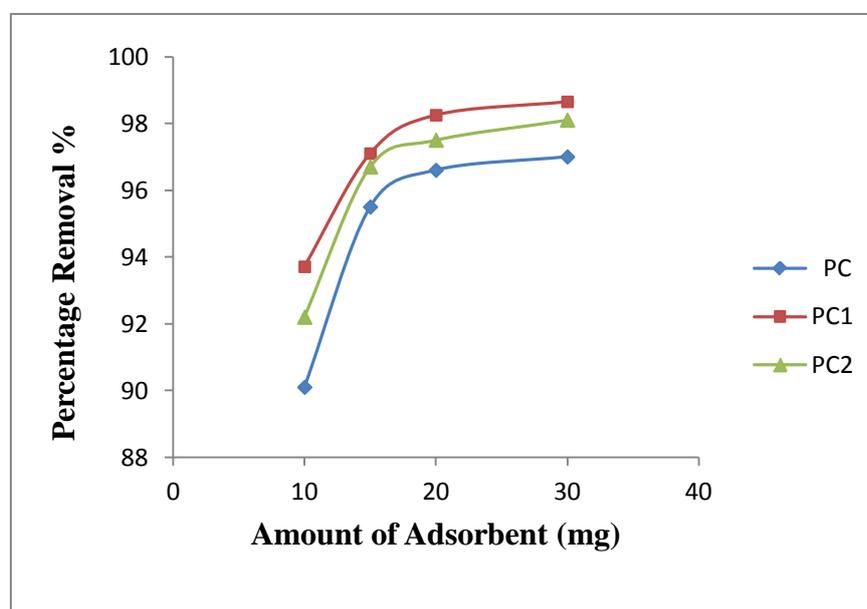


Figure 4.8b Effect of adsorbent pine cone materials dosage on the amount of adsorption of MB

(Volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= 30°C; shaker speed=150 rpm; pH=9.2; time 240 min)

#### 4.4.7 Effect of Agitation Speed on MB Dye Kinetic Adsorption

To determine the effect of agitation speed on the equilibrium adsorption, batch runs were conducted at different speeds ranging from 100 to 200 rpm. Fig (4.9) shows that the amount of adsorption of dye increased as the agitation speed increased for both the systems. This fact can be attributed to the increase in turbulence and the decrease in boundary layer thickness around the adsorbent particles. This result is also in agreement with that reported by (Ho et al., 2001, Tsai et al., 2008).

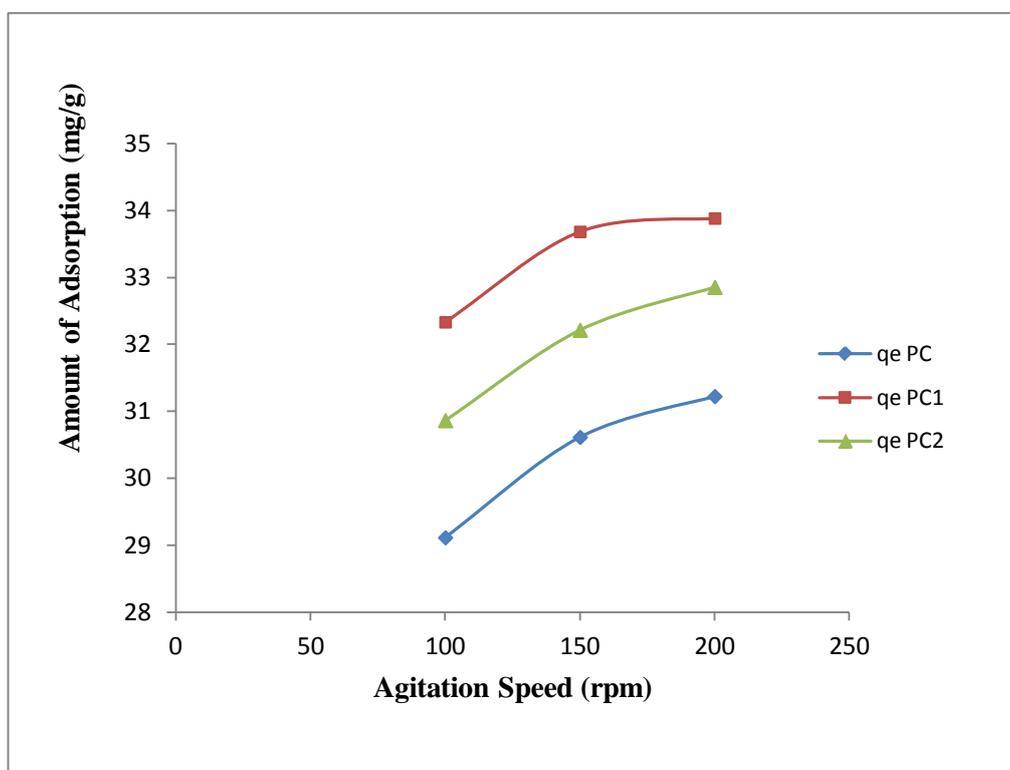


Figure 4.9 Effect of agitation speed on the adsorption of MB onto pine cone materials

(Volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= 30°C; pine cone dosage 15mg; pH=9.2; time 240 min)

## 4.5 MB Adsorption Mechanism and Application of Various Kinetics Models

Usually, the sorption of methylene blue by pine materials biomass is a rapid process which involves a combination of physical and chemical sorption mechanisms. Initially, the MB dye is to be transported from the bulk to the surface of the biomass which will then diffuse through the boundary layer to the surface of the sorption sites and intra-particle diffusion into the interior of the sorbent. Chemisorptions of MB involves functional groups from the pine materials surface including OH<sup>-</sup>, COOH<sup>-</sup>, C=O, as shown in the FTIR spectra which interact with the active amine groups in the dye by forming complexes either by hydrogen bonds. The physical sorption is an ion-exchange process where the functional groups from the biomass interact with the ions at the active site of the MB resulting in protonation. The thermodynamic results also indicate the mechanism of sorption is based on weak forces of ion exchange, hydrogen bond, or electrostatic forces which make regeneration are possible.



Adsorption kinetics in wastewater treatment is significant because it gives valuable insights into the mechanism of adsorption process, which is useful for adsorber design. The applicability of five models was tested for the adsorption of MB into raw and modified pine cone in this study. The best-fit model was selected based on the linear regression correlation coefficient  $R^2$  values and also Chi-square error function. The theory of these models is presented in section 2.5. These models have been fitted with experimental data at different physicochemical conditions.

There is several error analysis methods used to predict the best fit of models. In this work, the best fit of the equation to the experimental data was determined in two techniques; linear regression correlation coefficient values ( $R^2$ ) and error estimation technique.  $R^2$  value closest to unity is assumed to provide the best fit meanwhile for the error function, the minor value of the error indicates the better fit. The error estimation employed is Chi-square analysis (Ho, 2004) which is given below:

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \quad (4.6)$$

Where  $q_{e,m}$  equilibrium capacity obtained from model (mg/g) and  $q_e$  was the equilibrium capacity (mg/g) from the experimental data. If data from model were similar to the experimental data,  $\chi^2$  would be a small number and vice versa.

The linear fitting plots of pseudo-first-order kinetic model are presented in fig (4.10, 4.11, 4.12, 4.13). Similarly the linear fitting plots of pseudo-second-order kinetics model are shown in fig (4.14, 4.15, 4.16, 4.17). Also the linear fitting plots of intraparticle diffusion model are illustrated in fig (4.18, 4.19, 4.20, 4.21). In the same way the linear fitting plots of liquid film diffusion model are demonstrated in fig (4.22, 4.23, 4.24, 4.25).

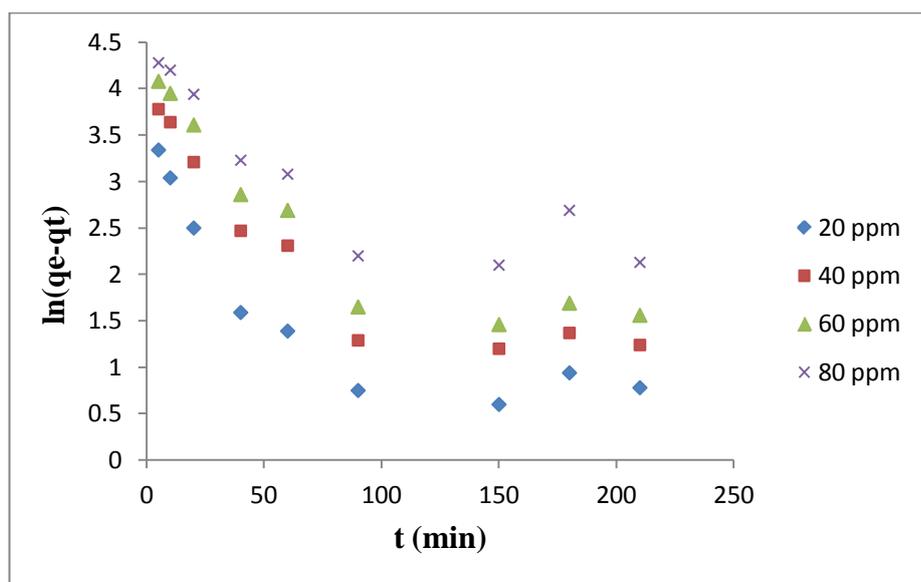


Figure 4.10 Pseudo-first-order plot for the adsorption of MB onto raw pine cone (PC) materials at different initial MB concentration

(Volume of dye solution=50 ml; temperature= 30°C; pine cone dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

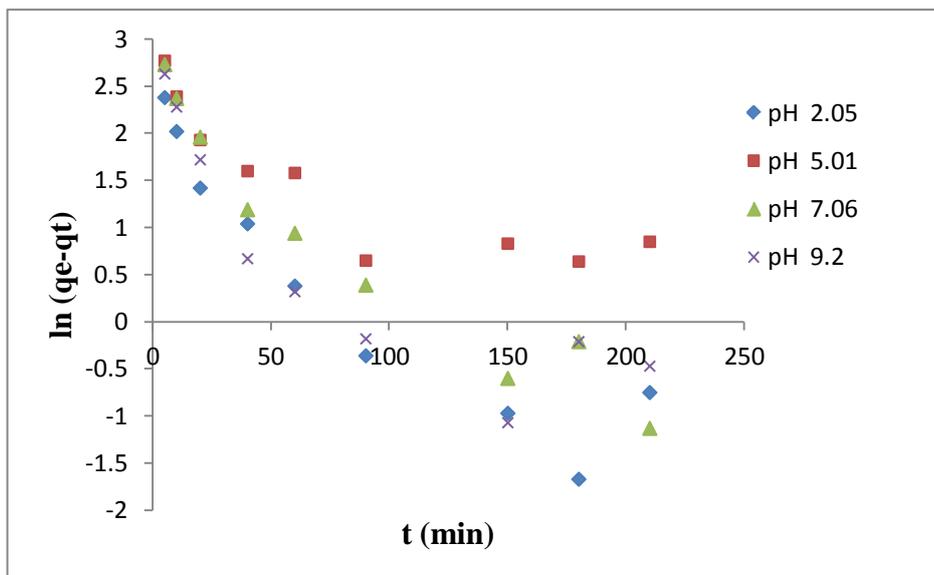


Figure 4.11 Pseudo-first-order plot for the adsorption of MB onto raw pine cone (PC) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine cone dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

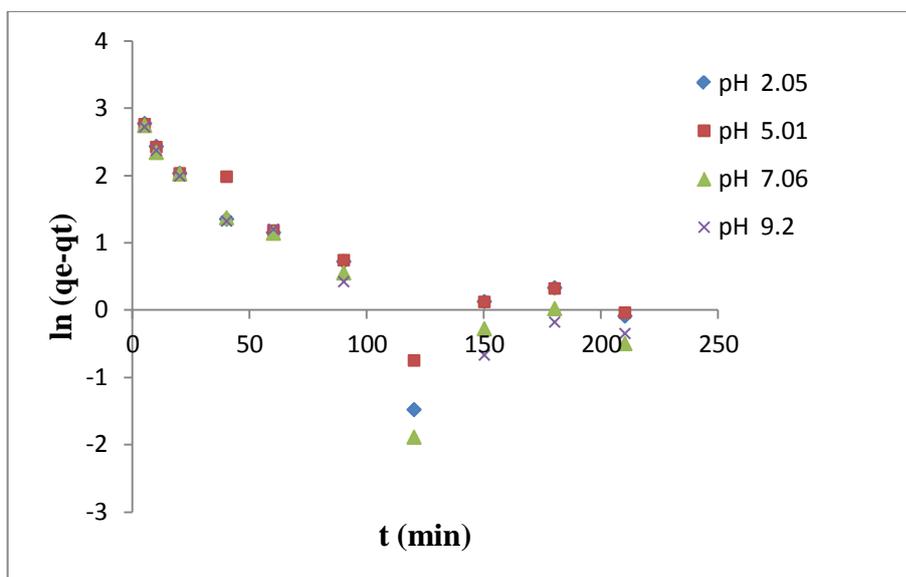


Figure 4.12 Pseudo-first-order plot for the adsorption of MB onto treated pine cone (PC1) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine cone dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

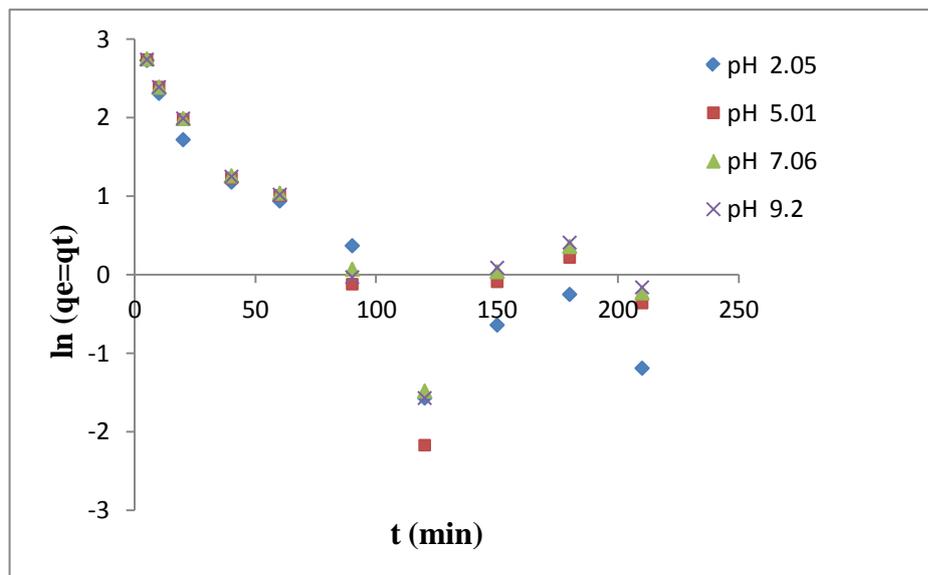


Figure 4.13 Pseudo-first-order plot for the adsorption of MB onto treated pine cone (PC2) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine cone dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

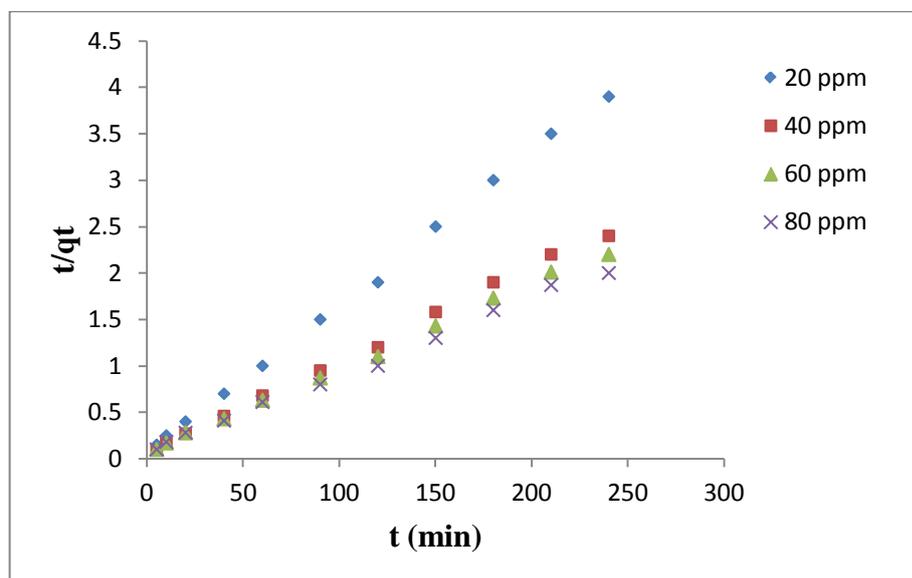


Figure 4.14 Pseudo-second-order plot for the adsorption of MB onto raw pine cone (PC) materials at different initial MB concentration

(Volume of dye solution=50 ml; temperature= 30°C; pine cone dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

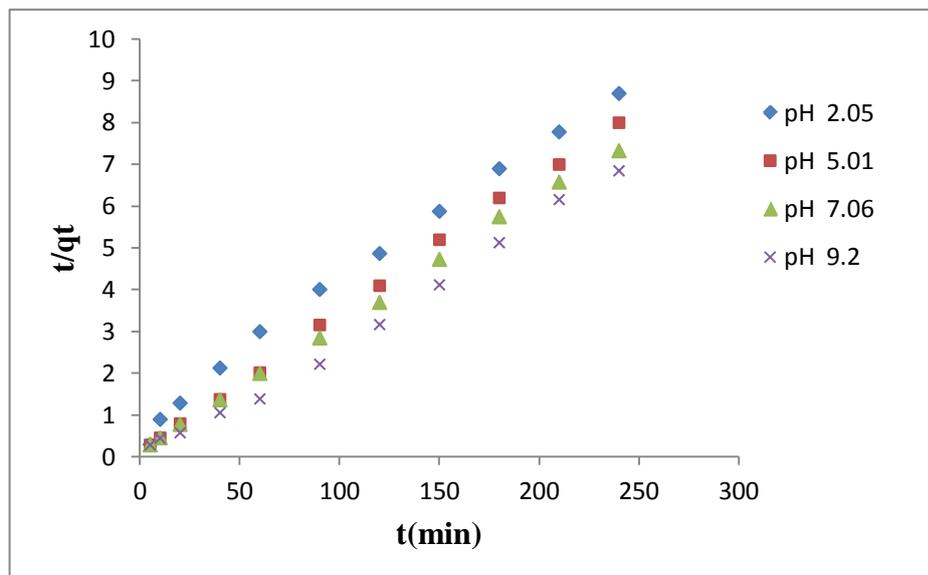


Figure 4.15 Pseudo-second-order plot for the adsorption of MB onto raw pine cone (PC) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine cone dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

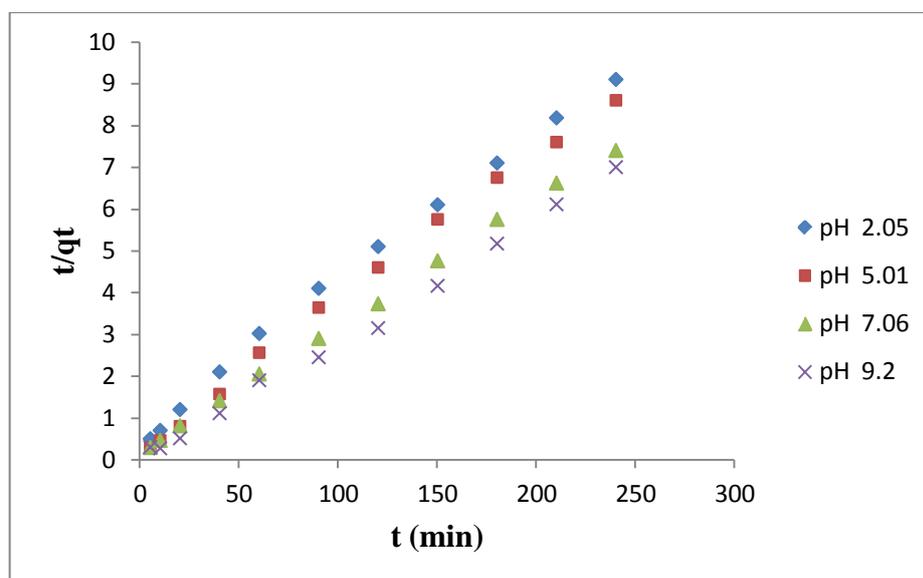


Figure 4.16 Pseudo-second-order plot for the adsorption of MB onto treated pine cone (PC1) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine cone dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

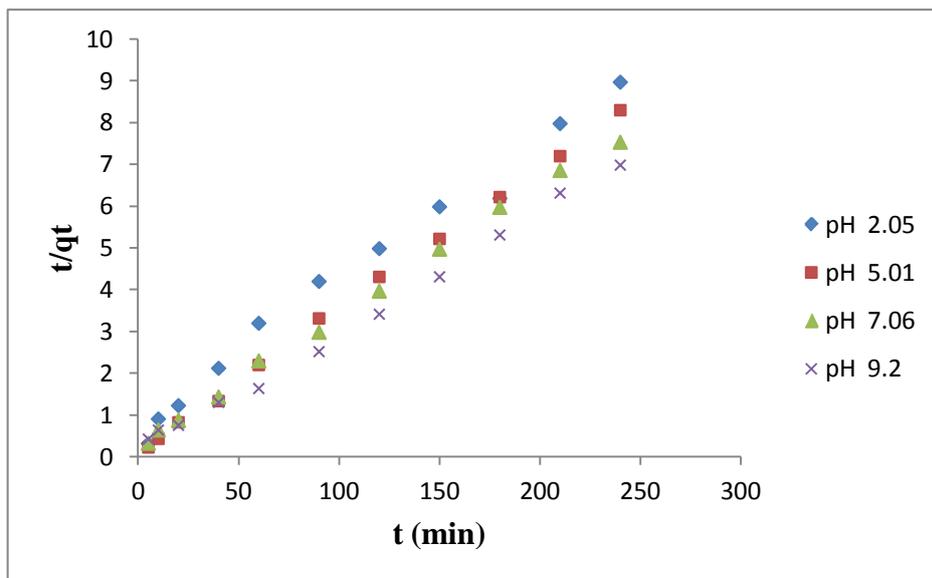


Figure 4.17 Pseudo-second-order plot for the adsorption of MB onto treated pine cone (PC2) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine cone dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

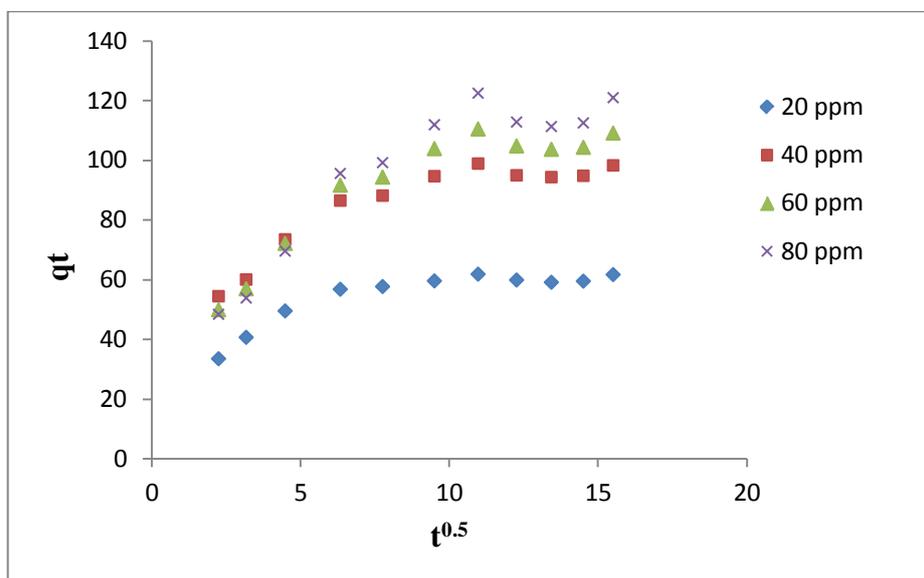


Figure 4.18 Intraparticle diffusion plot for the adsorption of MB onto raw pine cone (PC) materials at different initial MB concentration

(Volume of dye solution=50 ml; temperature= 30°C; pine cone dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

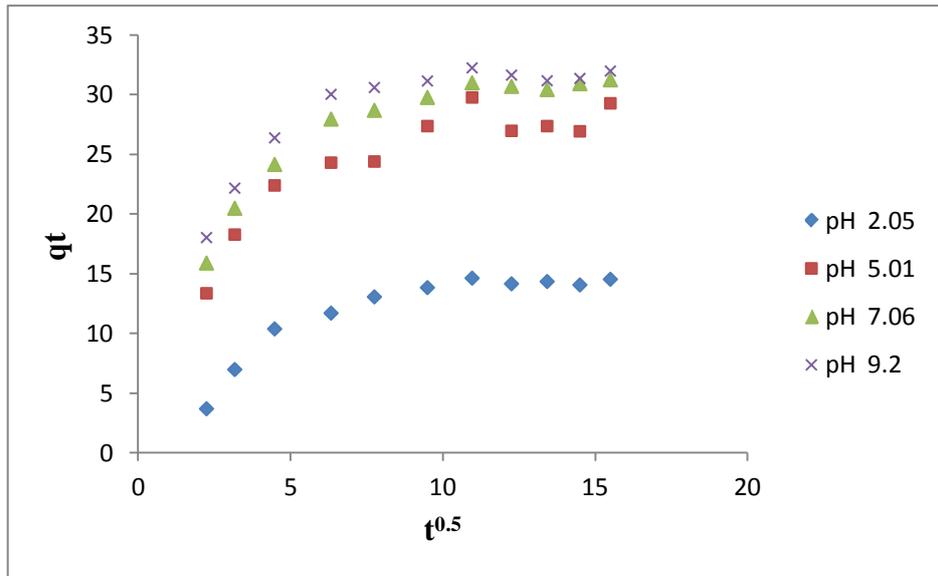


Figure 4.19 Intraparticle diffusion plot for the adsorption of MB onto raw pine cone (PC) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine cone dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

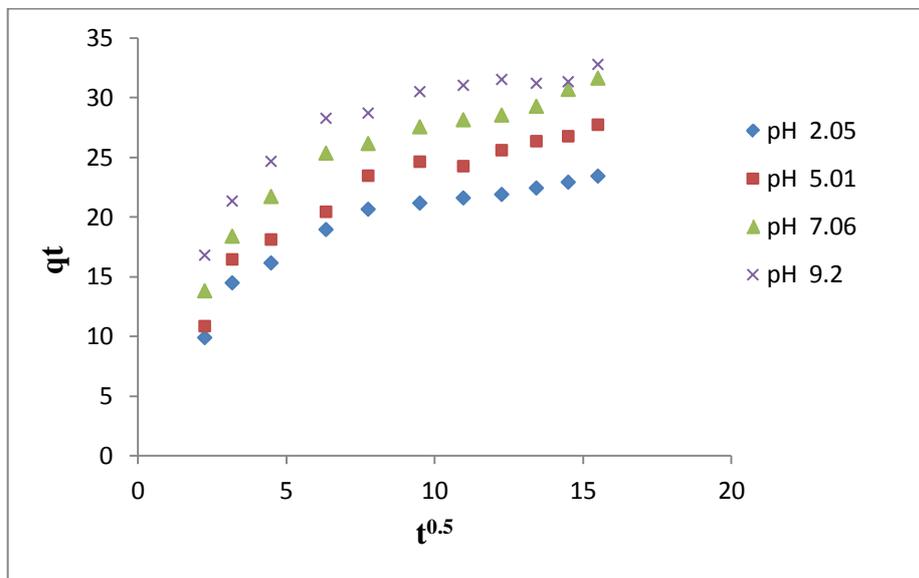


Figure 4.20 Intraparticle diffusion plot for the adsorption of MB onto treated pine cone (PC1) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine cone dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

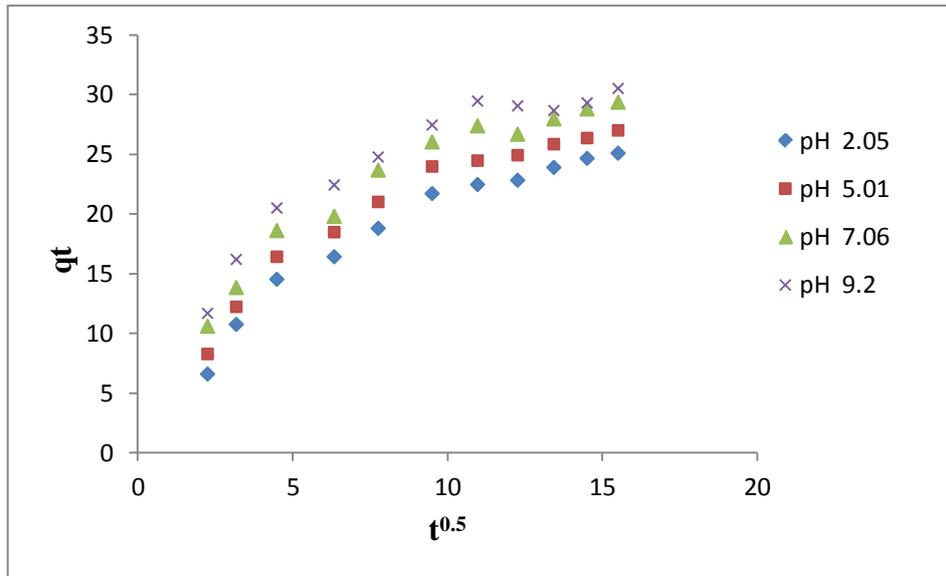


Figure 4.21 Intraparticle diffusion plot for the adsorption of MB onto treated pine cone (PC2) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine cone dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

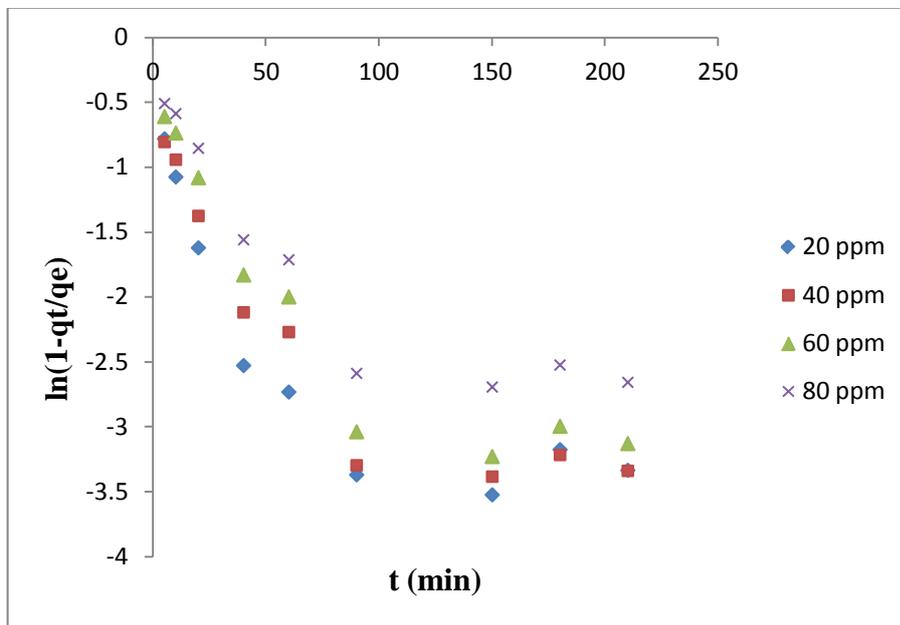


Figure 4.22 Liquid film diffusion plot for the adsorption of MB onto raw pine cone (PC) materials at different initial MB concentration

(Volume of dye solution=50 ml; temperature= 30°C; pine cone dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

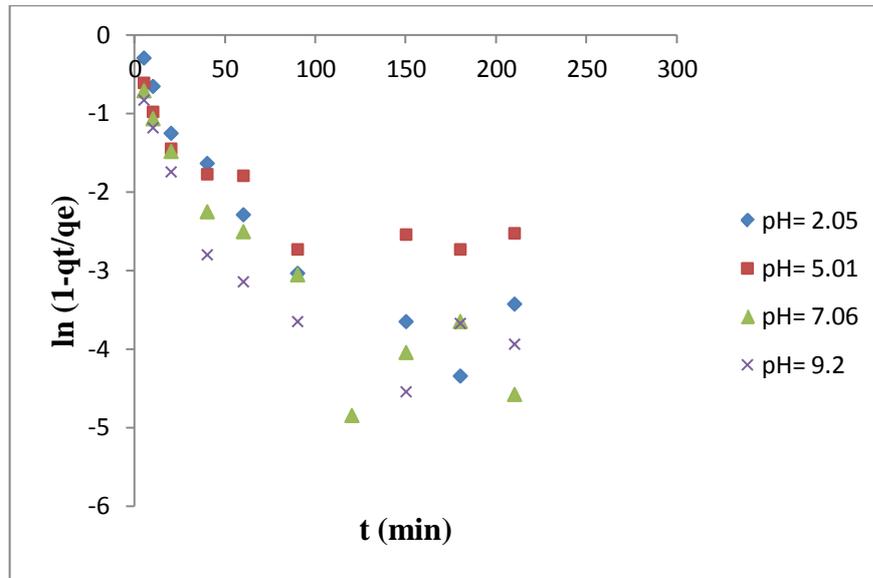


Figure 4.23 Liquid film diffusion plot for the adsorption of MB onto raw pine cone (PC) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine cone dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

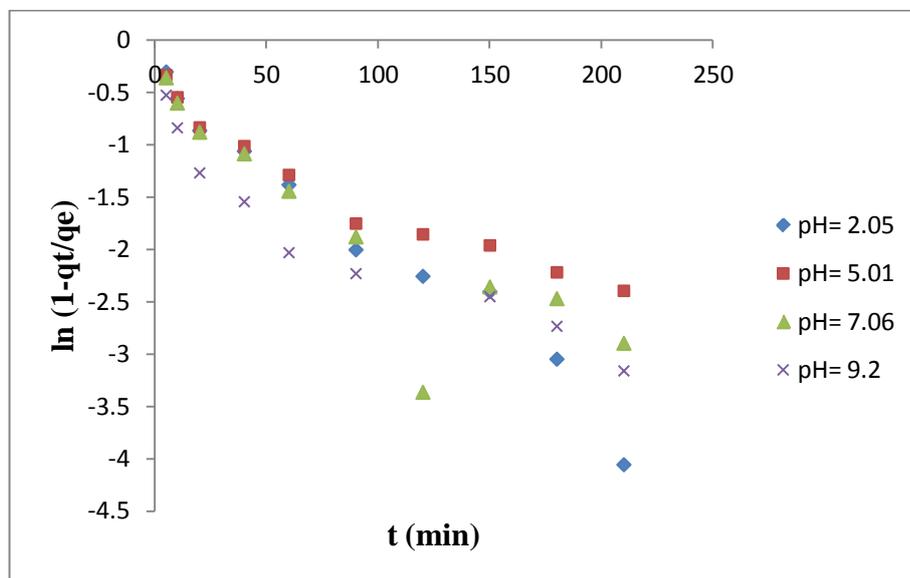


Figure 4.24 Liquid film diffusion plot for the adsorption of MB onto treated pine cone (PC1) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine cone dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

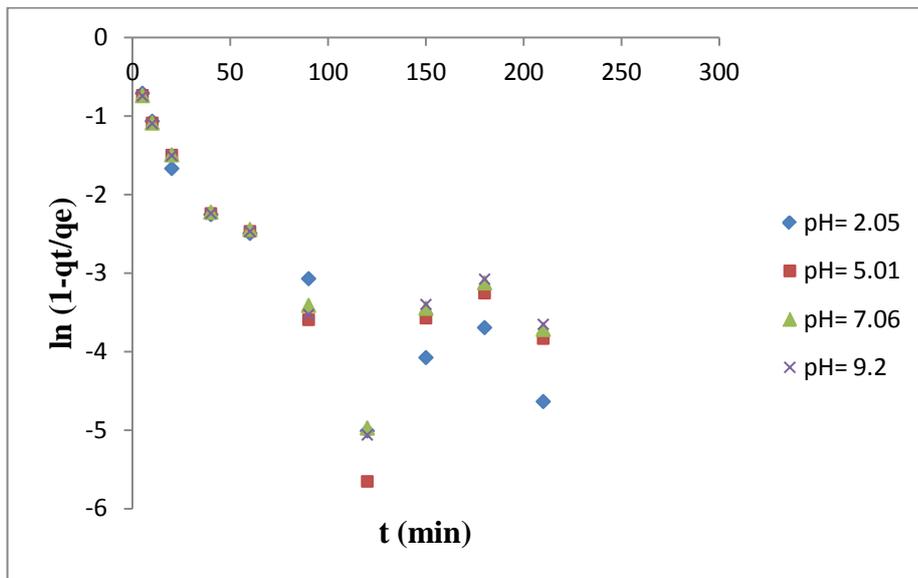


Figure 4.25 Liquid film diffusion plot for the adsorption of MB onto treated pine cone (PC2) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine cone dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

All kinetic parameters obtained from fitting model plots with experimental data under various conditions are tabulated in Tables 4.2 - 4.5. Higher linear regression coefficient  $R^2$  from pseudo-second-order kinetics model and the Chi-square error analysis  $\chi^2$  with respect to the other models, (Table 4.2 - 4.5) indicates the suitability of pseudo-second-order kinetics model over other models. In addition, the values of calculated  $q_e$  from pseudo-second-order model are very close to the experimental  $q_e$  value (Table 4.3) which gives more suitability of this model. While pseudo-first-order kinetic model, intraparticle diffusion model, and liquid film diffusion model give a much lower value of the equilibrium  $q_e$  than the experimental  $q_e$  value (Table 4.2, 4.4, and 4.5) therefore these models are not applicable for this system. Similar kinetic model parameters were obtained by different researchers for a few other systems reported in the literature (Dogan et al., 2004, Oladoja et al., 2008, Vadivelan and Kumar, 2005).

**Table 4.2** Pseudo-first -order kinetic parameters for adsorption of MB on pine cone and modified pine cone

<i>Pseudo-first-order kinetic parameters Model</i>					
<i>Parameters</i>	<i>q<sub>e</sub> (mg/g) experimental</i>	<i>q<sub>e</sub> (mg/g) calculated</i>	<i>K<sub>1</sub> (min<sup>-1</sup>)</i>	<i>R<sup>2</sup></i>	<i>x<sup>2</sup></i>
<b>Initial dye</b>					
<b>Conc.(ppm)</b>					
<b>20</b>	61.69	13.59	0.0112	0.6826	0.4251
<b>40</b>	98.28	39.41	0.0122	0.7860	0.4136
<b>60</b>	109.09	27.55	0.0124	0.8023	0.4032
<b>80</b>	120.97	50.61	0.0098	0.7293	0.4125
<b>Initial pH</b>					
<b>2.05</b>	14.55	6.19	0.0169	0.8501	0.4095
<b>5.01</b>	29.29	9.08	0.0087	0.7254	0.4125
<b>7.06</b>	31.26	9.67	0.0167	0.9170	0.3541
<b>9.2</b>	31.99	6.31	0.0142	0.7192	0.4117
<b>Temperature °C</b>					
<b>30</b>	32.84	8.74	0.0139	0.6278	0.4129
<b>40</b>	32.75	10.04	0.0139	0.7526	0.4114
<b>50</b>	32.31	8.77	0.0160	0.6695	0.4356
<b>60</b>	32.05	9.52	0.0150	0.8733	0.3989
<b>salt conc.mg NaCl</b>					
<b>50</b>	28.53	11.07	0.0108	0.8981	0.3999
<b>100</b>	27.38	16.10	0.0153	0.9795	0.3856
<b>150</b>	27.02	16.00	0.0151	0.9797	0.3699
<b>200</b>	25.11	16.89	0.0158	0.9703	0.3897
<b>Modified pine cone</b>					
<b>PC1- pH</b>					
<b>2.05</b>	13.45	5.32	0.0154	0.7401	0.4111
<b>5.01</b>	32.05	7.21	0.0075	0.8254	0.3877
<b>7.06</b>	32.08	7.89	0.0177	0.7370	0.4666
<b>9.2</b>	32.12	5.84	0.0156	0.7622	0.4585
<b>Modified pine cone</b>					
<b>PC2- pH</b>					
<b>2.05</b>	13.21	5.87	0.0168	0.7901	0.4253
<b>5.01</b>	31.77	8.12	0.0069	0.7654	0.4222
<b>7.06</b>	32.05	8.75	0.0156	0.8170	0.4002
<b>9.2</b>	32.07	6.01	0.0133	0.7322	0.4522

**Table 4.3** Pseudo- second-order kinetic parameters for adsorption of MB on pine cone and modified pine cone

<i>Pseudo-second-order kinetic parameters Model</i>						
<i>Parameters</i>	<i>q<sub>e</sub> (mg/g) experimental</i>	<i>q<sub>e</sub> (mg/g) calculated</i>	<i>K<sub>2</sub> (mg/g min)</i>	<i>h</i>	<i>R<sup>2</sup></i>	<i>x<sup>2</sup></i>
<b>Initial dye Conc.(ppm)</b>						
<b>20</b>	61.69	62.11	0.0044	16.97	0.9991	0.0855
<b>40</b>	98.28	100	0.0016	16.00	0.9983	0.0875
<b>60</b>	109.09	111.11	0.0011	13.58	0.9984	0.0901
<b>80</b>	120.97	121.95	0.0008	11.89	0.9964	0.0911
<b>Initial pH</b>						
<b>2.05</b>	14.55	15.19	0.0061	1.41	0.9985	0.0877
<b>5.01</b>	29.29	28.90	0.0053	4.43	0.9953	0.0902
<b>7.06</b>	31.26	31.74	0.0057	5.74	0.9998	0.0799
<b>9.2</b>	31.99	32.26	0.0080	8.32	0.9995	0.0899
<b>Temperature °C</b>						
<b>30</b>	32.84	33.11	0.0053	5.81	0.9994	0.0798
<b>40</b>	32.75	33.22	0.0043	4.74	0.9986	0.0878
<b>50</b>	32.31	32.78	0.0053	5.69	0.9995	0.0811
<b>60</b>	32.05	32.46	0.0054	5.69	0.9995	0.0903
<b>salt conc.mg NaCl</b>						
<b>50</b>	28.53	28.82	0.0039	3.23	0.9960	0.0876
<b>100</b>	27.38	28.82	0.0022	1.83	0.9971	0.0888
<b>150</b>	27.02	28.41	0.0021	1.69	0.9982	0.0813
<b>200</b>	25.11	26.67	0.0019	1.35	0.9973	0.0844
<b>Modified pine cone PC1- pH</b>						
<b>2.05</b>	13.45	13.19	0.0048	1.19	0.9986	0.0905
<b>5.01</b>	32.05	31.90	0.0047	4.11	0.9955	0.0898
<b>7.06</b>	32.08	32.74	0.0049	3.75	0.9997	0.0786
<b>9.2</b>	32.12	32.02	0.0062	6.55	0.9996	0.0788
<b>Modified pine cone PC2- pH</b>						
<b>2.05</b>	13.21	13.02	0.0052	1.23	0.9988	0.0859
<b>5.01</b>	31.77	31.21	0.0048	4.25	0.9959	0.0886
<b>7.06</b>	32.05	31.99	0.0051	4.54	0.9995	0.0849
<b>9.2</b>	32.07	32.88	0.0067	7.34	0.9997	0.0799

**Table 4.4** Intraparticle Diffusion Model kinetic parameters for adsorption of MB on pine cone and modified pine cone

<i>Intraparticle Diffusion Model</i>					
<i>Parameters</i>	<i>q<sub>e</sub> (mg/g) experimental</i>	<i>q<sub>e</sub> (mg/g) calculated</i>	<i>K<sub>id</sub> (min<sup>-1</sup>)</i>	<i>R<sup>2</sup></i>	<i>x<sup>2</sup></i>
<b>Initial dye Conc.(ppm)</b>					
<b>20</b>	61.69	14.85	2.4523	0.8522	0.4125
<b>40</b>	98.28	35.98	4.1002	0.8710	0.4111
<b>60</b>	109.09	30.25	3.9801	0.7892	0.4532
<b>80</b>	120.97	55.98	4.3598	0.7982	0.4587
<b>Initial pH</b>					
<b>2.05</b>	14.55	9.58	0.2978	0.8225	0.4101
<b>5.01</b>	29.29	8.32	0.7801	0.7788	0.4326
<b>7.06</b>	31.26	10.22	0.6301	0.8776	0.4111
<b>9.2</b>	31.99	7.85	0.6711	0.8782	0.4130
<b>Temperature °C</b>					
<b>30</b>	32.84	9.58	1.1812	0.8810	0.4101
<b>40</b>	32.75	9.99	1.1605	0.8745	0.3999
<b>50</b>	32.31	9.01	1.1465	0.8662	0.4015
<b>60</b>	32.05	8.77	1.1112	0.8856	0.4225
<b>salt conc.mg NaCl</b>					
<b>50</b>	28.53	10.99	0.8201	0.8682	0.4236
<b>100</b>	27.38	14.89	0.8421	0.8788	0.4521
<b>150</b>	27.02	14.55	0.8619	0.8735	0.4712
<b>200</b>	25.11	17.01	0.9579	0.7982	0.4581
<b>Modified pine cone PC1- pH</b>					
<b>2.05</b>	13.45	4.99	0.2545	0.7926	0.4222
<b>5.01</b>	32.05	8.03	0.7111	0.7856	0.4985
<b>7.06</b>	32.08	9.01	0.5896	0.8596	0.4528
<b>9.2</b>	32.12	6.11	0.6124	0.7989	0.4456
<b>Modified pine cone PC2- pH</b>					
<b>2.05</b>	13.21	7.11	0.2775	0.8111	0.4856
<b>5.01</b>	31.77	9.21	0.7498	0.8771	0.4199
<b>7.06</b>	32.05	8.25	0.6101	0.7998	0.4865
<b>9.2</b>	32.07	5.99	0.6321	0.8811	0.4856

**Table 4.5** Liquid Film Diffusion Model kinetic parameters for adsorption of MB on pine cone and modified pine cone

<i>Parameters</i>	<i>Liquid Film Diffusion Model</i>				
	<i>q<sub>e</sub> (mg/g) experimental</i>	<i>q<sub>e</sub> (mg/g) calculated</i>	<i>K<sub>fd</sub> (min<sup>-1</sup>)</i>	<i>R<sup>2</sup></i>	<i>x<sup>2</sup></i>
<b>Initial dye Conc.(ppm)</b>					
<b>20</b>	61.69	12.52	0.0123	0.8694	0.3986
<b>40</b>	98.28	26.98	0.0175	0.8749	0.3896
<b>60</b>	109.09	26.85	0.0222	0.7852	0.4011
<b>80</b>	120.97	55.36	0.0286	0.8574	0.3897
<b>Initial pH</b>					
<b>2.05</b>	14.55	6.98	0.0233	0.8678	0.4021
<b>5.01</b>	29.29	8.99	0.0196	0.8523	0.3999
<b>7.06</b>	31.26	8.78	0.0178	0.8884	0.3995
<b>9.2</b>	31.99	5.98	0.0156	0.8781	0.3899
<b>Temperature °C</b>					
<b>30</b>	32.84	7.89	0.0161	0.8766	0.3976
<b>40</b>	32.75	9.89	0.0173	0.8653	0.3895
<b>50</b>	32.31	7.89	0.0193	0.8975	0.3799
<b>60</b>	32.05	10.01	0.0213	0.8796	0.3894
<b>salt conc.mg NaCl</b>					
<b>50</b>	28.53	10.85	0.0378	0.8964	0.3756
<b>100</b>	27.38	15.96	0.0345	0.8875	0.3802
<b>150</b>	27.02	16.12	0.0189	0.7998	0.3833
<b>200</b>	25.11	17.23	0.0169	0.8999	0.3711
<b>Modified pine cone PC1- pH</b>					
<b>2.05</b>	13.45	6.02	0.0198	0.8777	0.3691
<b>5.01</b>	32.05	8.09	0.0144	0.8654	0.3699
<b>7.06</b>	32.08	7.99	0.0123	0.8698	0.3701
<b>9.2</b>	32.12	6.55	0.0111	0.8852	0.3951
<b>Modified pine cone PC2- pH</b>					
<b>2.05</b>	13.21	6.05	0.0201	0.8711	0.3888
<b>5.01</b>	31.77	9.12	0.0156	0.8632	0.3968
<b>7.06</b>	32.05	9.08	0.0163	0.8897	0.3874
<b>9.2</b>	32.07	5.91	0.0135	0.8699	0.3836

The time required for the adsorbent to remove half of the amount adsorbed at equilibrium is defined as the half-adsorption time of the dye,  $t^{1/2}$ , it is considered as a measure of the rate of adsorption and for the second-order process is given by the relationship (Sen et al., 2011)

$$t^{1/2} = 1/k_2qe \quad (4.7)$$

The calculated values of  $t^{1/2}$  for the MB adsorption by pine cone are 3.66 min, 6.25 min, 8.18 min, and 10.25 min for an initial MB concentration range of 20, 40, 60 and 80 ppm, respectively.

#### 4.5.1 Adsorption Mechanism

It is important to understand the underlying mechanism that results in the apparent dynamic behaviour of the system for the process design and control of adsorption systems. The adsorption of methylene blue by pine cone biomass was found to be rapid at the initial period of contact time and then become slow and stagnate with increase in contact time. For a solid/liquid sorption process, the solute transfer is usually described by either external mass transfer (boundary layer diffusion) or intra-particle diffusion or both. The mechanism of the removal methylene blue from its aqueous phase by adsorption is assumed to consists of four steps: movement of the MB molecules from the bulk solution to the surface of the pine cone, diffusion through the boundary layer to the surface of the pine cone, adsorption at sites and intra-particle diffusion into the inside of the pine cone. The rate controlling step for sorption is the slowest step. However, the controlling step might be distributed between intra-particle and external transport mechanisms. The adsorption of methylene blue onto pine cone biomass may be controlled due to film diffusion at first stage, and as the adsorbent particles are loaded with dye ions, the adsorption process may be controlled due to intra-particle diffusion (Kumar and Kumaran, 2005, Oladoja et al., 2008, Nandi et al., 2009b, Vimonses et al., 2009). The most commonly used technique to classify this mechanism in the adsorption process is given by fitting the experimental data to an intra-particle diffusion plot. Plot of  $t^{0.5}$  vs.  $q_t$  which are shown in fig (4.26) at different initial MB concentration for pine cone system. Fig (4.26) shows that adsorption plots are not linear under the whole

time range and can be divided into two or three linear regions which confirm the multistage nature of adsorption. This figure also represented the two different stages external mass transfer followed by intra-particle diffusion, signified the dye were transported to the external surface of the pine material through film diffusion and its rate was very fast. Generally, when adsorption steps are not dependent of one another, the plot of  $t^{0.5}$  against  $q_t$  showed give two or more intercepting lines depending on the actual mechanism (Weber and Morris, 1963). Furthermore, from Fig (4.26) conclusion can be made that none of the plot give linear straight line segment passing through the origin  $(0, 0)$ . This indicates that the intra-particle diffusion is involved in the adsorption process but the only rate-controlling step (Sen et al., 2011). As the extrapolation of the plots did not pass through the origin, they indicated that film diffusion and intra-particle diffusion occurred simultaneously (Sen et al., 2011).

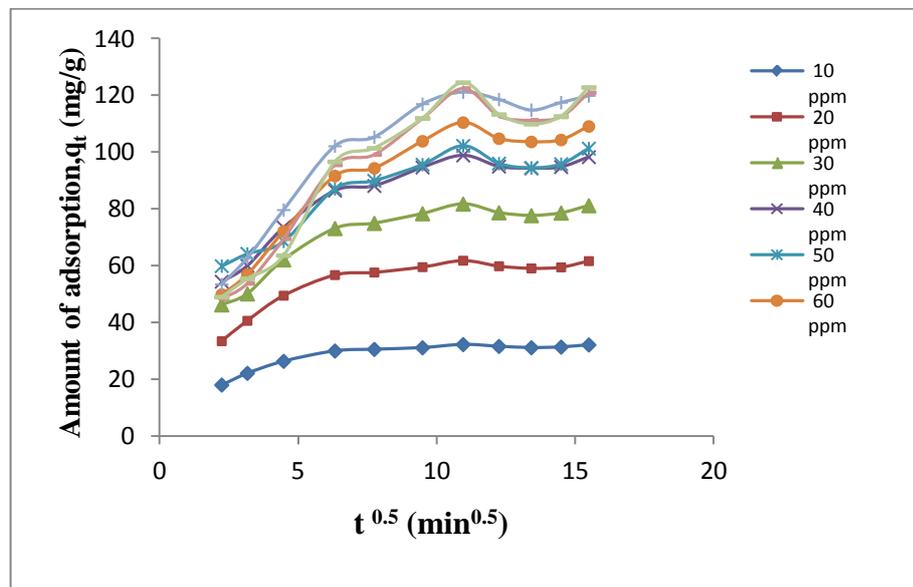


Figure 4.26 Intra-particle diffusion model on different initial dye concentration

The diffusion coefficient,  $D$ , for the intra-particle transport of different dye concentration was also calculated using the following relationship (Dogan et al., 2004):

$$t^{1/2} = \frac{0.03r_0^2}{D} \quad (4.8)$$

Where  $t^{1/2}$  is the half-life time in sec,  $r_0$  is the radius of adsorbent particle in cm and  $D$  is the diffusion coefficient in  $\text{cm}^2/\text{sec}$ . Here the mean diameter of pine cone particles is  $70.15 \mu\text{m}$  (radius= $35.075 \mu\text{m}=35.075 \times 0.0001 \text{ cm}=0.0035075 \text{ cm}$ ). The diffusion coefficients,  $D$  values, were found to be  $1.68\text{E}-9$ ,  $3.84\text{E}-9$ ,  $5.52\text{E}-9$ , and  $6.97\text{E}-9 \text{ cm}^2/\text{s}$  for an initial methylene blue dye concentration of 20, 40, 60 and 80 ppm, respectively, which increases with change in initial dye concentration.. These results agree with those of resulting by McKay and Allen, 1983 and Dogan et al., 2004 (McKay and Allen, 1983, Dogan et al., 2004). This was attributed to the larger molecular size of the present systems, the factor that slows down in diffusion rate (Dogan et al., 2004). In addition due to strong interaction between MB dye and pine cone, mobility was low.

## 4.6 Adsorption Equilibrium Isotherm Models

Equilibrium isotherm studies are important to describe how MB dye molecules interact with the pine cone biomass surface and determine the max adsorption capacity of adsorbent. The applicability of the isotherm equation is compared by judging the correlation coefficients,  $R^2$ . The theory of Langmuir and Freundlich models is presented in section 2.5.

Figures (4.27a-4.27c) showed Langmuir isotherm fittings for raw and treated pine cone biomass adsorbent with high linear regression. The maximum monolayer adsorption capacity of pine cone,  $q_m$ , and constant related to the binding energy of the sorption system,  $K_a$ , is calculated from the slop and intercept of this plot. The maximum monolayer adsorption capacity  $q_m$  of raw pine cone PC was 129.87 mg/g and the constant related to the binding energy of the sorption system,  $K_a$  was 0.2996, whereas the maximum monolayer adsorption capacity  $q_m$  for treated pine cone PC1 and PC2, were 142.86, and 135.13 mg/g and the constant related to the binding energy of the sorption system,  $K_a$  were 0.2734, and 0.3008 respectively.

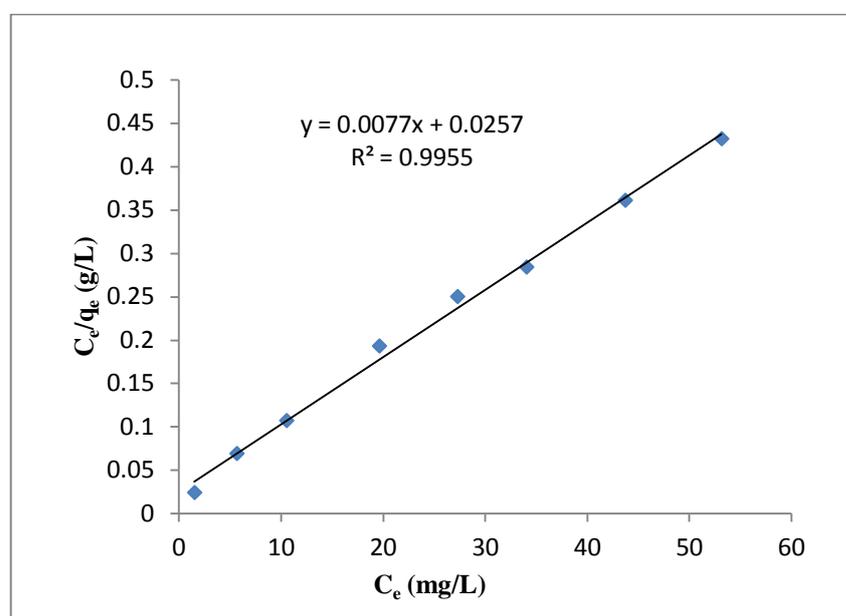


Figure 4.27a Langmuir plot: amount of adsorbent (pine cone PC)

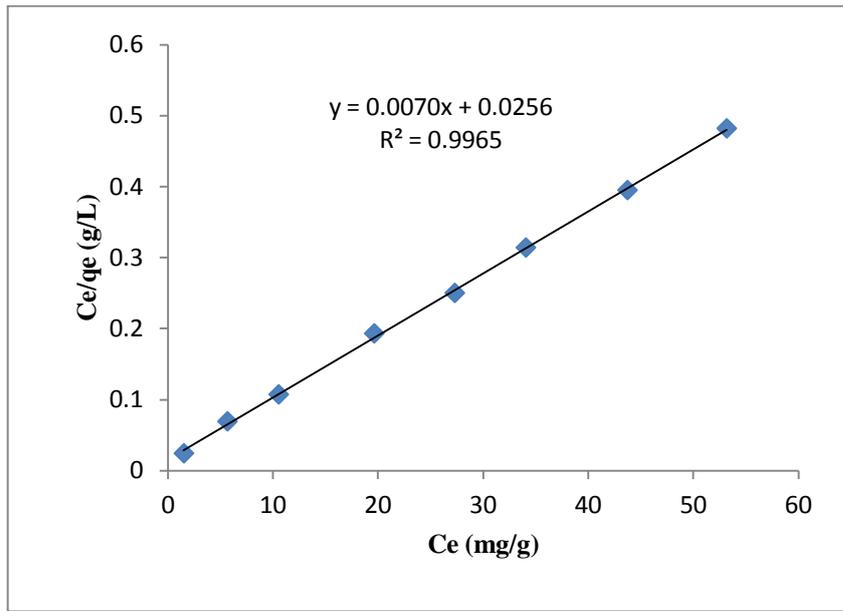


Figure 4.27b Langmuir plot: amount of adsorbent (treated pine cone PC1)

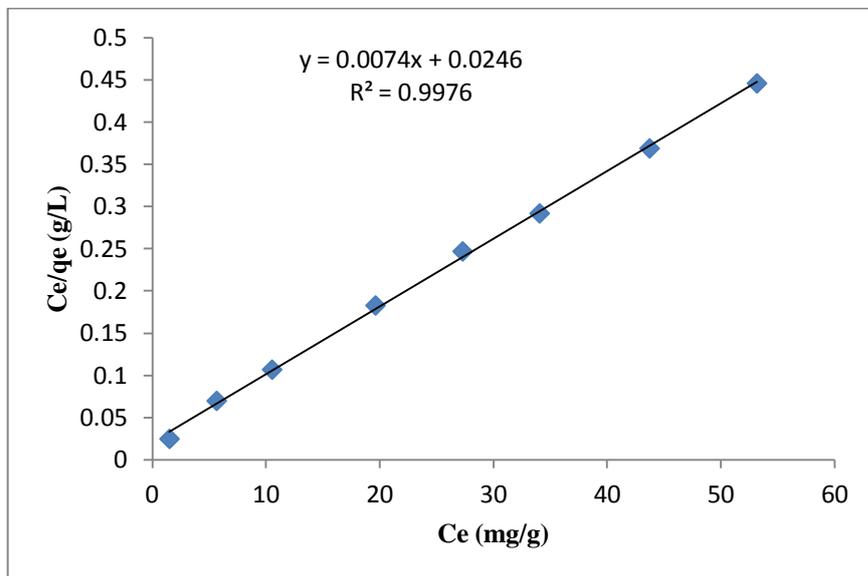


Figure 4.27c Langmuir plot: amount of adsorbent (treated pine cone PC2)

On the other hand, Freundlich isotherm fittings for raw and treated pine cone biomass adsorbent are shown in Figures (4.28a-4.28c). The linear correlation coefficients  $R^2$  are 0.9608, 0.9515, and 0.9274 for PC, PC1, and PC2 respectively. Freundlich constants, i.e., rate of adsorption,  $n$  and adsorption capacity  $K_f$ , are calculated from these plots, which is 5.13 and 58.23 mg/g, respectively for raw pine cone, whereas the adsorption capacity  $K_f$  and the rate of adsorption, ' $n$ ' for treated pine cone PC1 and PC2, were (54.24 and 4.68) and (53.96 and 4.81) respectively.

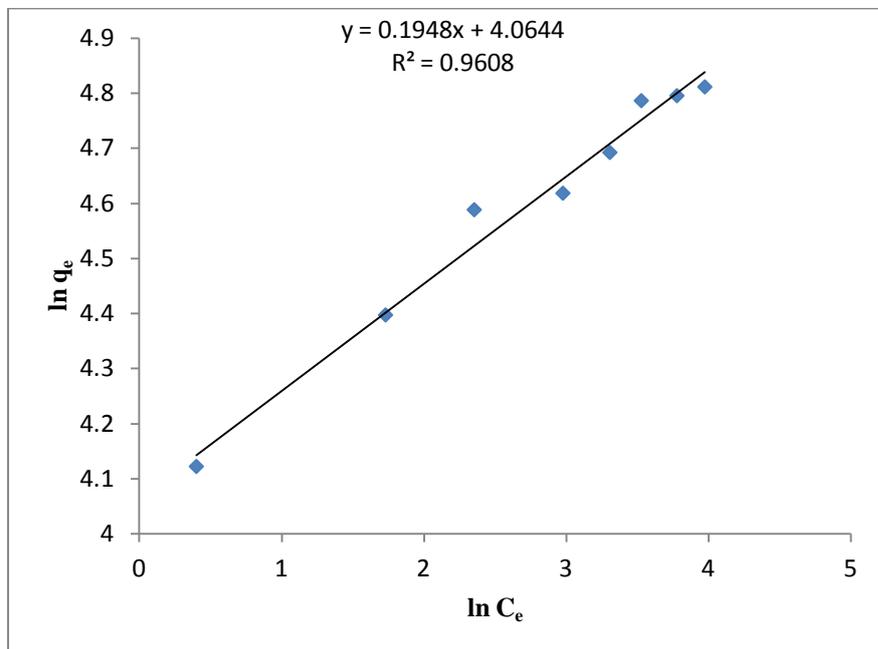


Figure 4.28a Freundlich plot: amount of adsorbent (pine cone PC)

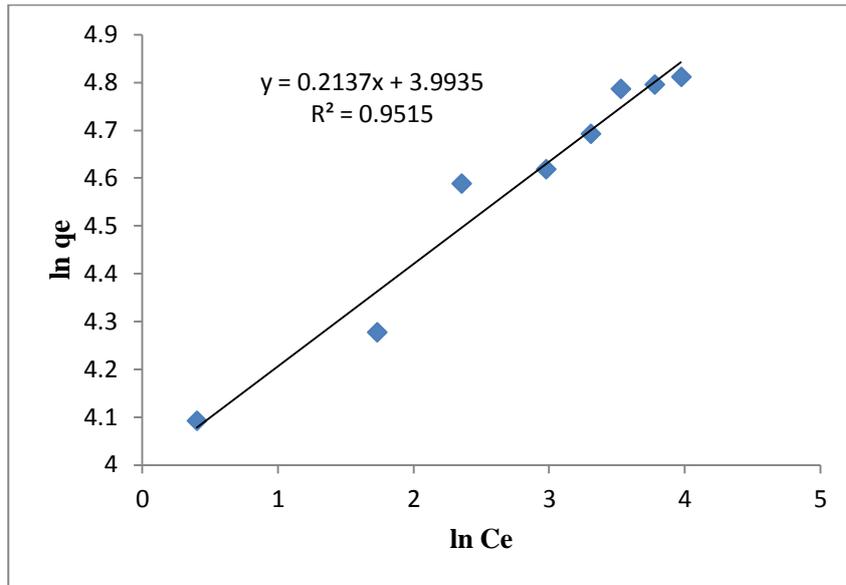


Figure 4.28b Freundlich plot: amount of adsorbent (treated pine cone PC1)

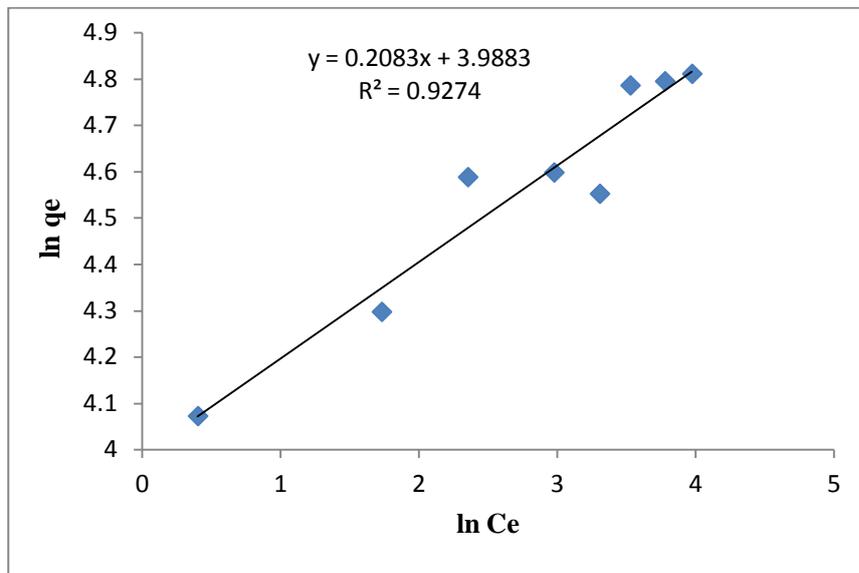


Figure 4.28c Freundlich plot: amount of adsorbent (treated pine cone PC2)

The separation factor,  $R_L$  for raw pine cone has been calculated from Langmuir plot as per the following relation

$$R_L = \frac{1}{1 + K_a C_0} \quad (4.9)$$

Where  $R_L$  values indicate the type of isotherm to be irreversible ( $R_L = 0$ ), favourable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) or unfavourable ( $R_L > 1$ ) (Mahmoode et al., 2011),  $K_a$  is the Langmuir constant and  $C_0$  is the initial MB dye concentration (ppm). The separation factor,  $R_L$ , has been calculated from Langmuir plot. It has been found that the calculated  $R_L$  values are 0.1431, 0.1001, 0.0771, 0.0626, 0.0527, 0.0455, 0.0401, and 0.0357 at initial dye concentration of 20, 30, 40, 50, 60, 70, 80 and 90 ppm, respectively. These  $R_L$  values indicate favourable adsorption as it lies in  $0 < R_L < 1$ . From Figs (4.27) and Figs (4.28),  $R^2$  values indicate the suitability of both isotherm models for their experiment data. It was also found that the adsorption equilibrium data fit both Langmuir and Freundlich equations with a correlation coefficient value of (0.9955, 0.9965, and 0.9976) and (0.9808, 0.9515, and 0.9274) respectively. Several studies have been investigated on the removal of MB from aqueous solution using low cost adsorbents. Table 4.6 summarises the adsorption capacity of different types of adsorbents for MB under more or less similar experimental conditions of adsorbents and it is compared with present study. It was found from Table 4.6, pine cone biomass and treated pine cone both are effective adsorbents in the removal of MB dye from aqueous solution. Table 4.6 also presents the pine cone biomass is better adsorbent compared to many other adsorbents in the removal of MB dye.

**Table 4.6** Comparative adsorption capacities of various adsorbents for removal of Methylene Blue dye

<i>Adsorbent</i>	<i>Adsorption capacity (<math>q_m</math> (mg/g))</i>	<i>Sources</i>
Peanut hull	68.06	(Gong et al., 2005)
Banana peel	20.8	(Annadurai et al., 2002)
Pineapple stem	119.05	(Hameed et al., 2009)
Coffee husk	90.1	(Oliveira et al., 2008)
Walnut sawdust	59.17	(Ferrero, 2007)
Rice husk	40.59	(Vadivelan and Kumar, 2005)
Egg shell	16.43	(Tsai et al., 2006)
Orange Peel	18.6	(Annadurai et al., 2002)
Mango seed kernel	142.86	(Kumar and Kumaran, 2005)
Coconut coir	15.59	(Sharma and Upadhyay, 2009)
Olive pomace	42.3	(Banat et al., 2007)
Raw pine cone	129.87	<b>Present Study</b>
Modified pine cone PC1	142.86	<b>Present Study</b>
Modified pine cone PC2	135.13	<b>Present Study</b>

## 4.7 Design of Single-Stage Batch Adsorber from Isotherm

### Data

The design of a single-stage batch adsorption system was determined from the Langmuir adsorption isotherm data by means of method developed by Vadivelan and Kumar (2005) and Sen et al (2011). Because of lack of extensive experimental data, based on adsorption isotherm studies empirical design procedures are the most common method to predict the adsorber size and performance. Fig (4.29) shows the diagram for a single-stage adsorption process as per Vadivelan and Kumar (2005). The design objective was to decrease initial dye concentration of  $C_0$  to  $C_t$  ( $\text{mg L}^{-1}$ ) for which total dye solution is  $V$  (L). The solute loading changes from  $q_o$  ( $\text{mg/g}$ ) to  $q_t$  ( $\text{mg/g}$ ) and the amount of added adsorbent was  $m$ . The mass balance for the methylene blue dye in the single-stage operation under equilibrium is given by:

$$V(C_o - C_e) = m(q_e - q_o) = mq_e \quad (4.10)$$

From isotherm experiments, it was found that equilibrium data for MB dye on raw pine cone are better fitted with Langmuir isotherm model, and therefore, Eq. 4.10 can be written and rearranged after putting the value of  $q_e$  as

$$\frac{m}{V} = \frac{C_o - C_e}{q_e} = \frac{C_o - C_e}{\frac{qmK_a C_e}{1 + K_a C_e}} \quad (4.11)$$

Figure (4.30) shows a series of plots derived from Eq. 4.11 between different solution volumes (2, 3, 4, 5, 6, 7 and 8 L) and the predicted amount of pine cone particles required to remove dye solutions of initial concentrations of 100 ppm for 95%, 85% and 75% dye removal. This is an outline of design procedure for a single-stage batch adsorption system by means of method developed by Vadivelan and Kumar (2005).

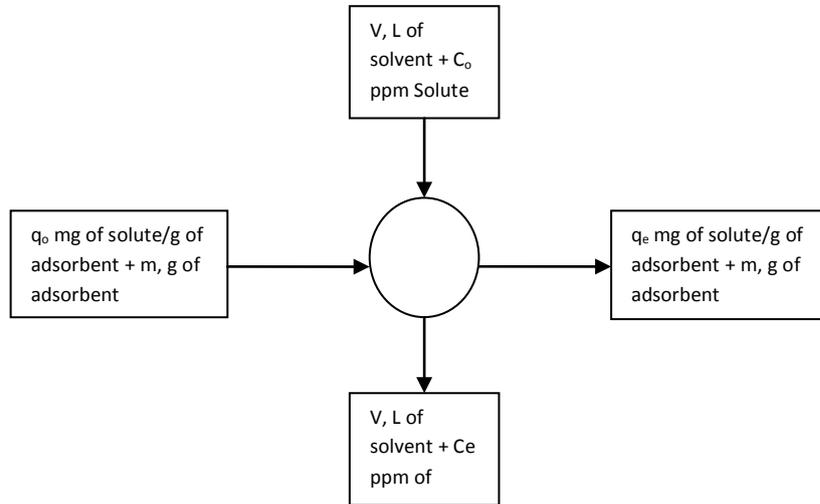


Figure 4.29 Schematic diagram of a single-stage batch adsorber

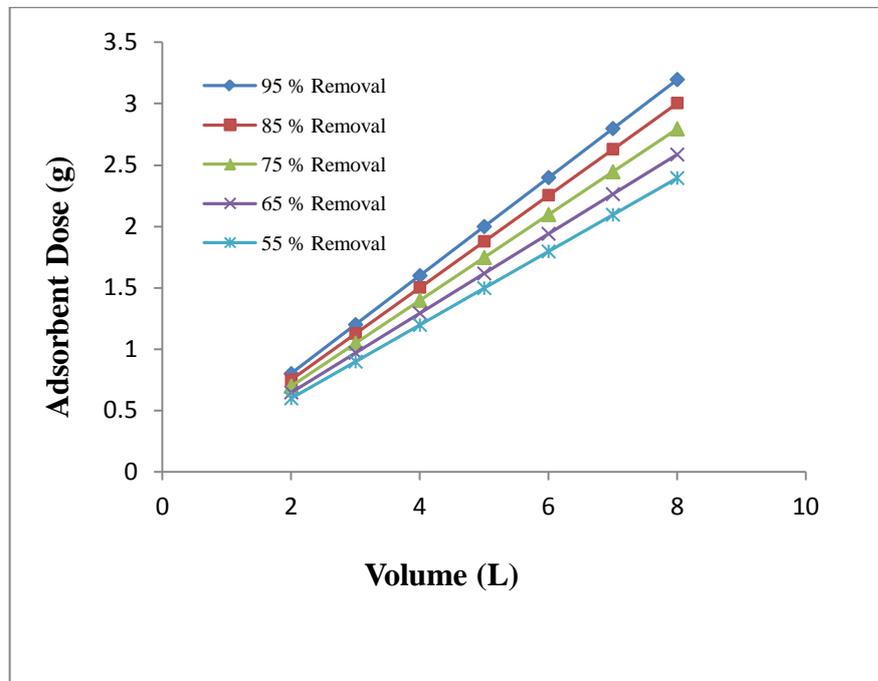


Figure 4.30 Volume of solution treated (litres) against adsorbent mass (grams)

## 4.8 Desorption Study

Desorption behaviour help to explain the mechanism and recovery of the adsorbate and adsorbent. In the desorption studies, the loaded raw and treated adsorbent that was used for the adsorption of dye solution was separated from solution by centrifugation and then dried. The dried adsorbent was agitated with 250 ml of distilled water at different pH values of 3, 5, 7 and 9 for the predetermined equilibrium time of the adsorption process. The desorbed dye was determined. It was found that percent desorption increased with decrease in pH of the aqueous medium figure (4.32). This figure shows that the percentages of dyes leached out at pH of 3, 5, 7 and 9 for PC were 74.22, 57.55, 43.48, and 31.51 %, whereas for modified pine cone PC1 and PC2 were 79.26, 63.25, 48.22, 38.58%, and 76.85, 59.56, 46.32, 34.78 % for PC1 and PC2 respectively.

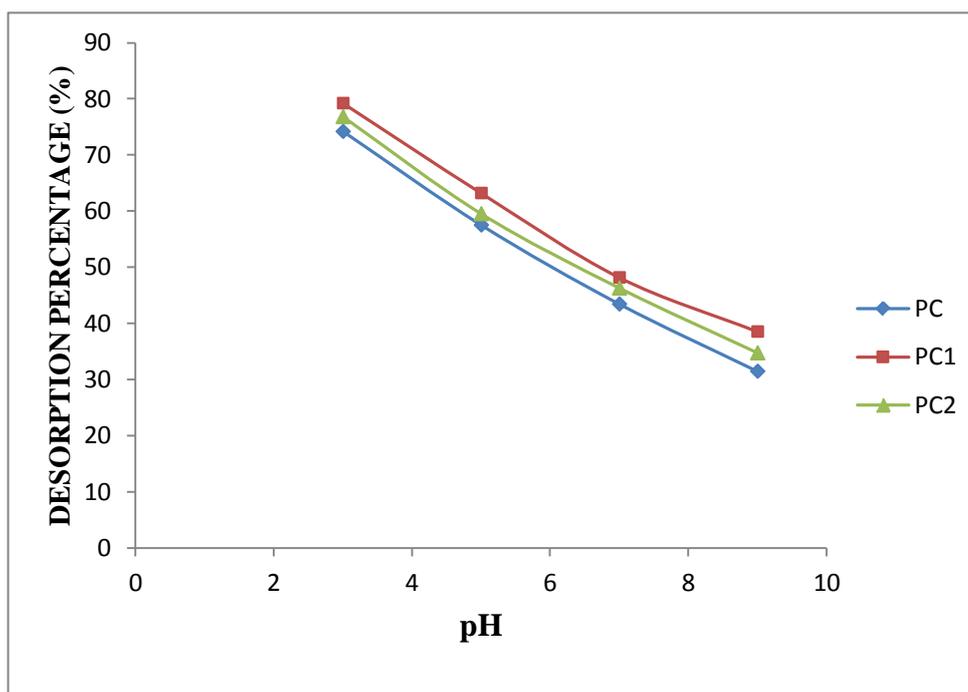


Figure 4.31 Desorption of raw and treated pine cone loaded MB at different pH solution

(Shaking speed: 150 rpm; Contact time: 5 hrs; dosage: 1 g L<sup>-1</sup>; Temperature: 30 °C)

## 4.9 Summary

In this study, the effectiveness of raw and modified biomass pine cone, PC, PC1, PC2 were tested for removal of Methylene Blue MB from aqueous solution and outcome of this chapter are as follows

- The amount of methylene blue dye uptake on raw and basic modified pine cone biomass were found to increase with increase in initial dye concentration, contact time, and solution pH but decreased with increase in, salt concentration and system temperature.
- In batch study, the kinetic experiments revealed that adsorption of dyes were rapid at initial stage followed by a slower phase where equilibrium uptake was achieved.
- The kinetic studies showed that the methylene blue adsorption process followed pseudo-second-order kinetics models.
- Langmuir and Freundlich equations both are applicable to describe the adsorption of methylene blue on raw and basic modified pine cone biomass within this initial dye concentration range. The maximum monolayer adsorption capacity was 129.87 mg/g occurred at pH of 9.02 for an initial dye concentration of 10 ppm by raw pine cone, whereas for base modified pine cone with two different NaOH concentrations were 142.25 mg/g and 139.23 mg/g at the same experimental conditions.
- The constant value, RL (low separation factor), in Langmuir isotherm and Freundlich constant, n, both give an indication of favourable adsorption.
- The thermodynamic analysis indicates that system is spontaneous, exothermic and physical processes in nature.
- A single stage batch adsorber design for the MB adsorption onto pine cone and modified pine cone have been presented based on the Langmuir isotherm model equation.
- Desorption experiments also showed that desorption increased as the pH decreased.

## **CHAPTER 5**

# **REMOVAL OF METHYLENE BLUE DYE (MB) FROM AQUEOUS SOLUTION BY RAW AND MODIFIED PINE LEAVES BIOMASS**

## 5.0 Abstract of article published from this chapter

The adsorption capacity of pine tree leaves for removal of methylene blue (MB) from aqueous solution was investigated in a batch system. The effects of the process variables, such as solution pH, contact time, initial dye concentration, amount of adsorbent, agitation speed, salt concentration and system temperature on the adsorption process were studied. The extent of methylene blue dye adsorption increased with increase in initial dye concentration, contact time, agitation speed, temperature, and solution pH but decreased with increased in amount of adsorbent and salt concentration. Equilibrium data were best described by both Langmuir isotherm and Freundlich adsorption isotherm. The maximum monolayer adsorption capacity of pine tree leaves biomass was 126.58 mg/g at 30°C. The value of separation factor,  $R_L$ , from Langmuir equation and Freundlich constant,  $n$ , both give an indication of favourable adsorption. The intraparticle diffusion model, Liquid film diffusion model, Double-exponential model, pseudo- first- order model and pseudo-second- order model were used to describe the kinetic and mechanism of adsorption process. A single stage batch absorber design for the MB adsorption onto pine tree leaves has been presented based on the Langmuir isotherm model equation. Thermodynamic parameters such as standard Gibbs free energy ( $\Delta G^0$ ), standard enthalpy ( $\Delta H^0$ ), and standard entropy ( $\Delta S^0$ ) were calculated.

YAGUB, M. T., SEN, T. K. & ANG, H. 2012. Equilibrium, Kinetics, and Thermodynamics of Methylene Blue Adsorption by Pine Tree Leaves. *Water, Air, & Soil Pollution*, 223, 5267-5282. (DOI 10.1007/s11270-012-1277-3)

## 5.1 Introduction

This chapter deals with the adsorptive parameters of raw and modified pine leaves in the removal of MB dye at various process conditions. Batch adsorption experiments were conducted to determine the effectiveness of the prepared adsorbents, raw pine leaves (PL), and chemically (base and acid) modified pine leaves (PLBT&PLAT). The effects of physiochemical process parameters conditions such as contact time, initial dye concentration, solution pH, amount of adsorbent, agitation speed, salt concentration and system temperature on dye removal were tested. The experimental data from batch experiments were analyzed with commonly used kinetic models; pseudo first-order model and pseudo- second- order model, intraparticle diffusion model, and liquid film diffusion model to provide better understanding of the adsorption process and mechanism. Two commonly used isotherm models, Langmuir and Freundlich models were selected to explain the dye–pine leaves biomass interaction and mechanism of adsorption. Thermodynamic parameters, standard Gibbs free energy change ( $\Delta G^{\circ}$ ), enthalpy change ( $\Delta H^{\circ}$ ), and entropy change ( $\Delta S^{\circ}$ ) were all calculated.

## 5.2 System Identification

Methylene blue (MB), the typical cationic dye was selected as the adsorbate. Raw and chemically modified pine leaves was selected as adsorbent.

## 5.3 Materials and Methods

### a) Pine leaves of adsorbent and its characterization

Pine tree leaves were collected locally from Curtin University campus, Perth, Western Australia. It was collected between April and May 2010. The leaves were washed several times with distilled water to remove impurity such as sand. Then direct it was dried in an oven at 65°C for 24 hr period. Dried pine leaves were cut into pieces and then ground by using a crusher. The resultant powders were passed through British Standard Sieves and particles below 350µm are collected in a plastic container and used as adsorbent for the adsorption experiments.

The preparation of base and acid modified pine leaves were the same as detailed section 4.3.a with 100 ml of 0.1M NaOH solution and with 100 ml of 0.1 M HCl solution.

### b) Adsorbate and other chemicals

The basic cationic dye, Methylene Blue (MB), was taken as the adsorbate in this study. The formula of methylene blue is  $C_{16}H_{18}N_3SCl \cdot 3H_2O$ , and molecular weight as 319.85 g. Preparation of stock solution, adjustment of the solution pH and the plot of calibration curve were the same as in section 4.3.b.

### c) Adsorption experiment

Adsorption measurements were conducted with known amount of the adsorbent in a 50 ml of aqueous methylene blue solutions of known concentration in a series of 250 ml conical flasks. The experiments were conducted as per the method mentioned in section 4.3.c

## 5.4 Results and Discussion

Some of the experimental data used to obtain the results of the study of the effect of pine leaves are listed in Appendix B1-23.

### 5.4.1 Effect of Initial Solution pH on MB Dye Adsorption

The effect of solution pH (2.05 to 9.20) on MB adsorption is presented in Fig 5.1a, b&c. for both raw and treated pine leaves. Solution pH is an important parameter in the adsorption process due to its influence on the surface properties of adsorbent (Quintelas et al., 2009).

From Figure (5.1a), it was found that the amount of dye adsorbed ( $q_t$  mg) increased with increase in pH or alkalinity for both the systems. The percentage removal of MB dye was also found to increase when the solution pH increased from pH 2.05 to pH 9.2, fig (5.1b). From Figs (5.1a, 5.1b), it was found that the amount of dye adsorption increased from 6.74 mg/g (20.24 % removal efficiency) to 26.81 mg/g (80.45 % removal efficiency) due to change in pH from 2.05 to 9.2 for a fixed initial MB dye concentration of 10 ppm at equilibrium for raw pine leaves (PL). Similarly from Fig (5.1a, 5.1b), it was also found that the amount of dye adsorbed increased from 7.82 mg/g (23.46% removal efficiency) to 27.51 mg/g (85.53% removal efficiency) for base modified pine leaves (PLBT) and from 11.38 mg/g (34.41% removal efficiency) to 31.72 mg/g (95.16% removal efficiency) for acid treatment pine leaves (PLAT) respectively, due to change in pH from 2.05 to 9.2 for a fixed initial MB dye concentration of 10 ppm at equilibrium. However the acid-treated pine leaves gives a higher MB dye sorption capacities than the others (Fig. 5.1a). This is because of increase of the internal surface size of acid treated sample ( $1.53 \text{ m}^2/\text{g}$ ) as compared to the raw and base treated pine leaves ( $1.17$  &  $1.21 \text{ m}^2/\text{g}$ ). The higher internal surface area led to increased adsorption of MB dye for the treated samples. Pine leaves comprises of different functional groups such as amino, hydroxyl and carbonyl groups which are affected by the pH of the solution. The point of zero charge,  $\text{pH}_{\text{PZC}}$  of pine leaves particles in aqueous solution is around 4.5 which has been discussed in section (3.3.4). Negative zeta potential increased with increasing alkaline solution pH (Nuhoglu and Oguz, 2003; Blazque et al., 2011). The surface charge of biomass change decreased  $\text{pH}_{\text{PZC}}$  and therefore points of zero charge,  $\text{pH}_{\text{PZC}}$  of modified pine leaves were 3.6 and 3.8 for PLAT and PLBT respectively.

Maximum adsorption of MB dye occurs at basic pH (Fig 5.1a, 5.1b). This can be explained by the electrostatic interaction of cationic dye methylene blue with negatively charged surface of the pine leaves. The negative charge on the leaves increased with increasing pH, which was reported by Ueun et al (2003) also. In addition, lower adsorption of methylene blue at acidic pH might be due to the presence of excess  $H^+$  ions competing with dye cations for the available adsorption sites (Bestani et al., 2008, Vadivelan and Kumar, 2005). The lower MB dye adsorption at acidic pH, due to electrostatic repulsion between positive surface charge and positive cationic dye MB molecule.

The results from pine cone systems (section 4.4.1) and pine leaves systems (section 5.4.1) showed the pine cone materials were better as compared to the pine leaves materials to remove the MB dye at the same condition.

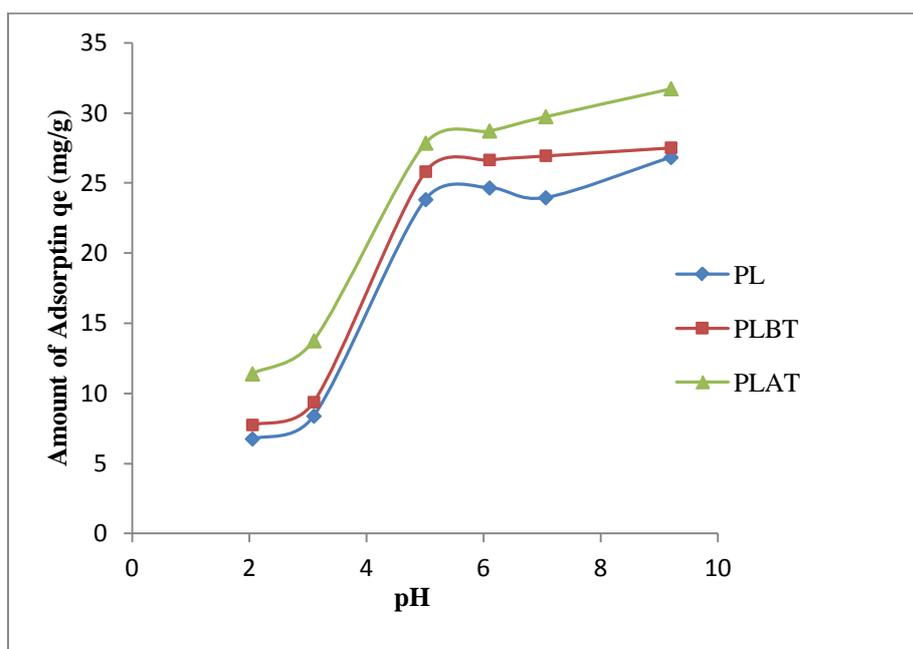


Figure (5.1a) Effect of initial solution pH on the amount of adsorption of MB onto raw and treated pine leaves

(Adsorbent=15mg; volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= 30°C; shaker speed=150 rpm; time 240 min)

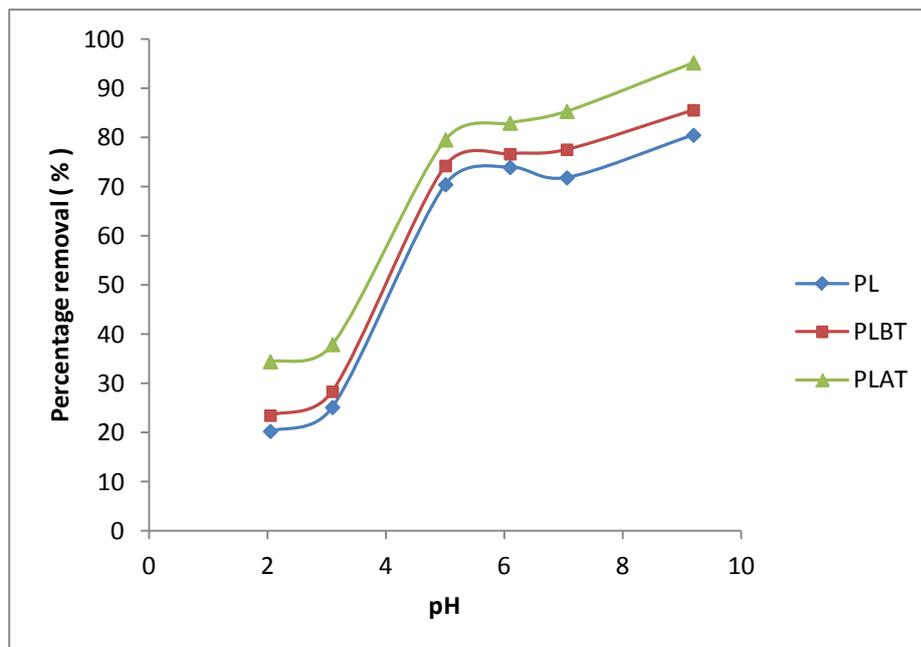


Figure 5.1b Effect of initial solution pH on the percentage removal of MB onto raw and treated pine leaves

(Adsorbent=15mg; volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= 30°C; shaker speed=150 rpm; time 240 min)

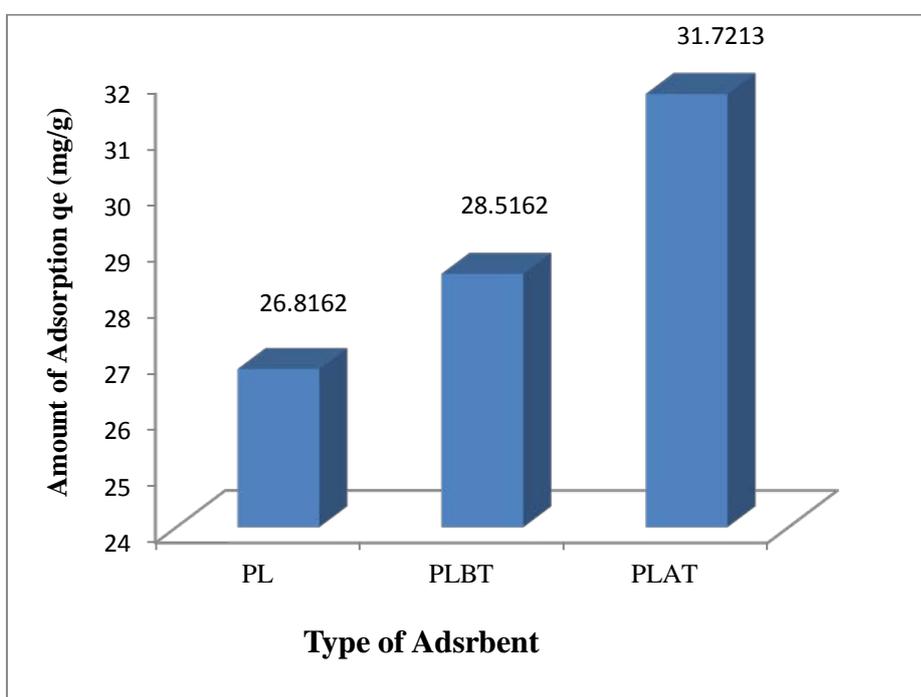


Figure 5.1c Effect of initial solution pH on the maximum amount of adsorption of MB onto raw and treated pine leaves

(Adsorbent=15mg; volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= 30°C; shaker speed=150 rpm; time 240 min)

### 5.4.2 Effect of Contact Time on MB Dye Adsorption Kinetics

Kinetic information is essential for economical wastewater treatment plant design applications (Saeprasearsit et al., 2010). Fig (5.2) shows the removal of MB dye solutions on to raw and modified pine leaves with time. A maximum adsorption of the MB takes place within 10min and thereafter the gradual increase in adsorption occurs with increasing contact time up to 90 min for both the systems. This kinetic experiment clearly indicated that adsorption of methylene blue dye on raw and modified pine leaves is followed by two-step process: a rapid adsorption of dye to the external surface followed by possible slow removal of MB dye. First step refers to the immediate availability of most active sites on the adsorbent surface. Second step, shows additional adsorption attributed to the intra-particle diffusion in the interior of the adsorbent stimulating further movement of MB molecules from the liquid phase onto adsorbent biomass surfaces.

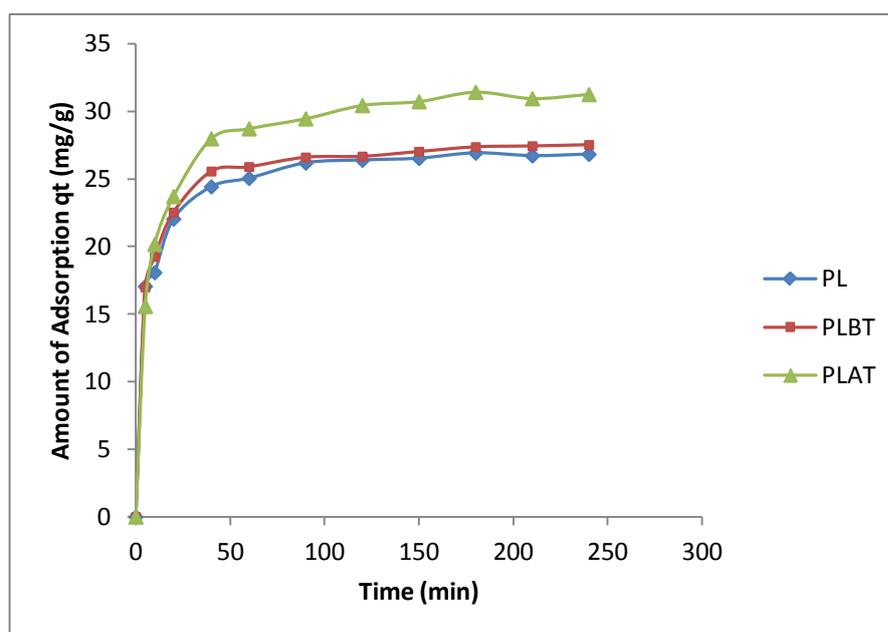


Figure 5.2 Effect of contact time on the adsorption of MB onto raw and treated pine leaves

(Sorbent=15mg; volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= 30°C; shaker speed=150 rpm)

### 5.4.3 Effect of Initial MB Dye Concentration on Adsorption

The initial dye concentration has strong effect on its removal from aqueous solutions. The effect of initial dye concentration on the adsorption of methylene blue dye was investigated at different initial dye concentration onto raw and treated pine leaves, and the results are presented in figures (5.3 a, b & c). Figures (5.3a) shows that the amount of adsorption  $q_e$  (mg/g) increased with increase in initial dye concentration for raw and modified pine leaves. As the initial dye concentration increased from 10 to 90 mg/L, the adsorption capacity of dye onto raw and treated pine leaves was increased from 26.81 to 146.38 mg/g. Furthermore, the adsorption capacity also increased with acid modified pine leaves. This indicates that the initial dye concentration plays a significant role in the adsorption ability of the leaves. Further, from figure (5.3b) both raw and modified pine leaves, the adsorption percentage decreased with increasing in initial MB dye concentration. The percentage removal of dye decreased from 72.2 to 27.3% for raw pine leaves (PL), from 77.2 to 33.5%, and from 85.9 to 39.9% for base and acid modified pine leaves (PLBT&PLAT) respectively, with increase in initial dye concentration from 10 to 90 mg/L Fig (5.3b).

This is because the initial dye concentration provides the driving force to overcome the resistance to mass transfer of dye between the aqueous and the solid phases. For constant dosage of adsorbent, at higher initial dye concentration, the available adsorption sites of adsorbent become less, and hence, the removal of MB dye depends upon the initial concentration (Shahryari et al., 2010). The increase in initial concentration also enhances the interaction between adsorbent and dye. Therefore, an increase in initial dye concentration leads to increase in the adsorption uptake of dye. Also kinetic experiments indicated that adsorption of MB on pine leaves followed a three-step processes, a rapid initial adsorption followed by a period of slower adsorption of MB and finally attain equilibrium. Similar types of results are reported by various researchers for methylene blue adsorption on activated carbon (Sharma, 2009), on carbon nanotube (Shahryari et al., 2010), on oak sawdust (Abd EI-Latif et al., 2010), on rice husk and rice husk ash (Sharma et al., 2010b), on water weeds biomass (Tarawou and Horsfall, 2007) and on cashew nut shell (Kumar et al., 2010). These results emphasised the removal of MB dye by pine leaves was less than the removal of MB dye by pine cone.

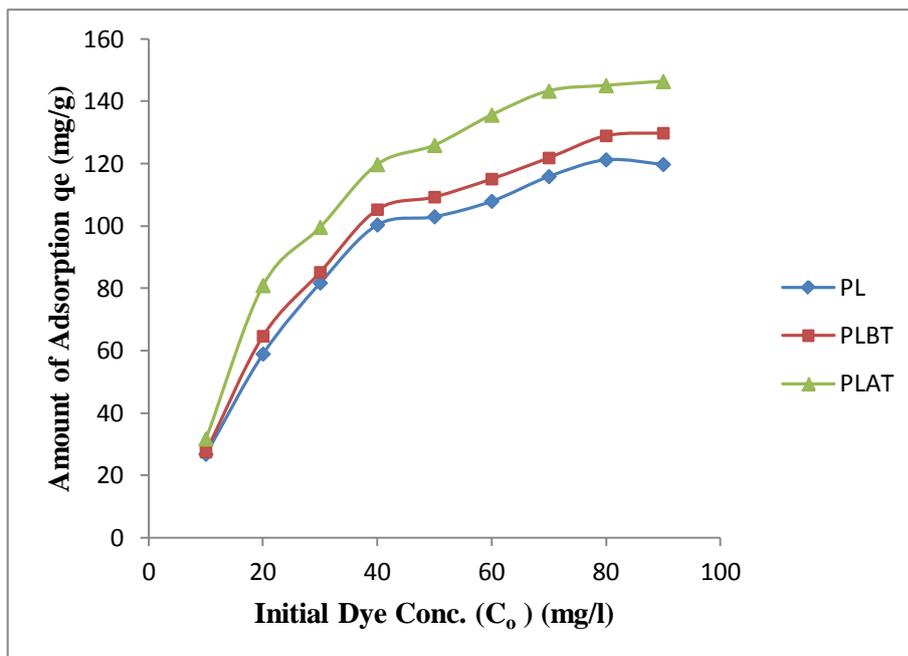


Figure 5.3a Effect of initial dye concentration on the amount of adsorption of MB onto raw and treated pine leaves

(Sorbent=15mg; volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= 30°C; shaker speed=150 rpm; time 240 min)

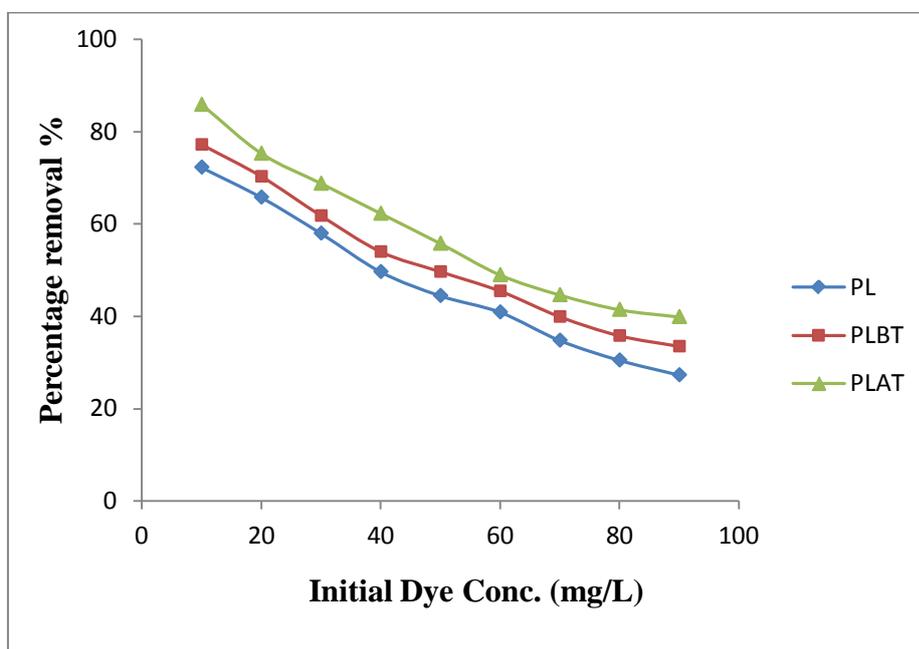


Figure 5.3b Effect of initial dye concentration on the percentage removal of MB onto raw and treated pine leaves

(Sorbent=15mg; volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= 30°C; shaker speed=150 rpm; time 240 min)

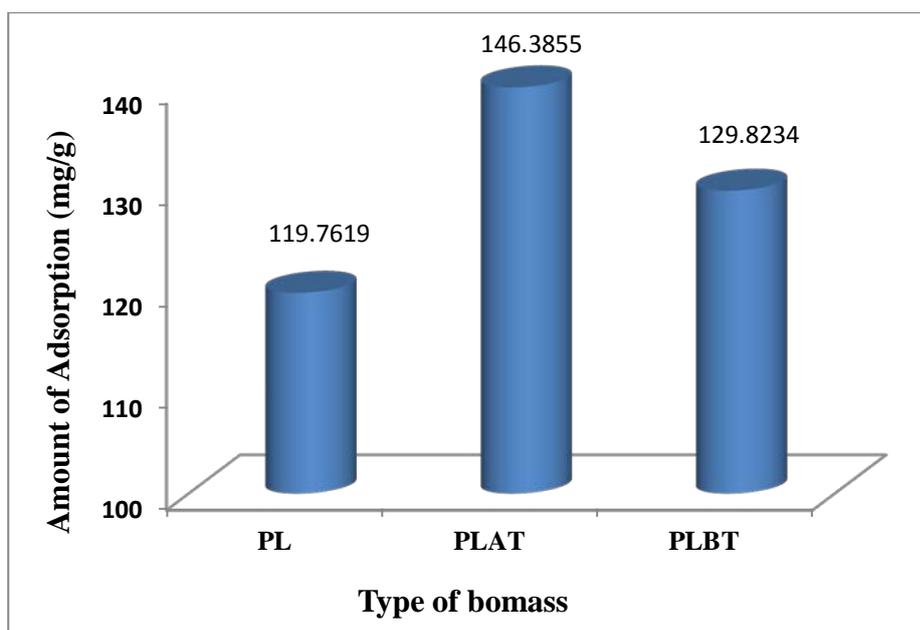


Figure 5.3c Effect of initial dye concentration on the maximum amount of adsorption of MB onto raw and treated pine leaves

(Sorbent=15mg; volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= 30°C; shaker speed=150 rpm; time 240 min)

#### 5.4.4 Effect of Inorganic Monovalent Salt Concentration on MB Dye Adsorption

The effect of salt concentration (NaCl) on removal of methylene blue MB was studied at different salt concentrations of 50, 100, 150, and 200 mg L<sup>-1</sup>. Figure (5.4) shows that the dye adsorption by raw and modified pine leaves decreased with increase of inorganic salt. This result indicates that the presence of external electrolyte, such as sodium chloride, has a limited effect on the binding efficiency between pine leaves materials and methylene blue. Na<sup>+</sup> of NaCl ions may compete with basic dye for binding sites on the adsorbent surface and hence less adsorption. Mahmood et al (2011) reported similar results for different system. Adsorption by pine cone also showed better results than that obtained using pine leaves.

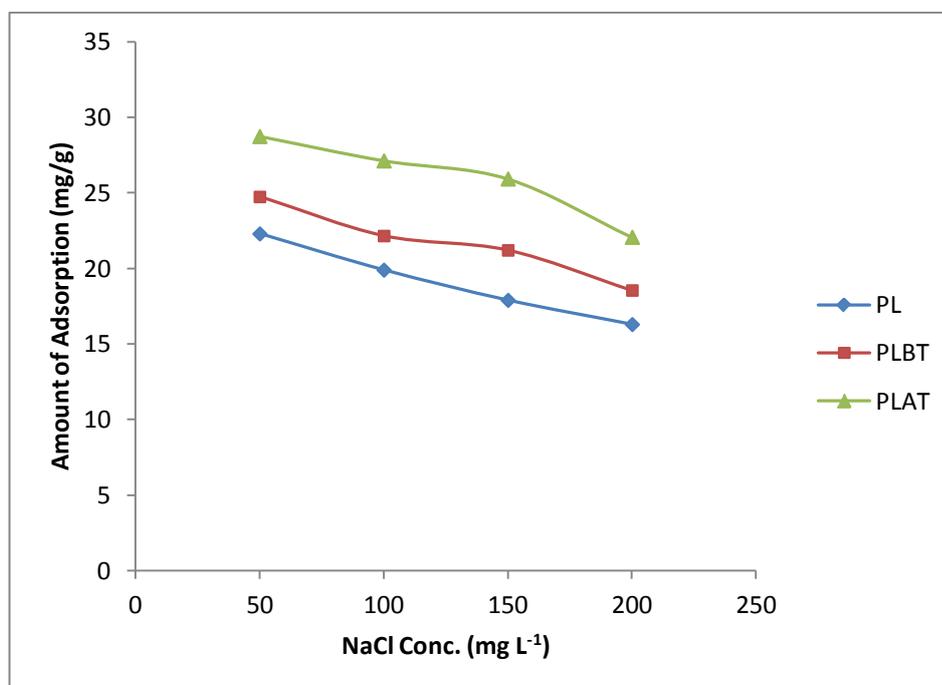


Figure 5.4 Effect of salt concentration on the amount of adsorption of MB onto raw and treated pine leaves

(Volume of dye solution=50 ml; temperature= 30°C; pine cone dosage 15mg; pH=9.2; agitation speed 150 rpm; and initial dye concentration 10 mgL<sup>-1</sup>; time 240 min)

### 5.4.5 Effect of Temperature on MB Dye Adsorption

Various dye effluents are produced at relatively high temperatures; therefore, temperature can be an important physical parameter for the real application of pine leaves materials. Effect of temperature is a good indicator for the adsorption to be either endothermic or exothermic process (Ghaedi et al., 2012). To study the effect of temperature on the adsorption of MB dye adsorption by pine leaves, the experiments were carried out at temperatures of 30, 40, 50, and 60°C. Figure (5.5), shows the influence of temperature on the adsorption of MB dye onto pine leaves and treated pine leaves. As it was observed, the equilibrium adsorption capacities onto raw and treated pine leaves increased with increasing temperature. This may be due to increasing the mobility of the dye molecules and an increase in the number of active sites for the adsorption with increasing temperature (Mahmoodi et al., 2010, Ghaedi et al., 2012). An increasing number of molecules may also acquire enough energy to undergo an interaction with active sites at the surface. Further, increasing temperature may create a swelling effect within the internal structure of the pine leaves materials enabling large dye molecule to penetrate further. It should be noted that contrary to the results obtained from pine cone, higher temperatures resulted in higher adsorption with pine leaves.

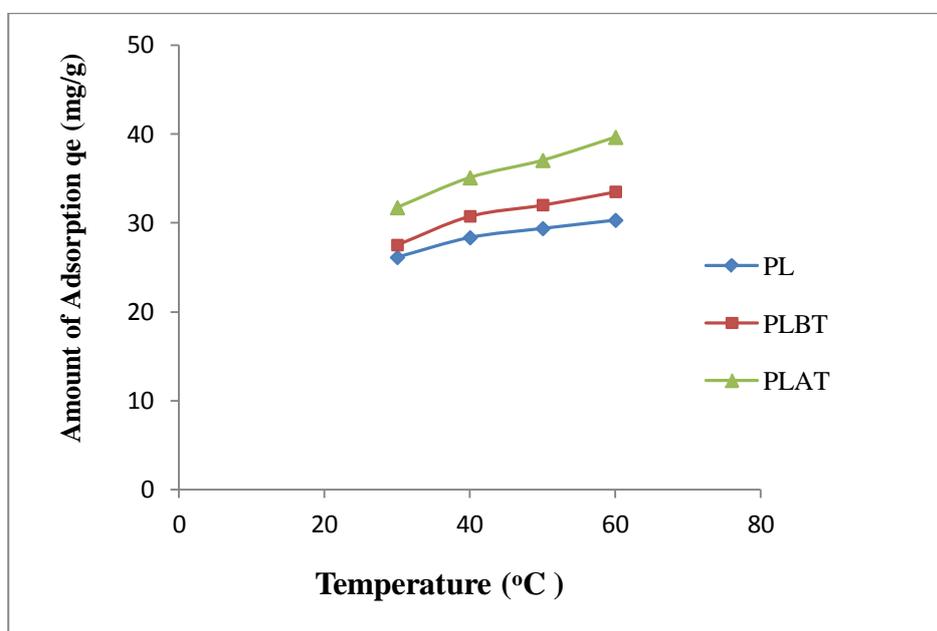


Figure 5.5 Effect of temperature on the amount of adsorption of MB onto raw and treated pine leaves

(Sorbent=15mg; volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= (30, 40, 50, 60 °C); shaker speed=150 rpm; pH=9.18; time 240 min)

#### 5.4.5.1 Calculation of Thermodynamic Parameters for MB Adsorption Process

Thermodynamic study of an adsorption process is needed to conclude whether the process is favourable or not. The thermodynamic parameters, namely free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ), and entropy change ( $\Delta S^\circ$ ) have an important function to determine heat change the adsorption process for dye and pine leaves. Assuming that the activity coefficients are unity at low concentrations (the Henry's law sense), the relationship of these thermodynamic was given by the equations (4.3, 4.4, and 4.5).

Gibbs free energy change  $\Delta G^\circ$ ; enthalpy change  $\Delta H^\circ$ , and entropy change  $\Delta S^\circ$  were obtained from the experimental study at different temperatures 303K, 313K, 323K and 333K by the application of Eqs. (4.3-4.5) and from Van't Hoff plot Fig (5.6). All thermodynamic parameters are tabulated in Table 5.1.  $\Delta G^\circ$  are ranged from (-53.8 KJ/mole) to (-57.8 KJ/mole) depending on temperature ranging from 303 K to 333 K.. The value of  $\Delta G^\circ$  increases thus indicating that the adsorption of MB on the pine leaves becomes more favourable with increasing temperature. The positive value of  $\Delta H^\circ$ , to the fact that the sorption process was endothermic and the reaction consumes energy, whereas the positive value of  $\Delta S^\circ$ , indicated increased randomness at the solid-solute interface during adsorption.

The comparison between pine leaves and pine cone in the removal of MB at different temperature was the adsorption capacities onto pine leaves materials increased with increasing temperature, whereas the adsorption capacities onto pine cone materials decreased with increasing temperature. These results are verified from the  $\Delta H^\circ$  values for each of the materials being positive in the case of pine leaves and negative for that of pine cone.

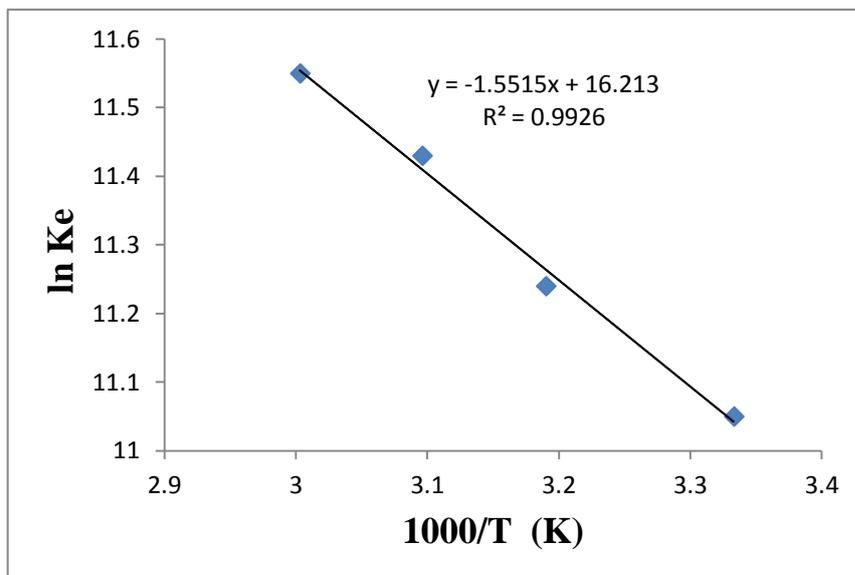


Figure 5.6 Van't Hoff plot for adsorption of MB into pine leaves

**Table 5.1** Thermodynamic parameters for adsorption of MB onto pine leaves at different temperatures

Temperature (K)	$\Delta G^\circ$ (KJ/mol <sup>-1</sup> )	$\Delta H^\circ$ (KJ/mol <sup>-1</sup> )	$\Delta S^\circ$ (KJ/mol <sup>-1</sup> K)
303	-53.8	12.9	0.135
313	-55.2	12.9	0.135
323	-56.5	12.9	0.135
333	-57.8	12.9	0.135

#### **5.4.6 Effect of Adsorbent Dosage on MB Dye Kinetics Adsorption**

Study of the effect of adsorbent dosage provides an idea of the effectiveness of an adsorbent and the ability of a dye to be adsorbed with a minimum dosage, so as to identify the ability of a dye from an economical point of view (Salleh et al., 2011). Fig (5.7a, b) shows that at equilibrium, the increase in adsorbent dosage from 10 to 30 mg resulted in decrease of amount of adsorbed dye for both raw and treated pine leaves. In Figure (5.7a), the increase in  $q_t$  (mg/g) with the time of contact is more pronounced for higher initial concentrations of MB, This is a common phenomenon observed for many systems. The reason is the higher driving force for mass transfer if the solute concentration is high. In fact the equilibrium adsorption generally levels off at a higher solute concentration generation an even higher driving force. A fixed mass of pine leaves materials can only adsorb a fixed amount of dye. This is because, at higher pine leaves materials to methylene blue concentration ratios, there is a very fast superficial sorption onto the raw and treated pine leaves surface that gives a lower methylene blue concentration in the solution compared to the lower biomass to methylene blue concentration ratio. The reduction in amount of dye adsorbed,  $q_e$  mg/g with rising adsorbent mass, is due to the split in the flux or the concentration gradient between solute concentration in the solution and the solute concentration in the surface of the adsorbent (Kumar et al., 2010, Vadivelan and Kumar, 2005). A similar behaviour was observed for methylene blue adsorption on rice husk (Sharma et al., 2010b, Vadivelan and Kumar, 2005), on cashew nut shell (Kumar et al., 2010) and on oak sawdust (Abd EI-Latif et al., 2010).

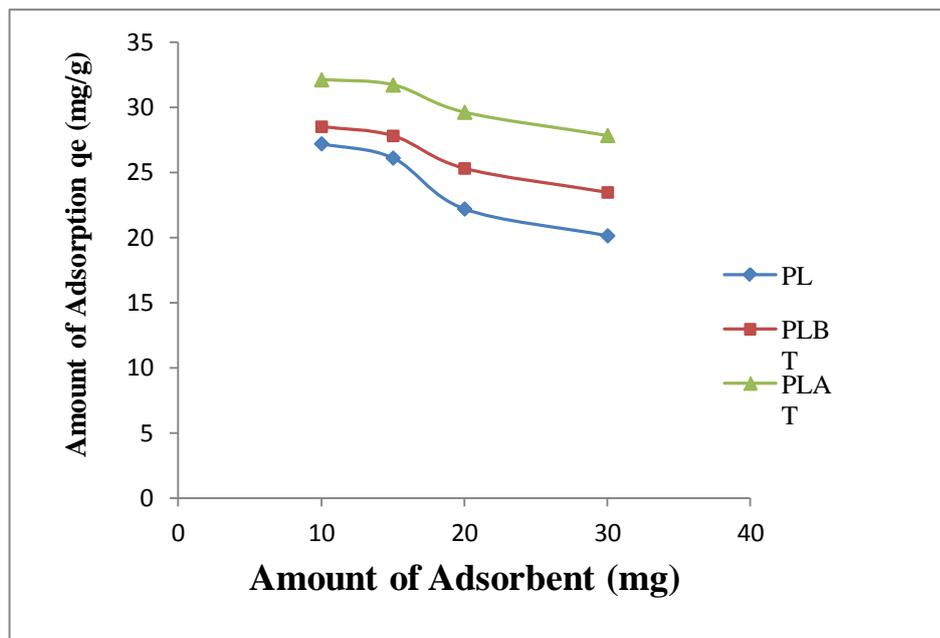


Figure 5.7a Effect of adsorbent pine leaves materials dosage on the adsorption of MB

(Volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= 30°C; shaker speed=150 rpm; pH=9.2; time 240 min)

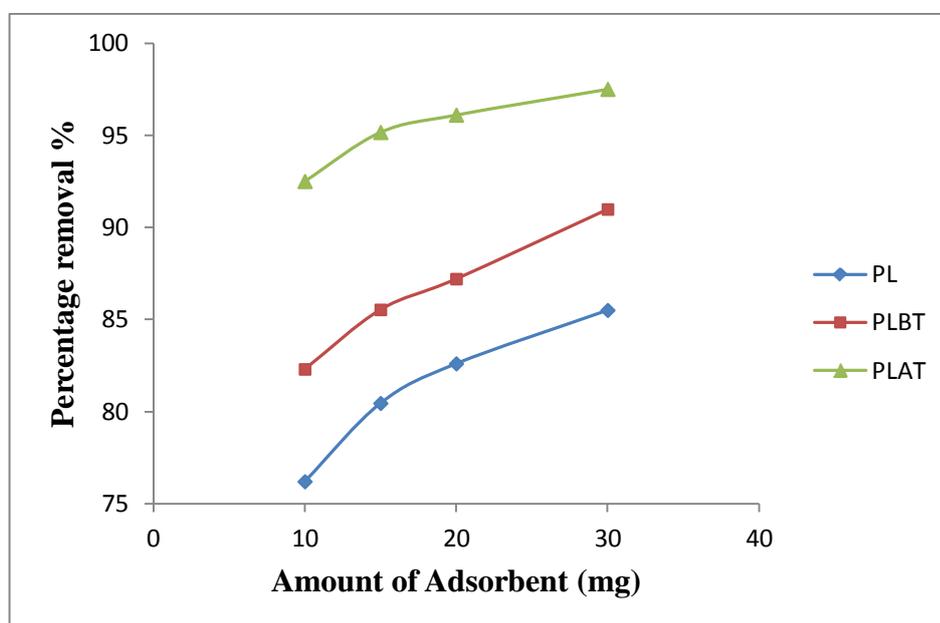


Figure 5.7b Effect of adsorbent pine leaves materials dosage on the adsorption of MB

(Volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= 30°C; shaker speed=150 rpm; pH=9.2; time 240 min)

### 5.4.7 Effect of Agitation Speed on MB Dye Kinetic Adsorption

The effect of agitation speed on removal efficiency of methylene blue was studied by varying the speed of agitation from 100 to 200 rpm, while keeping the optimum dose of adsorbents and optimum pH of solution. As can be seen from Figure (5.8) the methylene blue removal efficient generally increased with increasing agitation speed for raw and modified pine leaves. These results can be associated to the fact that the higher agitation speed, improves the diffusion of methylene blue ions towards the surface of the adsorbents. This also indicates that a shaking rate in the range 100-200 rpm is enough to assure that all the surface binding sites are made readily available for methylene blue uptake. This result is also in agreement with that reported by (Ho et al., 2001, Saifuddin M and Kumaran, 2005, Tsai et al., 2008).

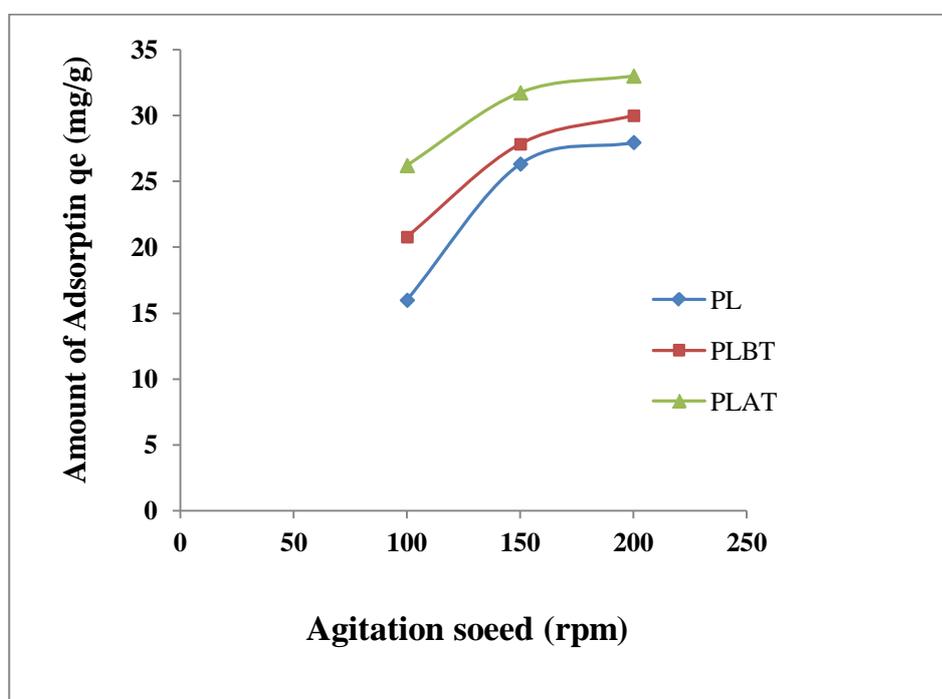


Figure 5.8 Effect of Agitation Speed on the adsorption of MB onto pine leaves materials

(Volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= 30°C; pine cone dosage 15mg; pH=9.2; time 240 min)

## 5.5 MB Adsorption Mechanism and Application of Various Kinetics Models

The prediction of batch adsorption kinetics is compulsory for the design of industrial adsorption columns. The nature of the adsorption process will depend on the system conditions and also on chemical or physical characteristics of the adsorbent system. In the present study, the applicability of the pseudo- first- order, pseudo- second-order, intraparticle diffusion, and liquid film diffusion models were tested for the adsorption of MB into raw and modified pine leaves biomass particles. The error analysis methods were used to calculate the best fit of models as mentioned in Section 4.5.

The linear fitting plots of pseudo-first-order kinetic model are presented in fig (5.9, 5.10, 5.11, and 5.12). Also the linear fitting plots of intraparticle diffusion model are shown in fig (5.13, 5.14, 5.15, and 5.16). In the same way the linear fitting plots of liquid film diffusion model are demonstrated in fig (5.17, 5.18, 5.19, and 5.20).

These plots give straight lines with very poor linear regression coefficient ( $R^2$ ) at different physico-chemical conditions. Moreover, these models predicted a significantly lower value of the equilibrium adsorption capacity ( $q_e$ ) than the experimental value and all kinetic parameters including linear correlation coefficient ( $R^2$ ) obtained from fitting these models plots with experimental data under different conditions were presented in Tables 5.2, 5.4, and 5.5 and low value indicate the inapplicability of these models on this system. The adsorption data were further analysed using the pseudo-second-order kinetic model. The plot  $t/q_t$  versus  $t$  figs (5.21, 5.22, 5.23, and 5.24) gives straight lines with higher linear correlation coefficients if pseudo second- order kinetics is applicable. The kinetic parameters  $q_e$ ,  $k_2$  and  $h$  can be determined from the slope and intercept of the plot respectively and also all kinetic parameters including linear correlation coefficient ( $R^2$ ) obtained from fitting model plots with experimental data under different conditions were presented in Table 5.3. It is important to note that the error function values using Chi-square analysis, of the pseudo second order model for raw and treated pine leaves were lower (than those of the other models) for all the dye adsorption, which further validates the better fit of the pseudo second order to the experimental data. The experimental adsorption uptake ( $q_{e,exp}$ ) were much closer to the calculated adsorption uptake ( $q_{e,cal}$ ) in Table 5.3 suggests the better fit of the second order model to the

kinetics data. These findings are the same for the case of pine cone as detailed in Section 4.5. Similar type kinetic model parameters were obtained by various researchers for a few other systems reported in the literature (Ofomaja and Naidoo, 2011, Sen et al., 2011, Dawood and Sen, 2012c), also similar results obtained from pine cone systems in the previous chapter

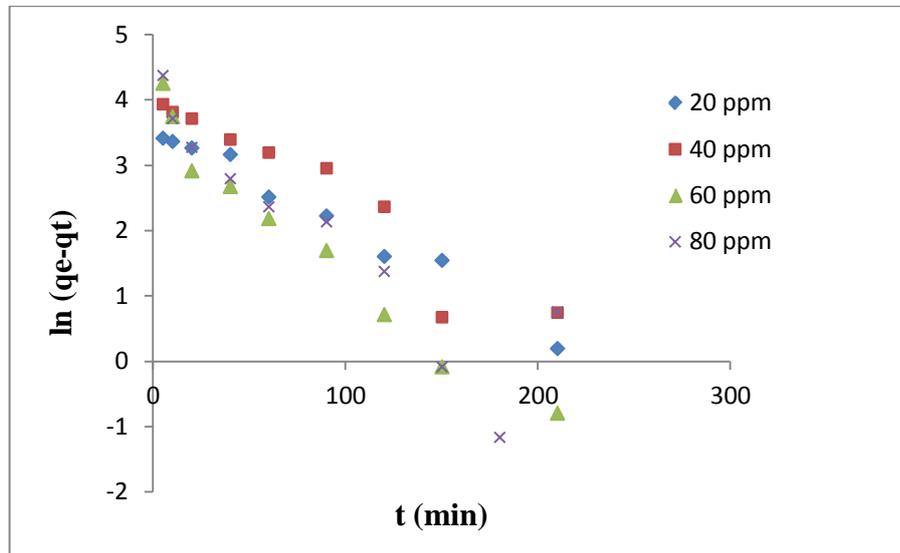


Figure 5.9 Pseudo-first-order plot for the adsorption of MB onto raw pine leaves (PL) materials at different initial MB concentration

(Volume of dye solution=50 ml; temperature= 30°C; pine leaves dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

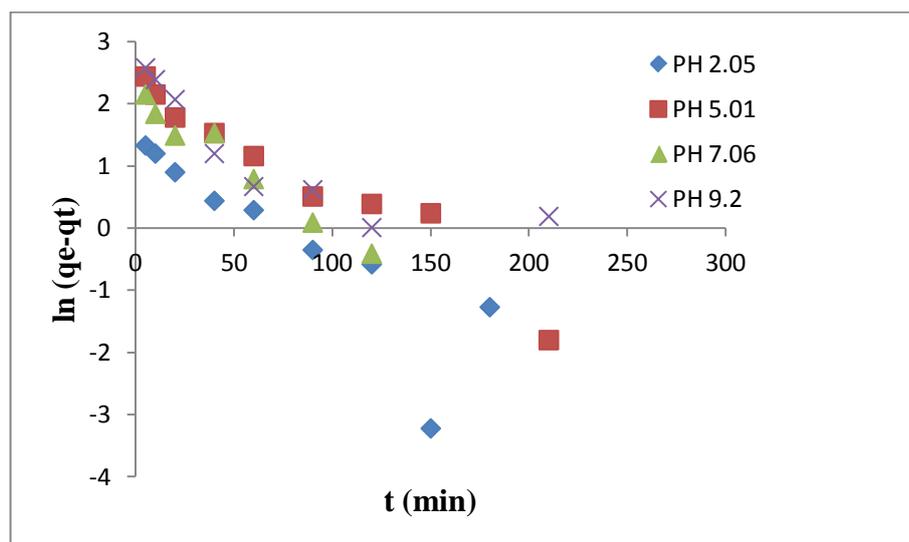


Figure 5.10 Pseudo-first-order plot for the adsorption of MB onto raw pine leaves (PL) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine leaves dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

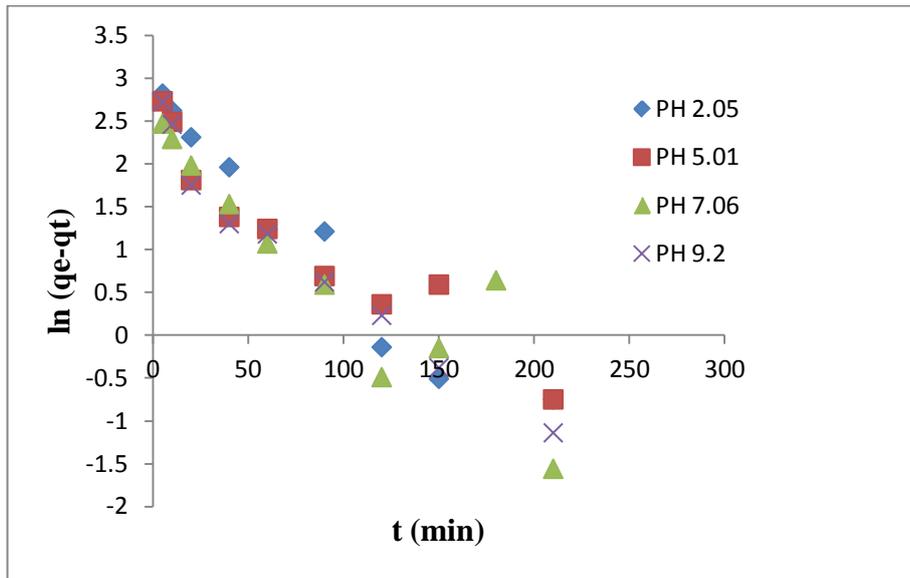


Figure 5.11 Pseudo-first-order plot for the adsorption of MB onto treated pine leaves (PLAT) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine leaves dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

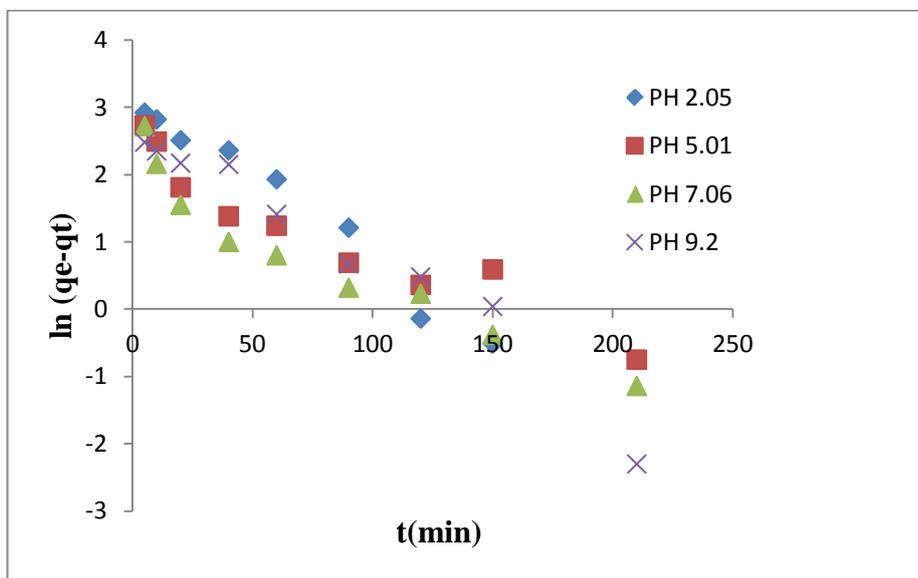


Figure 5.12 Pseudo-first-order plot for the adsorption of MB onto treated pine leaves (PLBT) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine leaves dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

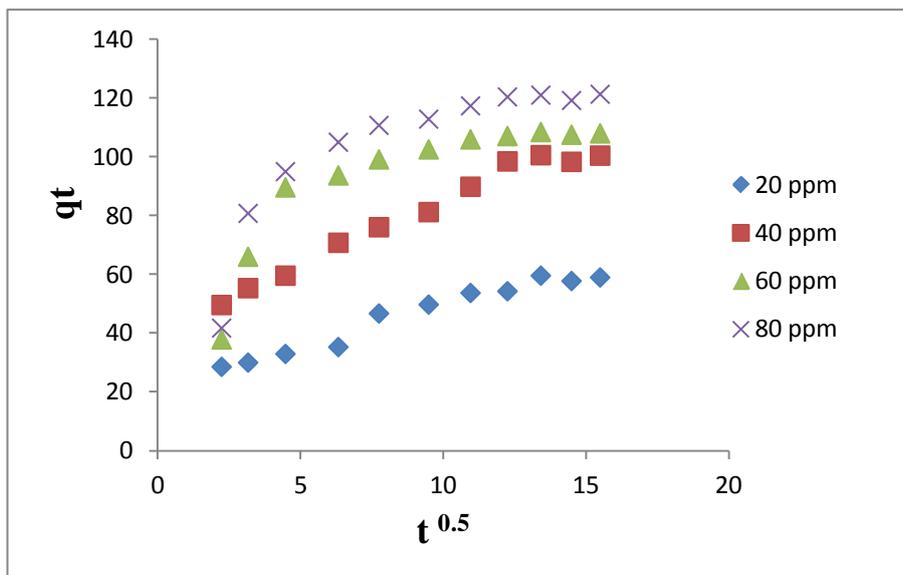


Figure 5.13 Intraparticle diffusion plot for the adsorption of MB onto raw pine leaves (PL) materials at different initial MB concentration

(Volume of dye solution=50 ml; temperature= 30°C; pine leaves dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

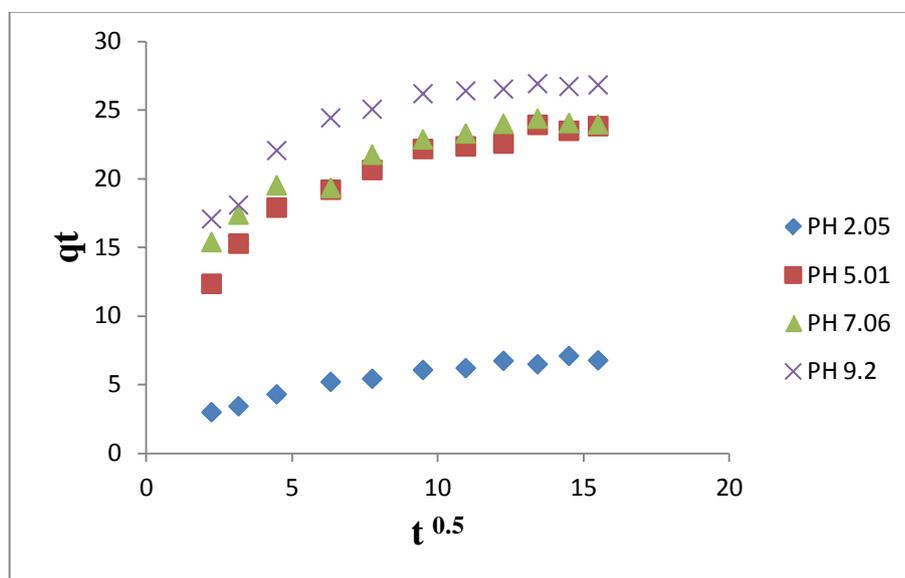


Figure 5.14 Intraparticle diffusion plot for the adsorption of MB onto raw pine leaves (PL) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine leaves dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

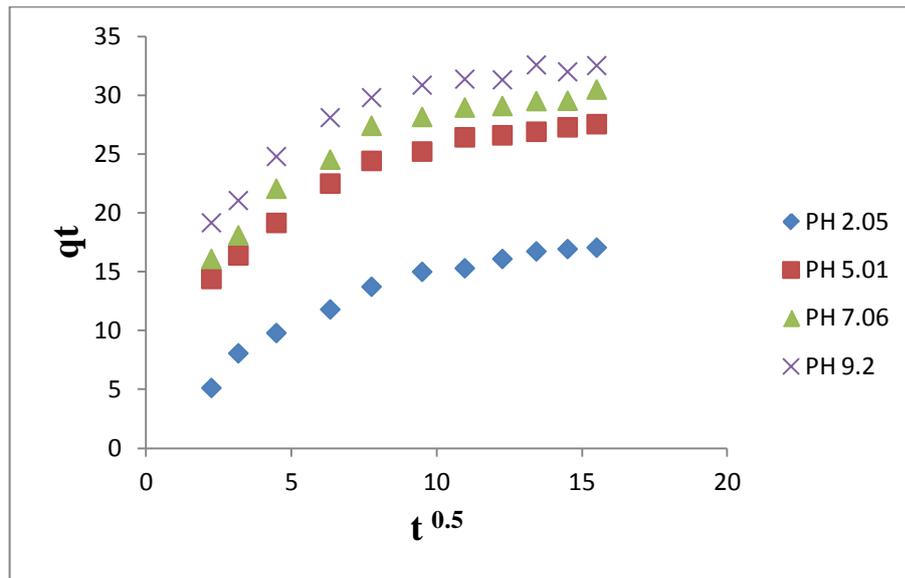


Figure 5.15 Intraparticle diffusion plot for the adsorption of MB onto treated pine leaves (PLAT) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine leaves dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

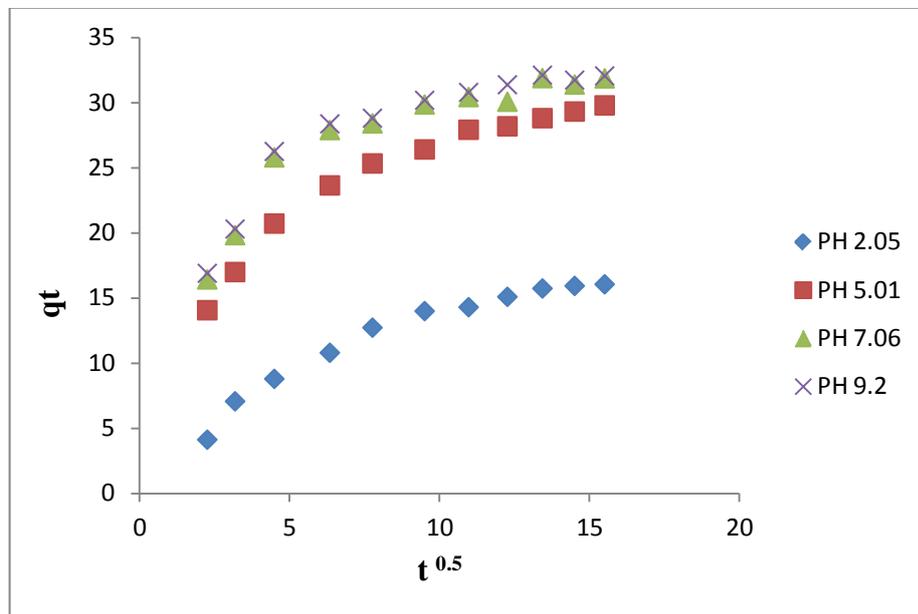


Figure 5.16 Intraparticle diffusion plot for the adsorption of MB onto treated pine leaves (PLBT) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine leaves dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

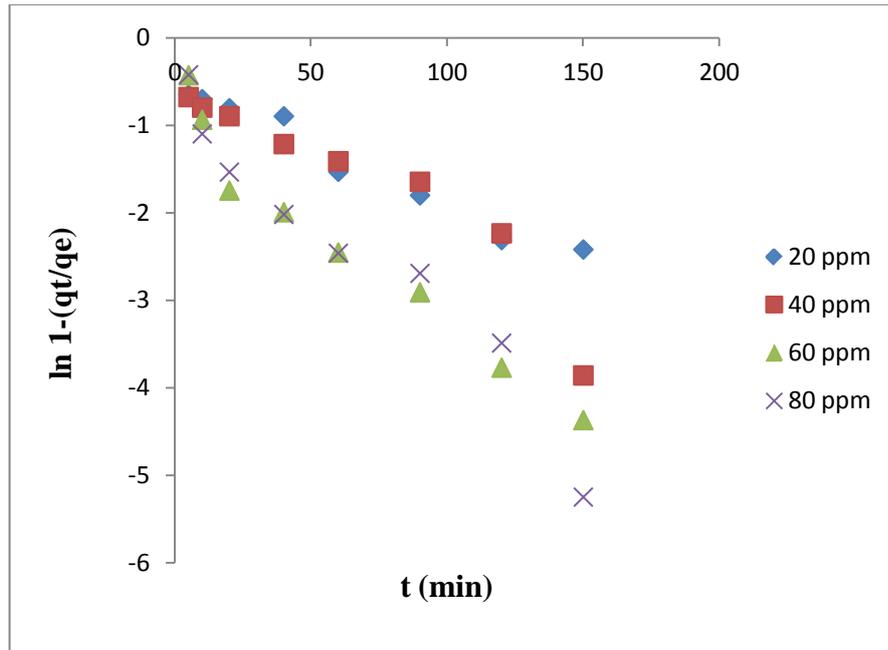


Figure 5.17 Liquid film diffusion plot for the adsorption of MB onto raw pine leaves (PL) materials at different initial MB concentration

(Volume of dye solution=50 ml; temperature= 30°C; pine leaves dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

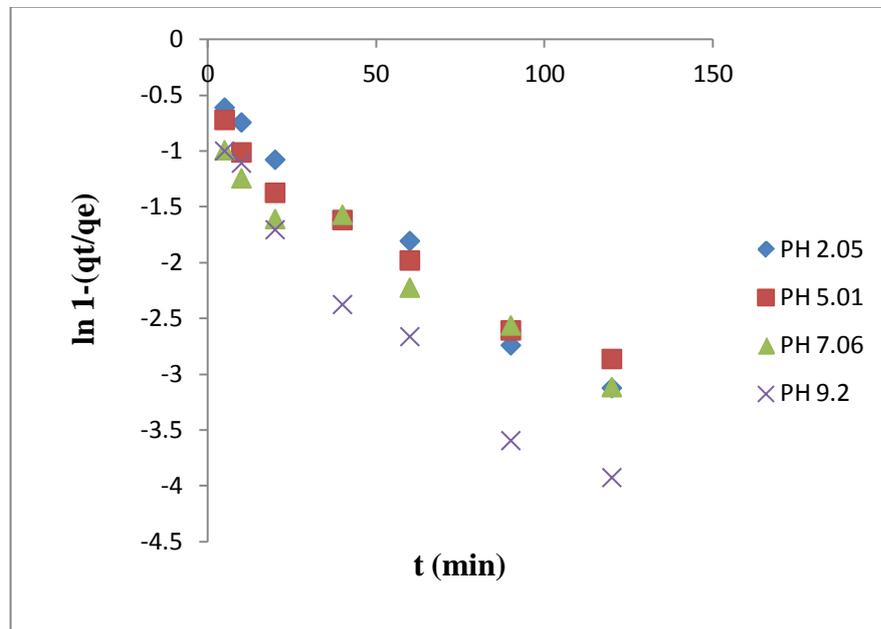


Figure 5.18 Liquid film diffusion plot for the adsorption of MB onto raw pine leaves (PL) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine leaves dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

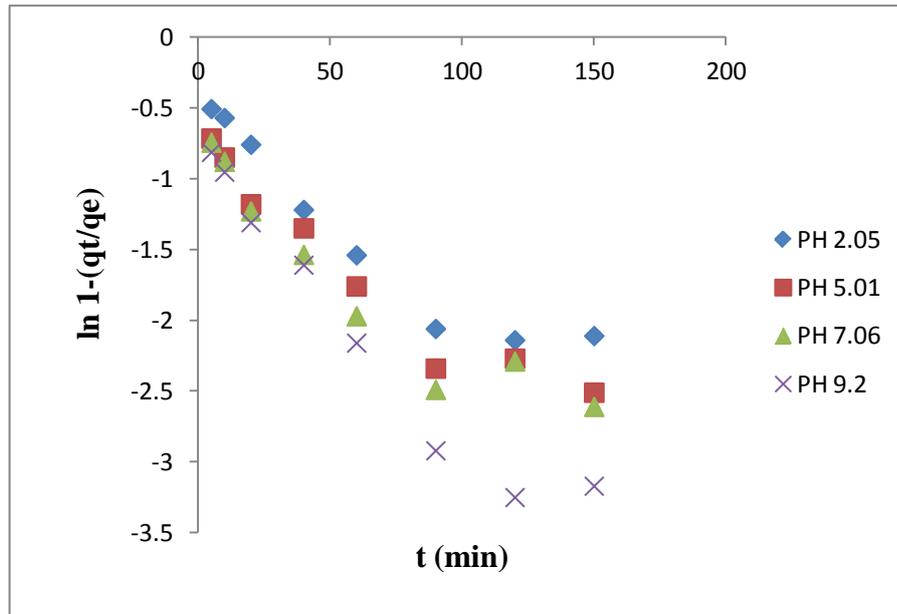


Figure 5.19 Liquid film diffusion plot for the adsorption of MB onto treated pine cone leaves (PLAT) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine leaves dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

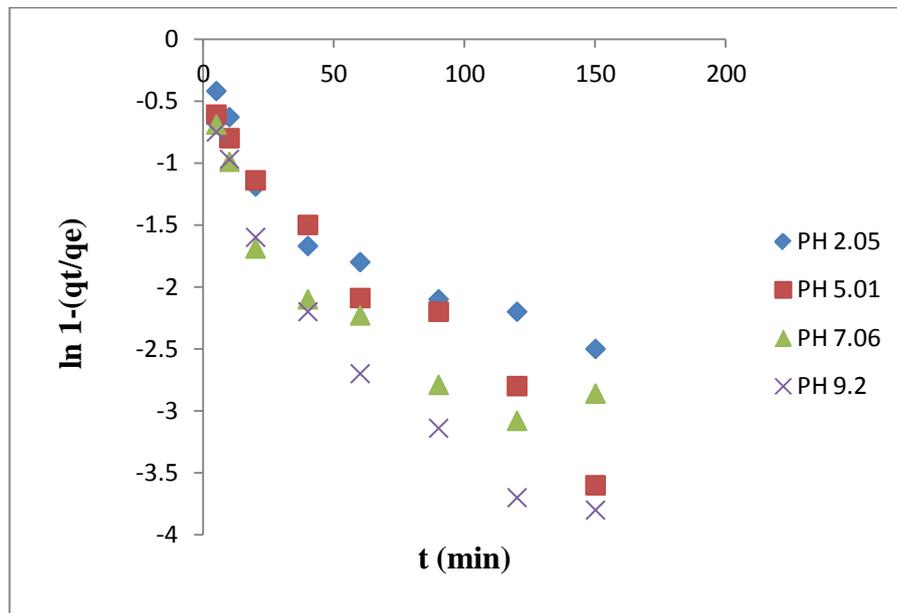


Figure 5.20 Liquid film diffusion plot for the adsorption of MB onto treated pine leaves (PLBT) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine leaves dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

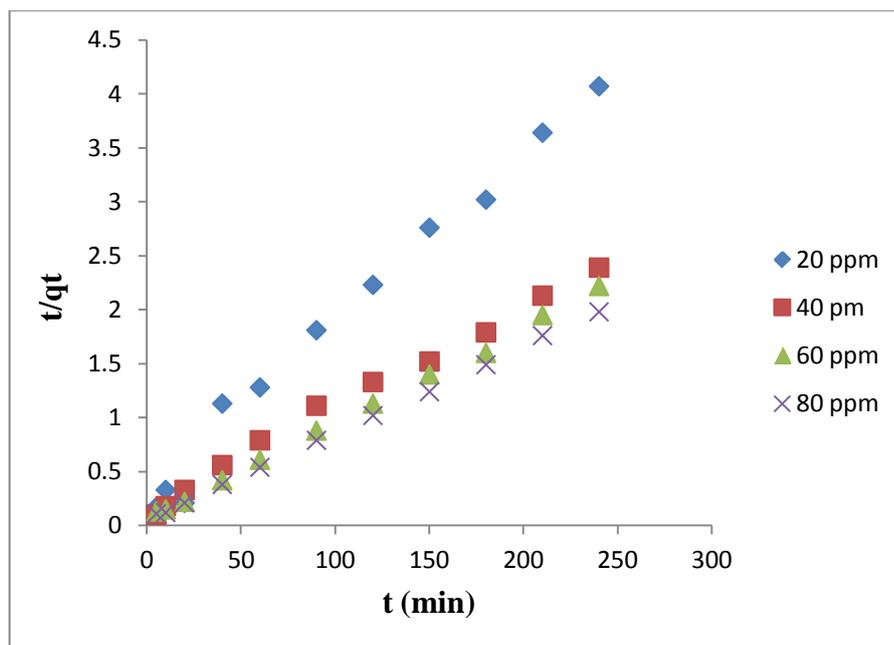


Figure 5.21 Pseudo-second-order plot for the adsorption of MB onto raw pine leaves (PL) materials at different initial MB concentration

(Volume of dye solution=50 ml; temperature= 30°C; pine leaves dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

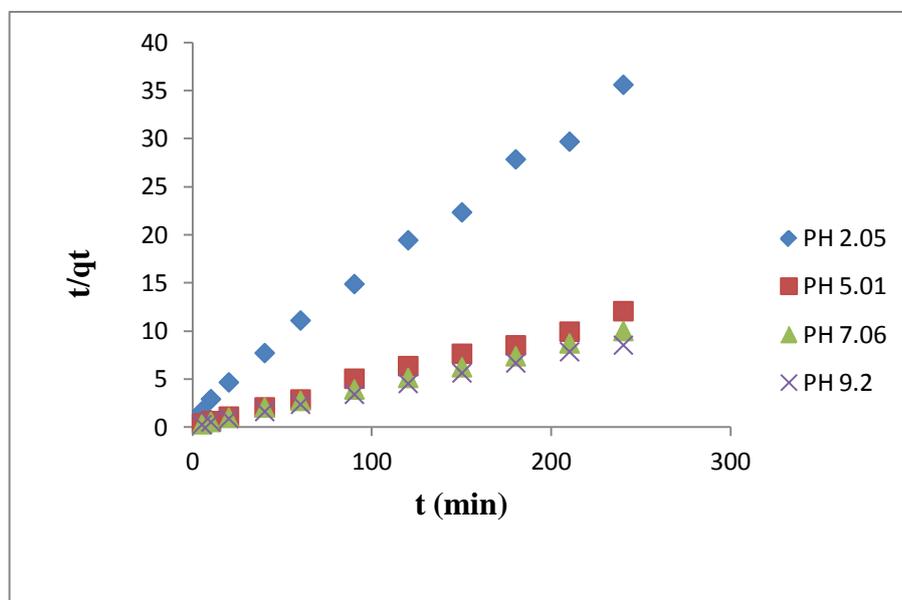


Figure 5.22 Pseudo-second-order plot for the adsorption of MB onto raw pine leaves (PL) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine leaves dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

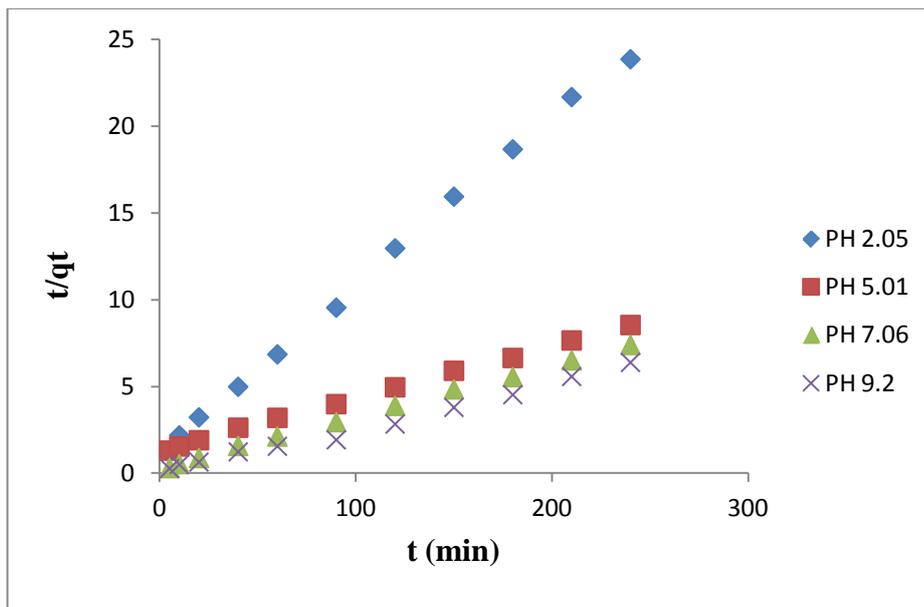


Figure 5.23 Pseudo-second-order plot for the adsorption of MB onto treated pine leaves (PLAT) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine leaves dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

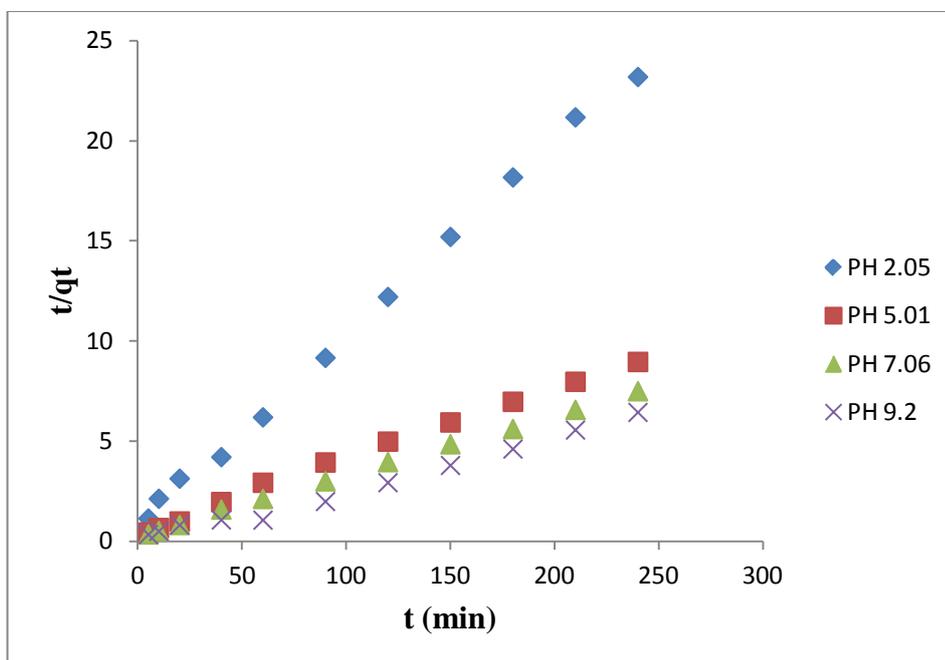


Figure 5.24 Pseudo-second-order plot for the adsorption of MB onto treated pine leaves (PLBT) materials at different solution pH

(Volume of dye solution=50 ml; temperature= 30°C; pine leaves dosage 15mg; pH=9.2; agitation speed 150 rpm; time 240 min)

**Table 5.2** Pseudo-first -order kinetic parameters for adsorption of MB on pine leaves and modified pine leaves

<i>Pseudo-first-order kinetic parameters Model</i>					
<i>Parameters</i>	<i>q<sub>e</sub> (mg/g) experimental</i>	<i>q<sub>e</sub> (mg/g) calculated</i>	<i>K<sub>1</sub> (min<sup>-1</sup>)</i>	<i>R<sup>2</sup></i>	<i>x<sup>2</sup></i>
<i>Initial dye Conc.(ppm)</i>					
<i>20</i>	58.96	35.36	0.0165	0.9804	0.3421
<i>40</i>	100.4	59.48	0.0094	0.9137	0.3586
<i>60</i>	107.96	43.84	0.0089	0.9610	0.3365
<i>80</i>	121.27	47.63	0.008	0.8389	0.3752
<i>Initial pH</i>					
<i>2.05</i>	6.74	3.86	0.0199	0.7767	0.3985
<i>5.01</i>	23.81	10.3	0.0179	0.9495	0.3255
<i>7.06</i>	23.94	8.43	0.0216	0.9724	0.3125
<i>9.2</i>	26.81	7.85	0.0122	0.7031	0.3985
<i>Temperature (°C)</i>					
<i>30</i>	26.11	16.12	0.0202	0.8206	0.3852
<i>40</i>	28.33	15.63	0.0212	0.8413	0.3652
<i>50</i>	29.36	16.67	0.0223	0.8578	0.3699
<i>60</i>	30.29	14.45	0.0205	0.8506	0.3854
<i>salt conc.mg NaCl</i>					
<i>50</i>	22.31	9.49	0.0160	0.8208	0.3865
<i>100</i>	19.91	12.83	0.0302	0.9060	0.3421
<i>150</i>	17.92	12.33	0.0209	0.9208	0.3301
<i>200</i>	16.33	14.59	0.0254	0.9572	0.3322
<i>Modified pine leaves PLAT- pH</i>					
<i>2.05</i>	11.38	6.42	0.0188	0.8368	0.3658
<i>5.01</i>	27.83	10.26	0.0148	0.8055	0.3698
<i>7.06</i>	29.72	12.58	0.0177	0.8571	0.3789
<i>9.2</i>	31.72	14.15	0.0175	0.8425	0.3888
<i>Modified pine leaves PLBT- pH</i>					
<i>2.05</i>	9.37	3.49	0.0160	0.8208	0.3985
<i>5.01</i>	25.81	10.83	0.0302	0.9860	0.3011
<i>7.06</i>	26.94	11.33	0.0209	0.8908	0.3965
<i>9.2</i>	27.51	12.59	0.0254	0.8872	0.3666

**Table 5.3** Pseudo- second-order kinetic parameters for adsorption of MB on pine leaves and modified pine leaves

<i>Pseudo-second-order kinetic parameters Model</i>						
<i>Parameters</i>	<i>q<sub>e</sub> (mg/g) experimental</i>	<i>q<sub>e</sub> (mg/g) calculated</i>	<i>K<sub>2</sub> (mg/g min)</i>	<i>h</i>	<i>R<sup>2</sup></i>	<i>x<sup>2</sup></i>
<i>Initial dye Conc.(ppm)</i>						
<i>20</i>	58.96	60.61	0.0011	5.14	0.9868	0.0856
<i>40</i>	100.4	106.38	0.0012	6.79	0.9935	0.0856
<i>60</i>	107.96	112.36	0.0014	15.15	0.9988	0.0901
<i>80</i>	121.27	125.00	0.0006	17.18	0.9997	0.0788
<i>Initial pH</i>						
<i>2.05</i>	6.74	7.17	0.0101	0.52	0.9957	0.0799
<i>5.01</i>	23.81	24.45	0.0049	2.93	0.9989	0.0896
<i>7.06</i>	23.94	24.75	0.0066	4.04	0.9991	0.0777
<i>9.2</i>	26.81	27.32	0.0083	6.19	0.9999	0.0776
<i>Temperature (°C)</i>						
<i>30</i>	26.11	27.68	0.0033	3.52	0.9992	0.0785
<i>40</i>	28.33	29.11	0.0033	3.62	0.9990	0.0794
<i>50</i>	29.36	31.22	0.0034	3.75	0.9993	0.0774
<i>60</i>	30.29	31.52	0.0037	4.08	0.9995	0.0771
<i>salt conc.mg NaCl</i>						
<i>50</i>	22.31	22.73	0.0047	2.43	0.9972	0.0784
<i>100</i>	19.91	20.98	0.0047	2.27	0.9989	0.0774
<i>150</i>	17.92	18.96	0.0036	1.58	0.9986	0.0764
<i>200</i>	16.33	16.92	0.0025	1.09	0.9997	0.0722
<i>Modified pine leaves PLAT- pH</i>						
<i>2.05</i>	11.38	12.23	0.0101	0.26	0.9989	0.0781
<i>5.01</i>	27.83	26.45	0.0049	1.98	0.9992	0.0769
<i>7.06</i>	29.72	29.75	0.0066	2.87	0.9997	0.0758
<i>9.2</i>	31.72	30.99	0.0083	4.75	0.9992	0.0761
<i>Modified pine leaves PLBT- pH</i>						
<i>2.05</i>	9.37	8.57	0.0101	0.35	0.9972	0.0745
<i>5.01</i>	25.81	24.45	0.0049	2.56	0.9989	0.0777
<i>7.06</i>	26.94	25.75	0.0066	3.23	0.9986	0.0795
<i>9.2</i>	27.51	27.22	0.0083	5.22	0.9997	0.0769

**Table 5.4** Intraparticle Diffusion Model kinetic parameters for adsorption of MB on pine leaves and modified pine leaves

<i>Intraparticle Diffusion Model</i>					
<i>Parameters</i>	<i>q<sub>e</sub> (mg/g) experimental</i>	<i>q<sub>e</sub> (mg/g) calculated</i>	<i>K<sub>id</sub> (min<sup>-1</sup>)</i>	<i>R<sup>2</sup></i>	<i>x<sup>2</sup></i>
<i>Initial dye Conc.(ppm)</i>					
<i>20</i>	58.96	40.25	2.5545	0.9522	0.3111
<i>40</i>	100.4	89.25	4.0622	0.9710	0.3101
<i>60</i>	107.96	52.36	3.9767	0.6892	0.4111
<i>80</i>	121.27	45.21	4.3666	0.6982	0.4001
<i>Initial pH</i>					
<i>2.05</i>	6.74	4.99	0.2898	0.9225	0.3099
<i>5.01</i>	23.81	13.25	0.7675	0.8788	0.3895
<i>7.06</i>	23.94	10.95	0.6265	0.8876	0.3652
<i>9.2</i>	26.81	9.36	0.6863	0.7882	0.3785
<i>Temperature (°C)</i>					
<i>30</i>	26.11	18.02	1.1741	0.8210	0.3852
<i>40</i>	28.33	17.01	1.1591	0.8385	0.3758
<i>50</i>	29.36	18.66	1.1456	0.8352	0.3856
<i>60</i>	30.29	17.25	1.1221	0.8236	0.3215
<i>salt conc.mg NaCl</i>					
<i>50</i>	22.31	9.99	0.8182	0.8542	0.3889
<i>100</i>	19.91	14.05	0.8359	0.8578	0.3915
<i>150</i>	17.92	15.02	0.8629	0.9135	0.3358
<i>200</i>	16.33	13.02	0.9584	0.9282	0.3232
<i>Modified pine leaves PLAT- pH</i>					
<i>2.05</i>	11.38	5.69	0.2525	0.7966	0.3985
<i>5.01</i>	27.83	9.89	0.7221	0.7911	0.3898
<i>7.06</i>	29.72	11.87	0.5788	0.8698	0.3859
<i>9.2</i>	31.72	13.99	0.6253	0.7999	0.3875
<i>Modified pine leaves PLBT- pH</i>					
<i>2.05</i>	9.37	4.52	0.2885	0.8212	0.3698
<i>5.01</i>	25.81	12.01	0.7501	0.8888	0.3888
<i>7.06</i>	26.94	13.11	0.6211	0.7999	0.3911
<i>9.2</i>	27.51	14.89	0.6422	0.8877	0.3859

**Table 5.5** Liquid Film Diffusion Model kinetic parameters for adsorption of MB on pine leaves and modified pine leaves

<i>Parameters</i>	<i>Liquid Film Diffusion Model</i>				
	<i>q<sub>e</sub> (mg/g) experimental</i>	<i>q<sub>e</sub> (mg/g) calculated</i>	<i>K<sub>fd</sub> (min<sup>-1</sup>)</i>	<i>R<sup>2</sup></i>	<i>x<sup>2</sup></i>
<i>Initial dye Conc.(ppm)</i>					
<i>20</i>	58.96	50.55	0.0134	0.9694	0.2969
<i>40</i>	100.4	62.35	0.0184	0.8849	0.3211
<i>60</i>	107.96	90.85	0.0245	0.9552	0.2985
<i>80</i>	121.27	98.22	0.0272	0.9374	0.2154
<i>Initial pH</i>					
<i>2.05</i>	6.74	5.66	0.0222	0.9848	0.2136
<i>5.01</i>	23.81	20.59	0.0181	0.9683	0.2111
<i>7.06</i>	23.94	21.01	0.0173	0.9664	0.2101
<i>9.2</i>	26.81	23.69	0.0261	0.9651	0.2114
<i>Temperature (°C)</i>					
<i>30</i>	26.11	13.36	0.0151	0.8936	0.3126
<i>40</i>	28.33	19.96	0.0163	0.9160	0.2986
<i>50</i>	29.36	23.69	0.0183	0.9480	0.2314
<i>60</i>	30.29	26.15	0.0202	0.9549	0.2412
<i>salt conc.mg NaCl</i>					
<i>50</i>	22.31	19.63	0.0362	0.9512	0.2021
<i>100</i>	19.91	17.98	0.0337	0.9910	0.2001
<i>150</i>	17.92	15.12	0.0191	0.9824	0.1999
<i>200</i>	16.33	14.25	0.0178	0.9681	0.2118
<i>Modified pine leaves PLAT- pH</i>					
<i>2.05</i>	11.38	5.98	0.0198	0.8777	0.3564
<i>5.01</i>	27.83	12.58	0.0144	0.8654	0.3259
<i>7.06</i>	29.72	14.58	0.0123	0.8698	0.3487
<i>9.2</i>	31.72	15.75	0.0111	0.8852	0.3852
<i>Modified pine leaves PLBT- pH</i>					
<i>2.05</i>	9.37	4.21	0.0201	0.8711	0.3549
<i>5.01</i>	25.81	11.98	0.0156	0.8632	0.3469
<i>7.06</i>	26.94	13.25	0.0163	0.8897	0.3569
<i>9.2</i>	27.51	13.88	0.0135	0.8699	0.3648

The values of the half-adsorption time of the dye ( $t^{1/2}$ ) for the methylene blue –pine leaves system estimated from equation (4.7) are 7.51 min, 7.68 min, 11.95 min, and 16.58 min for an initial concentration range of 20, 40, 60 and 80 ppm, respectively.

### 5.5.1 Adsorption Mechanism

The most generally used technique for identifying the mechanism involved in the sorption process is given by fitting the experimental data to intra-particle diffusion. Plot of  $q_t$  vs.  $t^{0.5}$  is shown in Fig (5.25) for pine leaves system at different initial dye concentration. Fig (5.25) provides that adsorption plots are not linear over the entire time range and can be separated into two or three linear regions which confirm the multistage nature of adsorption. This figure represented the two different stages viz external mass transfer followed by intra-particle diffusion, signified that the dye were transported to the external surface of the pine leaves through film diffusion and its rate was very fast. After that MB dye molecules were entered into the pine leaves adsorbent by intra-particle diffusion through pores. Generally, when adsorption steps are not dependent of one another, the plot of  $q_t$  against  $t^{0.5}$  showed two or more intercepting lines depending on the actual mechanism (Weber and Morris, 1963). Moreover, from fig (5.25) conclusion can be made that none of the plot gives linear straight line segment passing through the origin  $(0, 0)$ . This indicates that the intra - particle diffusion is involved in the adsorption process but the only rate-controlling step (Sen et al., 2011). As the extrapolated curves did not pass through the origin, this indicated that film diffusion and intra-particle diffusion occurred simultaneously. The results show that the adsorption mechanism is as the same compared with the system of pine cone.

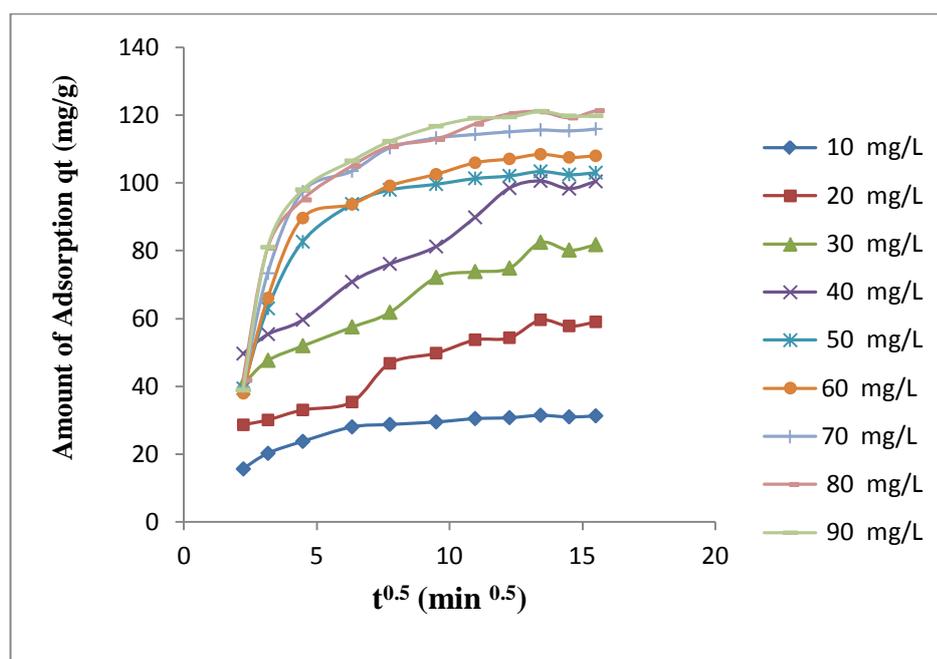


Figure 5.25 Intra-particle diffusion model on different initial dye concentration

The surface-weighted mean diameter of pine leaves particles of 95.68  $\mu\text{m}$  (radius=47.84  $\mu\text{m}$ =47.84 $\times$ 0.0001 cm=0.004784 cm) has been utilised, and the diffusion coefficients, D values, were calculated from equation (4.8) were 1.52E-9, 2.49E-9, 3.57E-9, 5.11E-9  $\text{cm}^2/\text{s}$  for an initial dye concentration of 20, 30, 40 and 50 ppm, respectively, which raises with change in initial dye concentration. This result agrees with those of Dogan et al. (2004), Haimour and Sayed (1997) and McKay and Allen (1983). This was attributed to the larger molecular size of the present systems, the factor that slows down in diffusion rate (Dogan et al., 2004).

As the same trend for the pine cone and the pine leaves, but the diffusion coefficients obtained from pine cone system was higher than the diffusion coefficients found from pine leaves, but as the same trend.

## 5.6 Adsorption Equilibrium Isotherm Models

The analysis of equilibrium adsorption data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes (Dawood and Sen, 2012b). The theory of Langmuir and Freundlich isotherm models is presented in section 2.5. The applicability of the isotherm equation is compared by the linear correlation coefficients,  $R^2$ .

Langmuir isotherm fitting for raw and treated pine leaves biomass adsorbent are shown in figure (5.26a-5.26 c). The maximum monolayer adsorption capacity of pine cone,  $q_m$ , and constant related to the binding energy of the sorption system,  $K_a$ , are calculated from the slope and intercept from these plots. The maximum monolayer adsorption capacity  $q_m$  for raw pine leaves PL was 126.58 mg/g and the constant related to the binding energy of the sorption system,  $K_a$  was 0.3435, whereas, the maximum monolayer adsorption capacity for treated pine leaves,  $q_m$ , and constant related to the binding energy of the sorption system,  $K_a$ , for modified pine leaves PLAT and PLBT are (140.84 and 0.239) and (131.58 and .3127) respectively. The results also showed that the maximum monolayer adsorption capacity for pine cone was high compared to the maximum monolayer adsorption capacity from the pine leaves.

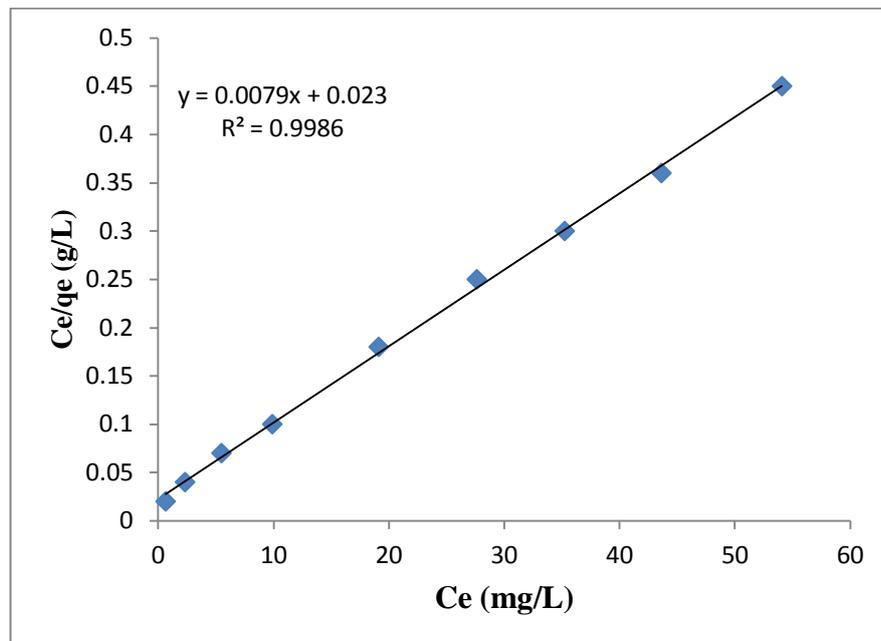


Figure 5.26a Langmuir plot: amount of adsorbent (pine leaves PL)

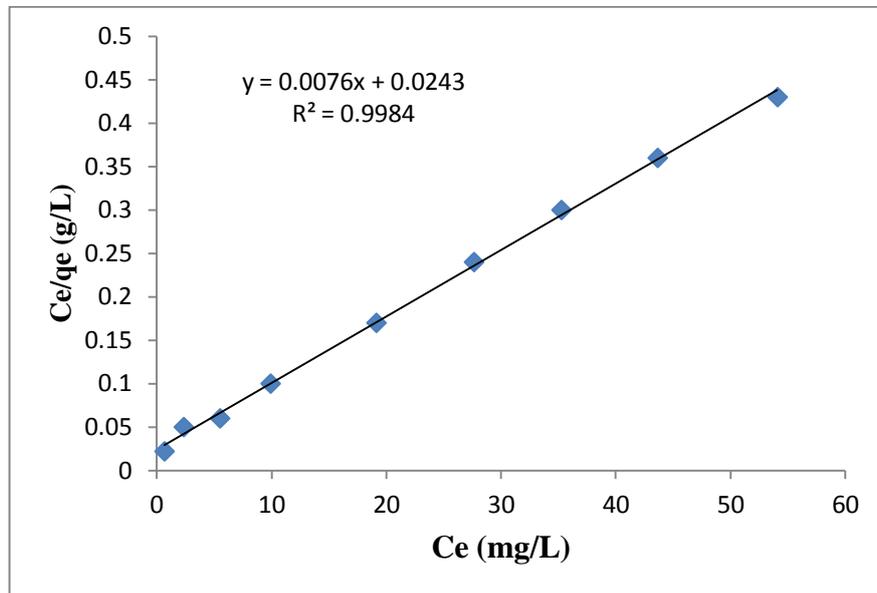


Figure 5.26b Langmuir plot: amount of adsorbent (modified pine leaves PLBT)

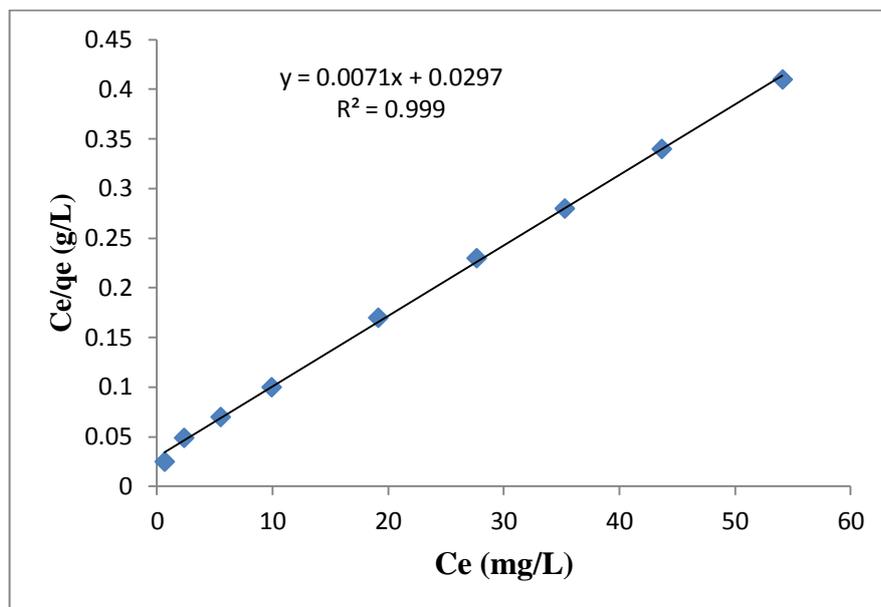


Figure 5.26c Langmuir plot: amount of adsorbent (modified pine leaves PLAT)

Figures (5.27a-5.27c) show Freundlich isotherm fittings for raw and modified pine leaves biomass adsorbent. Freundlich constants, i.e. adsorption capacity,  $K_f$ , and rate of adsorption,  $n$ , are calculated from these plots. For raw pine leaves the adsorption capacity,  $K_f$ , and rate of adsorption,  $n$ , are 43.18 and 3.5 respectively. Whereas the adsorption capacity  $K_f$ , and the rate of adsorption,  $n$  for modified pine leaves PLAT and PLBT, were (40.36 and 3.27) and (38.81 and 3.15) respectively. The value of 'n' is large than one which indicates the favourable native of adsorption and a physical process.

The equilibrium isotherm studies for the pine cone systems and pine leaves systems show that the MB dye adsorption on raw and treated pine cone was good represented by both the Langmuir and the Freundlich isotherm models, whereas, the adsorption of MB dye on raw and modified pine leaves was better represented by the Langmuir isotherm model rather than the Freundlich isotherm model.

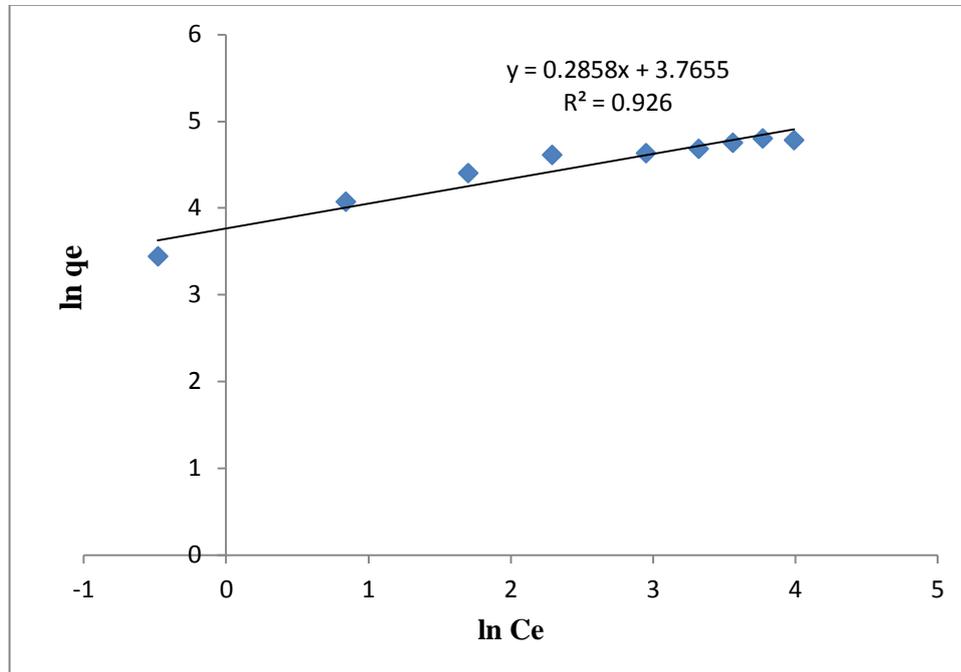


Figure 5.27a Freundlich plot: amount of adsorbent (pine leaves PL)

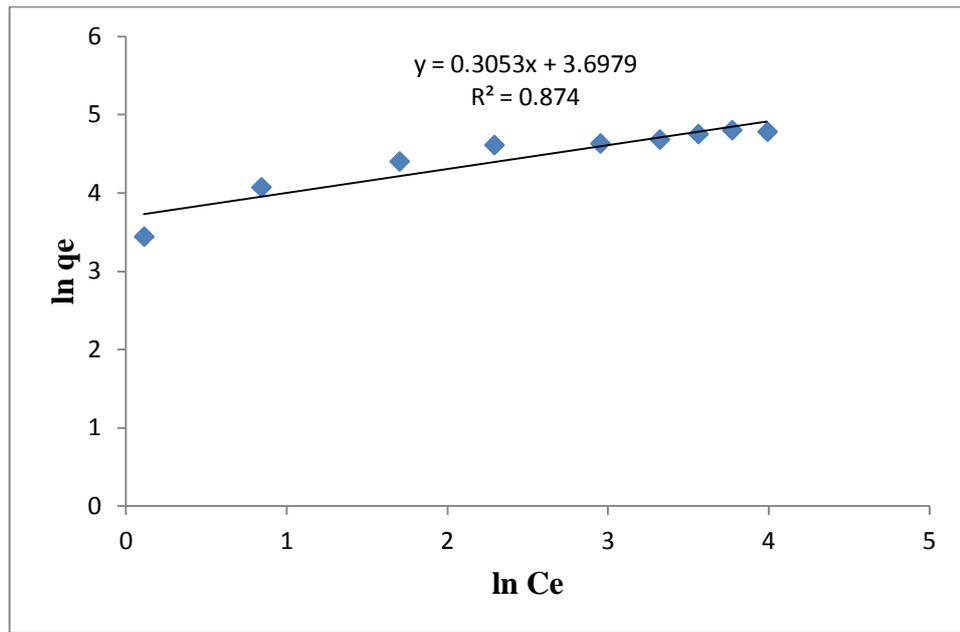


Figure 5.27b Freundlich plot: amount of adsorbent (treated pine leaves PLBT)

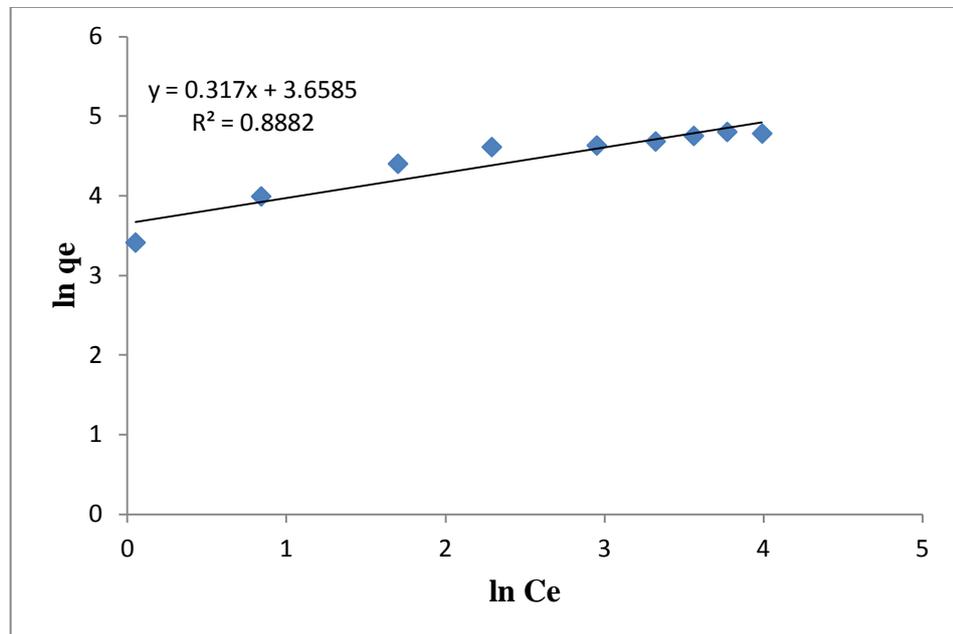


Figure 5.27c Freundlich plot: amount of adsorbent (treated pine leaves PLAT)

The separation factor,  $R_L$  has been determined from Langmuir plot for raw pine leaves as per the equation 4.9

The calculated separation factor,  $R_L$  values are 0.1271, 0.0884, 0.0678, 0.0550, 0.0462, 0.0399, 0.0351, and 0.0313 at initial dye concentration of 20, 30, 40, 50, 60, 70, 80 and 90 ppm, respectively. These  $R_L$  values indicate favourable adsorption as it lies in  $0 < R_L < 1$ . The best fit of equilibrium data in the Langmuir isotherm expression confirms the monolayer coverage of MB onto pine leaves particles. From the results the separation factor,  $R_L$  values for pine cone were more than the values from pine leaves. The adsorption capacity of other agricultural natural adsorbents to uptake of cationic dye reported as 67.6 mg/g of canola hull (Mahmoode et al., 2011), 114.9 mg/g of soy meal hull, 37.4 mg/g of pine cone (Mahmoode et al., 2011). Therefore, present results on the capacity of pine leaves for the removal of MB is comparable and also a better adsorbent. Table (5.6) presented the comparative results of MB adsorption by different adsorbents. It was found that similar to pine cone, pine leaves is also a good adsorbent for MB dye removal.

**Table 5.6** Adsorption capacities of different adsorbents for removal of Methylene Blue dye

<i>Adsorbent</i>	<i>Adsorption capacity (<math>q_m</math> (mg/g))</i>	<i>Sources</i>
Peanut hull	68.06	(Gong et al., 2005)
Banana peel	20.8	(Annadurai et al., 2002)
Pineapple stem	119.05	(Hameed et al., 2009)
Coffee husk	90.1	(Oliveira et al., 2008)
Walnut sawdust	59.17	(Ferrero, 2007)
Rice husk	40.59	(Vadivelan and Kumar, 2005)
Egg shell	16.43	(Tsai et al., 2006)
Orange Peel	18.6	(Annadurai et al., 2002)
Yellow passion fruit	44.7	(Pavan et al., 2008)
Coconut husk	99	(Oladoja et al., 2008)
Algal waste	104	(Vilar et al., 2007)
Raw pine cone	129.87	<b>Present Study</b>
Modified pine cone PC1	142.86	<b>Present Study</b>
Modified pine cone PC2	135.13	<b>Present Study</b>
Raw pine leaves PL	126.58	<b>Present Study</b>
Modified pine leaves PLAT	140.84	<b>Present Study</b>
Modified pine leaves PLBT	131.58	<b>Present Study</b>

## 5.7 Design of Single-Stage Batch Adsorber from Isotherm

### Data

Langmuir adsorption isotherm data have been used to design a single-stage batch adsorption system as per method mentioned in section 4.7.

A series of plots derived from Eq. 4.11 between different solution volumes and the predicted amount of pine leaves particles required to remove dye solutions of initial concentrations of 100 ppm for 95%, 85%, 75%, 65% and 55% dye removal is shown in figure (5.28).

Fig 5.28 and fig 4.30 for the volume of solution treated against mass of pine leaves and pine cone respectively showed that the mass needed from pine cone was less than the mass needed from pine leaves, this mean pine cone is more favourable compared to pine leaves.

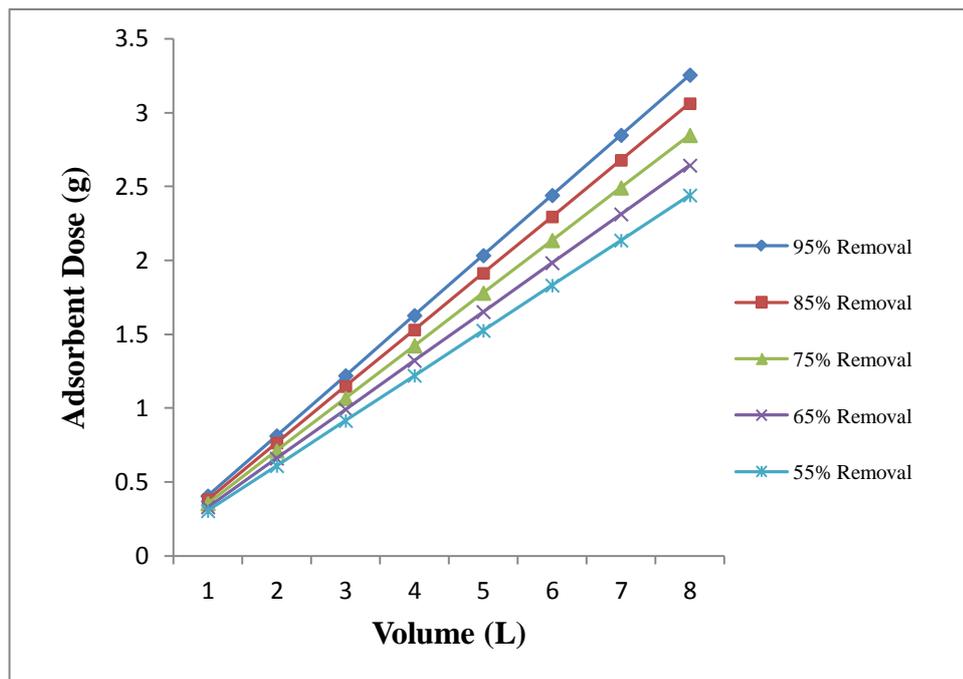


Figure 5.28 Volume of solution treated (litres) against adsorbent mass (grams)

## 5.8 Desorption Study

A desorption study is important for the determination of the amount of dye that will be possibly washed out when it is exposed to the natural erosion agent such as water. The desorption percentages of MB dye loaded on raw and treated pine leaves are shown in Figure (5.29) at different pH values of 3, 5, 7 and 9. It was found that the percentage desorption was decrease with increase pH of solution figure (5.29).

The percentages of MB dye desorbed out at the exposure time were 70.22, 75.26 and 72.85% at pH 3 for PL, PLAT, and PLBT respectively, meanwhile, for pH of 5 the percentages desorption of MB dye were 53.55, 59.25 and 56.25% for PL, PLAT, and PLBT respectively, whereas for pH at 7 the percentages desorption of MB dye were 39.48, 44.92 and 42.32%, and 27.51, 34.58 and 30.78 for PL, PLAT, and PLBT respectively at pH 9. It is clear that the percentage of desorption is decrease with increasing initial solution pH. This suggests that as the pH of solution decreases the net positive charge on adsorbent surface decreases.

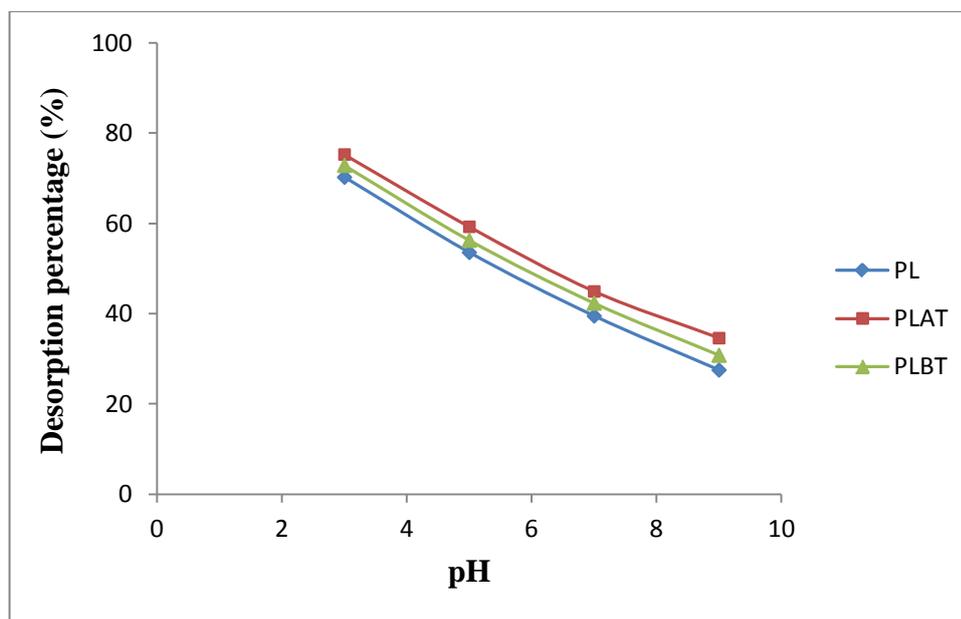


Figure 5.29 Desorption of raw and treated pine leaves loaded MB at different pH solution

(Shaking speed: 150 rpm; Contact time: 5 hrs; dosage: 1 g L<sup>-1</sup>; Temperature: 30 °C)

## 5.9 Summary

The effectiveness of raw and treated pine leaves biomass, PL, PLAT and PLBT for the removal of Methylene Blue MB from its aqueous solution and was concluded experimentally, the following conclusion can be made from this study:

- The effectiveness of raw and modified pine leaves, PL, PLAT and PLBT for removal of methylene blue was studied under various experimental conditions such as initial dye concentration, contact time, solution pH, salt concentration and system temperature.
- In batch study, the kinetic experiment revealed that adsorption of dye was rapid at initial stage followed by a slower phase where equilibrium removal was achieved.
- The amount of methylene blue dye adsorption was found to increase with increase in initial dye concentration, contact time, amount of adsorbent, agitation speed, system temperature, and solution pH but decrease with increase in salt concentration.
- It was also observed that the adsorption was pH dependent and the maximum adsorption of 126.58 mg/g occurred at pH of 9.2 for an initial dye concentration of 10 ppm by raw pine leaves, whereas for treated pine leaves the maximum adsorption of 140.84 and 131.58 mg/g for PLAT and PLBT respectively at the same experimental conditions, whereas the maximum monolayer adsorption capacity were 129.87, 142.25 and 139.23 mg/g by raw and treated pine cone PC, PC1, PC2 respectively.
- Overall, the kinetic studies showed that the MB dye adsorption process followed pseudo-second-order kinetics models and the adsorption was controlled by chemisorptions process, and the pine cone study gives the same trend.

- Langmuir model gives a better fit with experimental data, but in the pine cone the Langmuir and Freundlich equations both are applicable to describe the adsorption within the same conditions
- The thermodynamic analysis indicates that system was endothermic and physical processes in nature. In contrast, pine cone study of chapter 4 indicated that adsorption was exothermic.
- A single stage batch adsorber design for the methylene blue MB adsorption onto pine leaves have been presented based on the Langmuir isotherm model equation
- Desorption experiments also showed that desorption of methylene blue decreased as the pH increased.

## **CHAPTER 6**

# **FIXED BED DYNAMIC COLUMN ADSORPTION STUDY OF METHYLENE BLUE (MB) ONTO PINE CONE BIOMASS**

## 6.1 Introduction

Both raw pine cone and leaves and chemically treated pine cone and leaves were used as adsorbents to remove MB from its aqueous solution in a batch mode (Yagub et al., 2012, Yagub et al., 2013). It was found that there was higher adsorption capacity for pine cone biomass and it was a function of various physio-chemical process parameters such as initial MB concentration, solution pH, adsorbent dose, contact time, and temperature. There are many reported results on the removal of MB from aqueous solution by a wide range of adsorbents which has been reviewed by (Crini, 2006, Rafatullah et al., 2010, Ali et al., 2012) and (Yagub et al., 2013). However, most of the earlier investigations on MB adsorption were restricted to batch equilibrium studies. The adsorption capacity of various adsorbents obtained from batch equilibrium experiments is useful to determine the effectiveness of adsorbents under various physio-chemical conditions. It also provides the fundamental information of dye adsorption mechanism and kinetic parameters and to determine the optimum value of various process parameters. However the data may not be applicable to most of the treatment system (such as column operations) where contact time is not sufficient for the attainment of equilibrium (Agrawal and Bajpai, 2011, Sadaf and Bhatti, 2013b). Moreover, batch experimental data are often not easy to apply directly to fixed bed column performance because isotherms are unable to give accurate data for scale up since a flow column is not at equilibrium. Hence there is a need to perform adsorption study using fixed bed columns. This fixed bed column with adsorbents offer easy continuous operation and scale up which is an important aspect of adsorption process. But lesser number of results on column study compared to vast batch adsorption study on inorganic/organic removal by various adsorbents were reported which is also mentioned in recent review article by Yagub et al 2013. Therefore it is imperative to describe dynamic behaviour in a fixed bed column condition. The major characteristics of fixed bed adsorption are the history of effluent concentration (Tien, 1994). These concentration-time curves (or their equivalent) are commonly referred to as the breakthrough curves (BTC) and the time at which the effluent concentration reaches the threshold value is called the breakthrough time. The rational design of adsorption systems is based on accurate predictions of breakthrough curves (BTC) at specified condition. Despite the usefulness of fixed bed mode, its analysis is usually complex (Nwabanne and

Igbokwe, 2012). The effectiveness of an adsorbent can be obtained from the BTC of effluent concentration where a typical S-shaped breakthrough curve is commonly observed (Cruz-Olivares et al., 2013). Fixed bed operation is influenced by equilibrium (isotherm and capacity), kinetics (diffusion and convection co-efficient) and hydraulic hold up, geometric analysis and mal-distribution) factors (Inglezakis and Pouloupoulos, 2006).

The aim of the present work is to investigate the effects of flow rate, bed depth and MB concentration on adsorption capacity of pine cone biomass in a dynamic fixed-bed column operation. Thomas, Yoon-Nelson, and Bed Depth Service Time (BDST) models were used to analyse the column performance for the removal of MB dye from aqueous solution using pine cone biomass. The results of the parameters obtained with modelling the continuous process can be scaled to an actual industrial column operation (Cruz-Olivares et al., 2013).

## 6.2 Materials and methods

### a) Syntheses of adsorbent and its characterization

Pine cones were collected locally from Curtin University campus, Perth, Western Australia, between April and May 2010, and they prepared for column use the same manner as detailed in section 4.3

### b) Adsorbate and other chemicals

Methylene Blue (MB) was taken as the adsorbate in this study. Preparation of stock solution, adjusted the solution pH and the plot of calibration curve were mentioned in section 4.3.b.

## 6.3 Fixed Bed Adsorption Column Design and Experimental Procedure

A fixed bed adsorption column was used to evaluate dynamic behaviour of dye MB removal by pine cone biomass. The column studies were carried out using a Perspex glass column of 2.5 cm internal diameter and 30 cm long and is shown in Figure (6.1). The column was packed with the adsorbent between two supporting layers of pre-equilibrated glass wool as shown in Fig (6.1). Both the ends of the column were connected with circular threaded caps. The column was packed with known quantity of pine cone biomass to obtain a particular bed height. Various packed bed of pine cone packing materials were made by wet packing method as per Sen et al (2002). Influent feed solution was injected into column at a fixed discharge rate by a variable speed peristaltic pump which was placed at the bottom of the vertical column Fig (6.1). The column was operated at room temperature. The bed porosity was measured by the following equation (6.1).

$$\varepsilon = 1 - \frac{m_p}{\rho_p A H} \quad (6.1)$$

where  $\varepsilon$ ,  $H$  and  $A$  are the porosity, height (cm) and cross sectional area (cm<sup>2</sup>) of the bed in Column respectively.  $m_p$  and  $\rho_p$  are the mass (g) and bulk density (g/cm<sup>3</sup>) of pine cone respectively. The initial MB dye concentration used was in the range of (50 mg/L) to (100 mg/L).

At the flow rate was also determined at the exit end of the column so as to get steady state flow conditions in the column. The effluent samples were collected at certain time intervals and concentrations of dye were measured. Sampling of column effluent was done at certain time intervals in order to investigate the breakthrough point or column service time and shape of breakthrough curve (BTC). The effect of inlet flow rate (10, 12 and 15 ml/min), bed height (10, 12, and 15 cm) and initial MB concentration (50, 70, and 100 mg/L) were evaluated using BTC. The Column data were applied to the various dynamic Column performance model and to determine various model parameters and mass transfer adsorption parameters.

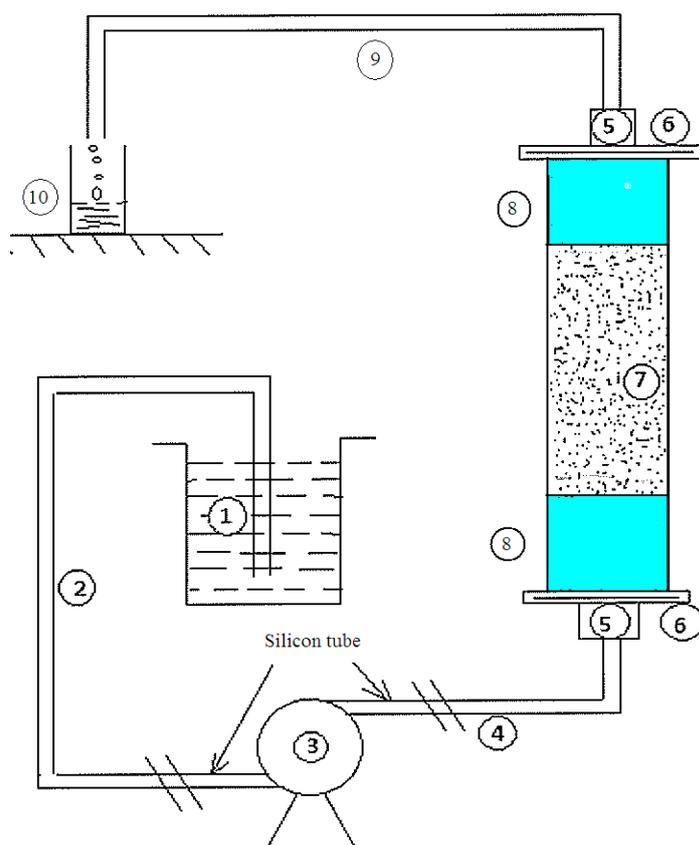


Figure 6.1 Schematic diagram of the column

1. Reservoir
2. Inlet silicon tube
3. Peristaltic Pump
4. Pump outlet silicon tube & Column inlet
5. Nozzles
6. Circular threaded Caps with 60 μm wire mesh
7. Packed Column
8. Glass wool
9. Column outlet plastic tube
10. Effluent collector tubes

## 6.4 Modelling and Column Adsorption Process Analysis

### 6.4.1 Theory of Breakthrough Curve (BTC)

The performance of fixed bed is described through the theory of the breakthrough curve. The time for breakthrough appearance and shape of BTC are very important characteristics for determining the operation and the dynamic response of an adsorption column (Agrawal and Bajpai, 2011, Nwabanne and Igbokwe, 2012). Both the time until the sorbed species are detected in the column effluent (breakthrough point) at a given concentration and the shape of the concentration-time profile or breakthrough curve (BTC) are important characteristics for operation, dynamic response and process design of an adsorption column as they directly affect the feasibility and economics of the adsorption process (Agrawal and Bajpai, 2011). A breakthrough plot (BTC) is usually expressed in terms of adsorbed pollutant concentration,  $C_{ad}$  where  $C_{ad} = \text{inlet pollutant concentration } (C_o) - \text{outlet pollutant concentration } (C_i)$  or normalized concentration defined as the ratio of effluent dye concentration ( $C_i$ ) to the inlet dye concentration ( $C_o$ ) i.e.  $(C_i/C_o)$  as a function of time,  $t$  or volume of effluent for a given bed height (Aksu et al., 2007). A typical BTC is shown in Fig (6.2).

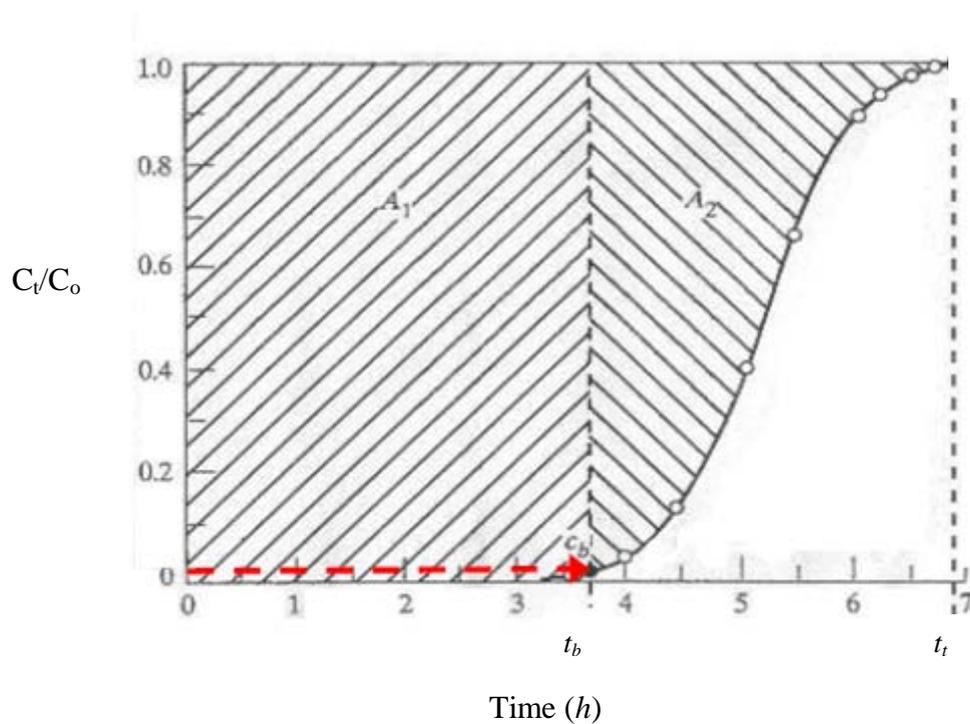


Figure 6.2 Typical Breakthrough Curve

Time equivalent to total or Stoichiometric Capacity is:

$$t_t = \int_{t=0}^{t=\infty} \left(1 - \frac{c_t}{c_0}\right) dt = A_1 + A_2 \quad (6.2)$$

Time equivalent to usable capacity is:

$$t_u = \int_{t=0}^{t_b} \left(1 - \frac{c_t}{c_0}\right) dt = A_1 \quad (6.3)$$

Usable capacity of bed up to the breakthrough point time,  $t_b$

$$t_u \approx t_b$$

Area under the curve gives,  $\int_{t=0}^{t=\infty} \left(1 - \frac{c_t}{c_0}\right) dt$ ,  $t_t$  value (total time), whereas area under curve  $\int_{t=0}^{t_b} \left(1 - \frac{c_t}{c_0}\right) dt$  gives,  $t_u$  value  $t_u/t_t$  is the fraction of the total bed capacity or length utilized up to break point. Area under the curve can be determined either graphically or by numerical integration.

Also the unused bed length  $H_{UNB}$  or Mass Transfer Zone (MTZ) can be calculated as:

$$H_{UNB} = (1 - t_u/t_t) H_T = (1 - t_b/t_t) H_T \quad (6.4)$$

where  $H_T$  = Total bed height

$$MTZ = H_{UNB} \quad (6.5)$$

The used bed length  $H_B$  (up to the break point) can be calculated as:

$$H_B = (t_b/t_t) H_T \quad (6.6)$$

Whenever BTC is expressed, the following parameter calculations are applicable.

Effluent volume ( $V_{\text{eff}}$ ) can be estimated as follows:

$$V_{\text{eff}} = Q t_{\text{total}} \quad (6.7)$$

where  $Q$  and  $t_{\text{total}}$  are the volumetric flow rate (mL/min) and the total flow time (min) respectively.

The area under the breakthrough curve ( $A$ ) obtained by integrating the adsorbed concentration  $C_t/C_o$  (mg/L) versus  $t$  (min) the plot can be used to find the total adsorbed MB quantity (maximum column capacity). The total adsorbed MB quantity ( $q_{\text{total}}$ ) in the column for a given feed concentration and flow rate is determined as (Aksu et al., 2007):

$$q_{\text{total}} = QA/1000 = (QC_o/1000) \int_{t=0}^{t=t_{\text{total}}} \left( \frac{c_t}{c_o} \right) dt \quad (6.8)$$

The total amount of MB dye sent to column ( $m_{\text{total}}$ ) is estimated as:

$$m_{\text{total}} = C_o Q t_{\text{total}} / 1000 \quad (6.9)$$

The total percent removal of MB dye can also be found from the ratio of total adsorbed quantity ( $q_{\text{total}}$ ) to the total amount sent to column ( $m_{\text{total}}$ ) as:

$$\% \text{ Removal} = (q_{\text{total}} / m_{\text{total}}) \times 100 \quad (6.10)$$

## 6.4.2 Modelling of Fixed Bed Column Breakthrough

Various kinetic and mass transfer models have been developed to predict the dynamic behaviour of the column. These models have been utilized to determine breakthrough performance and also to calculate the column kinetic parameters and adsorption capacity of the fixed bed column. These models are as follows:

### 6.4.2.1 Thomas Model

Thomas model has been used by many researchers to study packed bed adsorption kinetics (Aksu and Gönen, 2004, Öztürk and Kavak, 2005, Baral et al., 2009, Ahmad and Hameed, 2010). Thomas model (Thomas, 1944) assumes the Langmuir kinetics of adsorption – desorption and no axial desorption and is derived from the assumption that the rate driving force obeys second order reversible reaction kinetics. The linearized form of the Thomas Model is as follows:

$$\ln \left( \frac{C_0}{C_t} - 1 \right) = \left( \frac{K_{Th} q_0 m}{Q} \right) - \left( \frac{K_{Th} C_0 V}{Q} \right) \quad (6.11)$$

where  $K_{Th}$  is the Thomas rate constant (mL/mg min),  $q_0$  is the equilibrium adsorbate uptake (mg/g),  $m$  is the amount of adsorbent in the column (g),  $C_0$  inlet or initial concentration (mg L<sup>-1</sup>),  $C_t$  effluent phenol concentration (mg L<sup>-1</sup>),  $Q$  is the flow rate (ml min<sup>-1</sup>), and  $V$  is effluent volume (ml).

A linear plot of  $\ln (C_0/C_t - 1)$  vs. time  $t$  will give the Thomas rate constant  $K_{Th}$  and the adsorption capacity of column  $q_0$  from intercept and slope of the plot.

### 6.4.2.2 Yoon-Nelson model

(Yoon and Nelson, 1984) developed a model based on the assumption that the rate of decrease in the probability of adsorption of adsorbate molecule is proportional to the probability of the adsorbate adsorption and the adsorbate breakthrough on the adsorbent. The linearized Yoon-Nelson model for a single component system is expressed as (Hamdaoui, 2006b).

$$\ln \left( \frac{C}{C_0 - C_t} \right) = K_{YN} t - K_{YN} \tau \quad (6.12)$$

where  $K_{YN}$  is the Yoon and Nelson rate constant (min<sup>-1</sup>),  $C_0$  inlet or initial concentration (mg L<sup>-1</sup>),  $C_t$  effluent phenol concentration (mg L<sup>-1</sup>),  $t$  is the breakthrough (sampling) time (min), and  $\tau$  the time required for 50% adsorbate breakthrough (min).

From a linear plot of  $\ln [C_i / (C_o - C_i)]$  against sampling time,  $t$ , values of  $K_{YN}$  and  $\tau$  can be obtained from the intercept and slope of the plot.

#### 6.4.2.3 Bed Depth Service Time (BDST) Model

Bed Depth Service Time (BDST) approach is based on Bohart and Adams (1920) equation and it is a widely used model (El-Kamash, 2008). It gives an idea of the efficiency of the column under constant operating conditions for achieving a desired breakthrough level (Sadaf and Bhatti, 2013b). Service time is the time period for adsorbent that will be able to adsorb a specific amount of pollutant from solution before regeneration is needed. BDST model gives relationship between bed height ( $H_T$ ) and service time ( $t$ ) in terms of process concentrations and other adsorption parameters. A linear relationship between bed height ( $H_T$ ) and service time ( $t$ ) is given by (Sadaf and Bhatti, 2013b).

$$t = \left( \frac{N_o H_T}{C_o U} \right) - \left( \frac{1}{K_o C_o} \right) \ln \left( \frac{C_o}{C_t} - 1 \right) \quad (6.13)$$

where  $C_t$  effluent concentration of solute in the liquid phase (mg/L),  $C_o$  inlet solute concentration (mg/L),  $U$  influent linear velocity (cm/min),  $N_o$  adsorption capacity (mg/L),  $K_o$  rate constant in BDST model (L/mg min),  $t$  = time (min),  $H_T$  = bed height of column (cm).

A plot of  $t$  vs. bed height  $H_T$  should yield a straight line where  $N_o$  and  $K_o$  can be determined. A simplified form of the BDST model is as follows:

$$t = az - b \quad (6.14)$$

where  $a$  is slope  $N_o/C_o U$ , and  $b$  = intercept  $(1/K_o C_o) \ln((C_o/C_t) - 1)$

## 6.5 Results and Discussion

All of the experimental data used to obtain the results of the study of the effect of pine cone are listed in Appendix C1-9.

### 6.5.1 Effect of Initial Flow Rate on MB Dye Adsorption

Flow rate is an important parameter for evaluating the efficiency of adsorbents in a continuous industrial scale packed bed operation. The effect of the flow rate on the adsorption of methylene blue MB dye using the raw pine cone was investigated by varying the flow rate (10, 12 and 15 ml/min) while the bed height and initial MB dye concentration was held constant at 12 cm and at  $70 \text{ mg l}^{-1}$ , respectively. The breakthrough curve of comparative normalized dye concentration ( $C_t/C_0$ ) versus time (min) at different flow rates are shown in figure (6.3).

From the BTCS, it was found that the breakthrough occurred faster with higher flow rate i.e.  $\text{MB}^{2+}$  eluted more rapidly as the velocity is increased. The breakthrough time decreased from 115 to 39 min for the flow rates ranging between 10 and 15 ml/min respectively (Table 6.1). This may be due to the increase in speed of adsorption zone at increased flow rate which resulted in a decrease in the time required to reach the specific breakthrough concentration. Further from Table 6.1, it was observed that the adsorption capacity,  $q_{\text{total}}$  and dye removal percentage of column decreases with increase of flow rate. Similar type of observations was reported by various researchers for different systems (Kahraman et al., 2012, Cruz-Olivares et al., 2013, Sadaf and Bhatti, 2013b). As the velocity increases the rate of mass transfer increases and thereby enhancing the rate of adsorption. As a result early breakthrough occurs at higher flow rates (Sen et al 2002). Further, retention time of dye molecules in the column depends on flow rate and decreases contact time between adsorbent and dye with increasing flow rate. Hence, MB dye molecules do not have sufficient time to penetrate and diffuse deeply into the pores of adsorbents. Therefore, lower adsorption capacity ( $q_{\text{total}}$ ) was obtained at higher flow rate and equilibrium does not take place. This was further supported by unused ( $H_{\text{UNB}}$ ) or used bed (HB) which are presented in Table 6.1. At a lower flow rate, contact time between MB and pine cone was higher resulting in higher removal of MB in column (Table 6.1). This was also supported by mass transfer zone (MTZ) (Table 6.1) or unused bed which increased with increasing flow rate. Overall, Table 6.1 indicates that the packed bed column

gives better performance in the removal of MB at lower solution flow rate, which is not favourable for large effluent treatment systems.

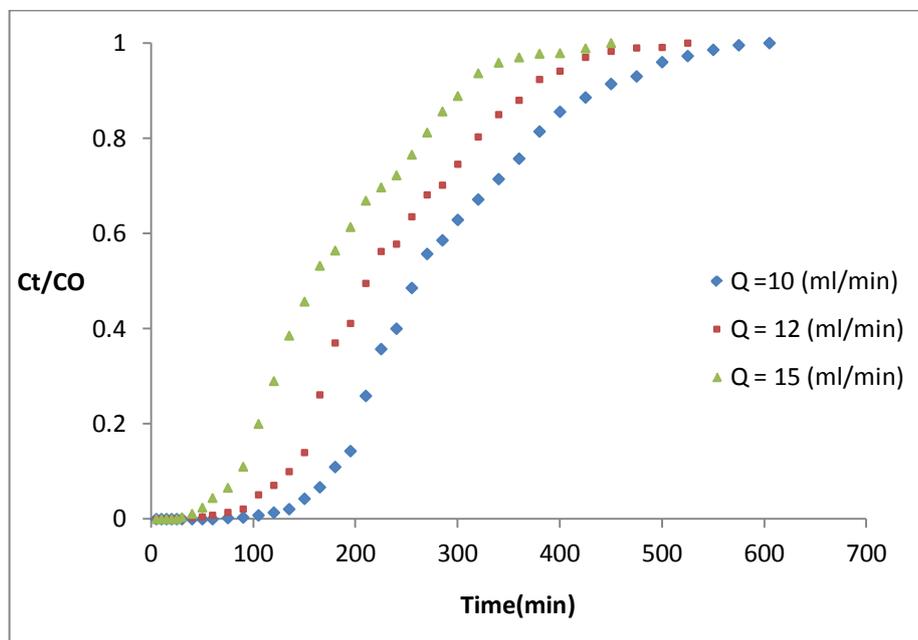


Figure 6.3 Comparison of predicted breakthrough curves of MB dye adsorption on raw pine cone at different flow rates.

(Inlet MB dye concentration = 70 mg/L, bed height = 12 cm, temperature = 25±1 °C)

**Table 6.1** Parameters of breakthrough curves (BTCS) of packed bed column for MB removal by pine cone

<b>Q</b> (ml/min)	<b>t<sub>b</sub></b> (min)	<b>V<sub>eff</sub></b> (mL)	<b>t<sub>total</sub></b> (min)	<b>m<sub>total</sub></b> (mg)	<b>q<sub>total</sub></b> (mg)	<b>% Removal</b>	<b>MTZ or H<sub>UNB</sub></b> (cm)	<b>H<sub>B</sub></b> (cm)
<b>10</b>	115	2811.8	281.1	423.5	196.8	46.5	7.1	4.9
<b>12</b>	65	2650.8	220.9	441	185.5	42.1	8.5	3.5
<b>15</b>	39	2551.5	170.1	467.2	176.5	38.2	9.25	2.7

### 6.5.2 Effect of Initial MB Dye Concentration

The effect of initial MB dye concentration on the BTCS at bed height of 12 (cm) and flow rate of 12 (ml/min) are shown in fig 6.4. The curves have relatively the same shape for all initial MB dye concentration and resulting more shortened mass transfer zone. As expected, a decreased initial dye concentration gave a slower breakthrough curve since the lower concentration gradient led to a slower transport due to lower diffusion coefficient or mass transfer. BTCS parameters of packed bed column for the removal of MB by pine cone at different MB solution concentration are presented in Tabla 6.2. The Table shows that the amount of total sorbed dye, equilibrium dye uptake, MTZ, and total percent removal increased with increasing initial MB dye concentration.

The increase in total amount of adsorbed MB ( $q_{total}$ ) and hence percentage removal of MB (Table 6.2) was obtained with increasing MB dye concentration. This is because of increasing mass transfer concentration driving force and dye loading rate. These results are in agreement with many investigations for different system (Al-Degs et al., 2009, Han et al., 2009, Saha et al., 2012a). In many cases the diffusion process is concentration dependent (Cruz-Olivares et al., 2013). On the other hand, decreasing the MB dye concentration increased the treated volume ( $V_{eff}$ ) that can be processed and shifted the BTC to the right. The larger influent MB dye concentration, the steeper is the scope of BTC and smaller is the breakthrough time ( $t_b$ ) (Table 6.2) i.e. the diffusion process is concentration dependent. A decreased initial MB dye concentration gave an extended breakthrough curve, since the lower concentration gradient caused a slower transport due to reduced diffusion coefficient and reduced mass transfer coefficient. Available adsorbent sites are quickly filled at high initial dye concentration resulting in reduced breakthrough time. From Table 6.2, it was observed that the highest uptake and highest percent removal of MB (47.6%) were obtained for the high dye concentration. However, percentage removal obtained from column study was lower than that obtained from batch study for the same initial dye concentration (Yagub et al., 2013). This may be due to insufficient contact time. Thus high dye loading rate and high concentration driving force resulted in a better column performance. Similar trends were obtained for adsorption of Reactive Black 5 dye by granular activated carbon (Ahmad and Hameed, 2010), removal of Methylene blue dye using cedar sawdust and crushed briq (Hamdaoui, 2006b).

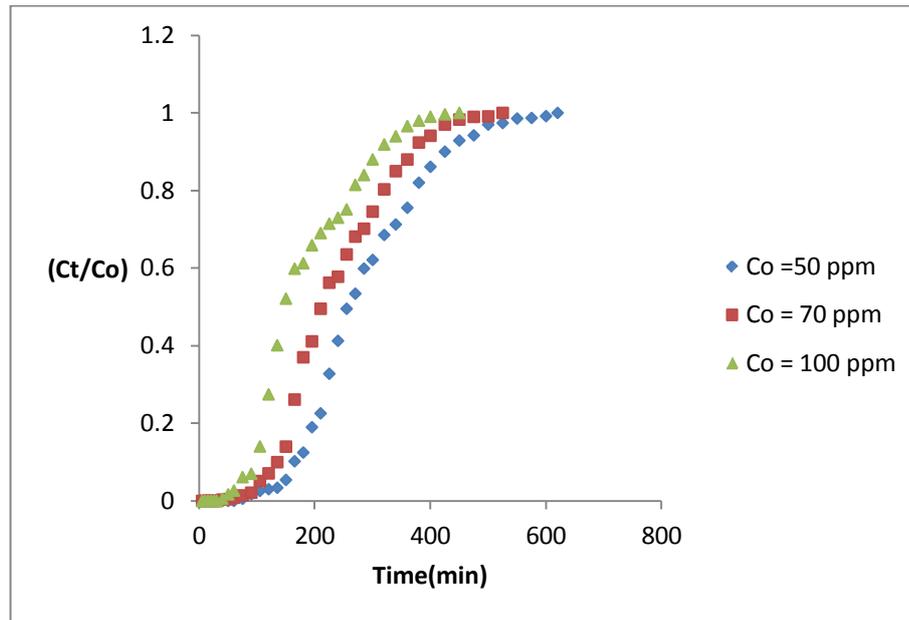


Figure 6.4 Comparison of predicted breakthrough curves of MB dye adsorption on raw pine cone at different initial MB dye concentration

(MB dye flow rate = 12 ml/min, bed height = 12 cm, temperature =  $25 \pm 1^\circ\text{C}$  )

**Table 6.2** Parameters of breakthrough curves (BTCS) of packed bed column for MB removal by pine cone

$C_o$ (mg/L)	$t_b$ (min)	$V_{eff}$ (mL)	$t_{total}$ (min)	$m_{total}$ (mg)	$Q_{total}$ (mg)	% Removal	MTZ or $H_{UNB}$ (cm)	HB (cm)
<b>50</b>	85	3001.2	250.1	372	150.1	40.3	7.92	4.08
<b>70</b>	64	2650.8	220.9	441	185.5	42.1	8.5	3.5
<b>100</b>	46	2286	190.5	480	228.6	47.6	9.16	2.84

### 6.5.3 Effect of Bed Height

Figure (6.5) shows the breakthrough curve (BTCs) obtained for MB adsorption on the pine cone for different bed heights of 10, 12, and 15 cm, at a constant flow rate of 12 ml/min and initial MB dye concentration of 70 mg/l.

Breakthrough curve (BTCs) parameters for MB column study were tabulated in Table 6.3. The results revealed that by increasing the bed height, the breakthrough time also shifted increased. By increasing bed height from 10 cm to 15 cm, the percentage dye removal also increased from 38.9 to 46.1 % (Table 6.3). This is also supported by used bed (HB). Detected breakthrough time ( $t_b$ ) with increase in bed height is an expected result. As the bed height is increased, the adsorbent pine cone load also increased and hence total adsorption capacity of the bed increases. With higher adsorbent loading, the contact time increased and in turn increases the “sweep efficiency” (Sen et al 2002). As a result, more adsorbent surface are exposed to flow and hence an increase in the removal of dye adsorption,  $q_{total}$  (Table 6.3). Further, it was supported by increased used bed (HB) from 2.19 cm to 4.47 cm (Table 6.3). Further, higher breakthrough time gives better intra-particle diffusion phenomena and higher will be the adsorption capacity of column (Sadaf and Bhatti, 2013b). Moreover, more volume of effluent ( $V_{eff}$ ) can be treated with high MB removal efficiency by increasing bed height which is advantageous for adsorption column operation.

Similar observation was reported by various researchers (Tan et al., 2008, Han et al., 2009).

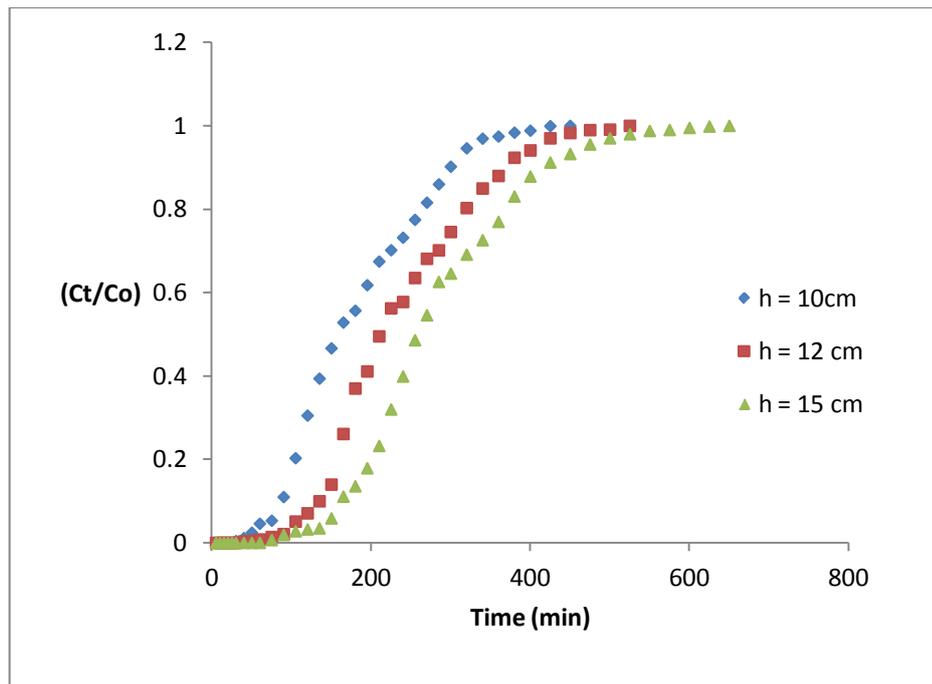


Figure 6.5 Comparison of predicted breakthrough curves of MB dye adsorption on raw pine cone at different bed height

(Inlet MB dye concentration = 70 mg/L, MB dye flow rate = 12 ml/min, temperature =  $25 \pm 1$  °C)

**Table 6.3** Parameters of breakthrough curves (BTCS) of packed bed column for MB removal by pine cone

<b>h</b> (cm)	<b>t<sub>b</sub></b> (min)	<b>V<sub>eff</sub></b> (mL)	<b>t<sub>total</sub></b> (min)	<b>m<sub>total</sub></b> (mg)	<b>Q<sub>total</sub></b> (mg)	<b>% Removal</b>	<b>MTZ or H<sub>UNB</sub></b> (cm)	<b>H<sub>B</sub></b> (cm)
<b>10</b>	38	2088	174	378	147	38.9	7.81	2.19
<b>12</b>	65	2650.8	220.9	441	185.5	42.1	8.5	3.5
<b>15</b>	85	3427.2	285.6	520.8	239.9	46.1	10.53	4.47

## 6.5.4 Kinetic Modelling of Fixed Bed Column Operation

### 6.5.4.1 Application of Thomas Model

The BTC column experimental data were fitted to the Thomas model to determine the Thomas rate constant ( $K_{Th}$ ) and maximum solid-phase concentration ( $q_0$ ). The determined coefficients and relative constants were obtained using linear regression analysis according to Eq. (6.11).

The predicted curves of a linear plot of  $\ln((C_0/C_t) + 1)$  against time ( $t$ ) at various experimental conditions (different flow rate, different initial MB concentration, and different bed height) according to the Thomas model are shown in Figures (6.6-6.8) to determine values of  $K_{Th}$  and  $q_0$  from the intercepts and slopes of the plot. The results of  $K_{Th}$ ,  $q_0$ , and  $R^2$  are given in Table (6.4). From the results in Table (6.4), it can be seen from the regression coefficient  $R^2$ , that the Thomas model fitted the experimental data well.

As shown in Table (6.4) as the initial MB dye concentration increased, the value of maximum solid-phase concentration ( $q_0$ ) increased but the value of Thomas rate constant ( $K_{Th}$ ) decreased. This is because the driving force for biosorption is the concentration difference between the dye in the solution and the dye on the biosorbent (Aksu and Gönen, 2004, Han et al., 2007a). Thus the high driving force due to the higher MB concentration resulted in better column performance. As flow rate increased, the value of Thomas rate constant ( $K_{Th}$ ) increased but the value of maximum solid-phase concentration ( $q_0$ ) decreased. With the bed depth increased, the value of maximum solid-phase concentration ( $q_0$ ) increased whereas the value of Thomas rate constant ( $K_{Th}$ ) decreased. So higher initial MB dye concentration, lower flow rate, and higher bed depth would increase the adsorption of MB on the pine cone powder column. Similar type of Thomas constants for different systems were reported by (Han et al., 2007) and (Aksu and Gönen, 2004).

**Table 6.4** Thomas kinetic parameters at different experimental condition by non linear regression analysis

<i>Thomas Parameter</i> <i>s</i>	<i>Flow Rate (ml/min)</i>			<i>Initial MB dye Concentration (mg/L)</i>			<i>Bed Height (cm)</i>		
	10	12	15	50	70	100	10	12	15
$K_{Th}$ (ml/min mg)	0.28	0.286	0.293	0.354	0.286	0.258	0.36	0.286	0.265
$q_0$ (mg/g)	55.35	44.39	38.23	38.95	44.39	55.68	48.75	44.39	42.49
$R^2$	0.997	0.997	0.998	0.985	0.997	0.989	0.995	0.997	0.99

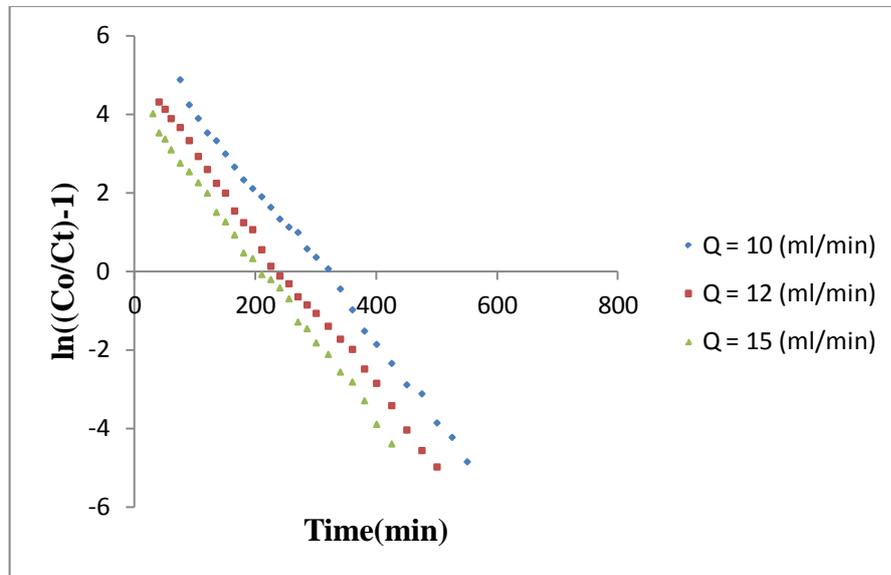


Figure 6.6 Thomas kinetic plot for the adsorption of MB on pine cone: Effect of flow rate

(Inlet MB dye concentration = 70 mg/L, bed height = 12 cm, temperature =  $25 \pm 1^\circ\text{C}$  )

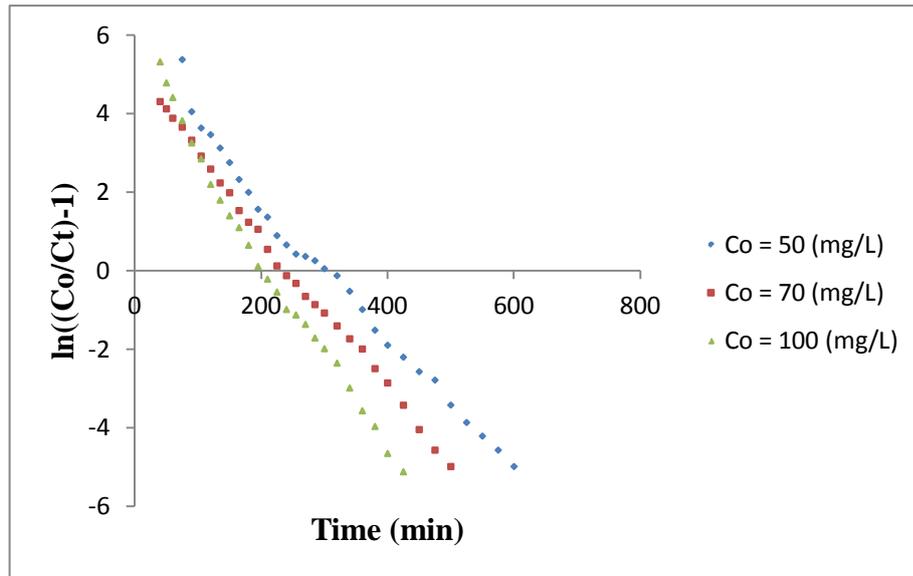


Figure 6.7 Thomas kinetic plot for the adsorption of MB on pine cone: Effect of initial dye concentration

(MB dye flow rate = 12 ml/min, bed height = 12 cm, temperature =  $25 \pm 1^\circ\text{C}$  )

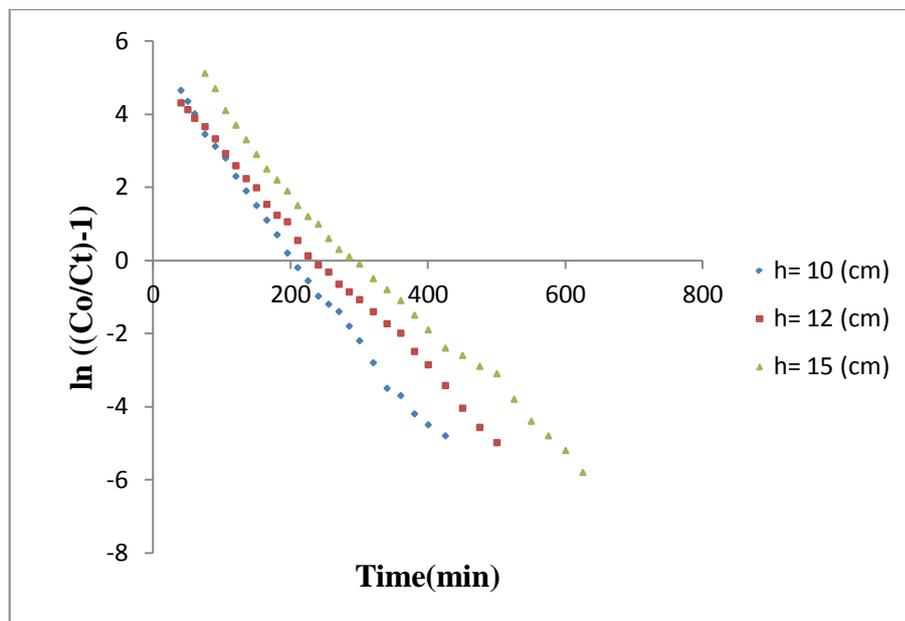


Figure 6.8 Thomas kinetic plot for the adsorption of MB on pine cone: Effect of bed height

(Inlet MB dye concentration = 70 mg/L, MB dye flow rate = 12 ml/min, temperature =  $25 \pm 1^\circ\text{C}$ )

### 6.5.4.2 Application of Yoon-Nelson Model

A simple theoretical model developed by Yoon–Nelson was used to study the breakthrough behaviour of MB dye on pine cone powder. The values of  $K_{YN}$  (a rate constant) and  $\tau$  (the time required for 50% MB breakthrough) were obtained from In  $(C_t / (C_0 - C_t))$  versus  $t$  plots at different flow rates different (10, 12, and 15 ml min<sup>-1</sup>) and at different initial dye MB concentration (50, 70, and 100 (mg/L), also at different bed heights varied between 10 and 15 (cm) according to Eq. (6.12). This plot will result in a straight line with slope of  $K_{YN}$  and intercept of  $\tau K_{YN}$  Figure (6.9-6.11). The values of  $K_{YN}$  and  $\tau$  are listed in Table (6.5).

Table (6.5), shows that the rate constant  $K_{YN}$  increased with both increasing initial MB dye concentration and flow rate, whereas the 50% breakthrough time  $\tau$  decreased with both increasing flow rate and initial MB concentration. With the bed mass increasing, the values of  $\tau$  increased while the values of  $K_{YN}$  decreased. This is due to the fact that increase in initial ion concentration increases the competition between adsorbate molecules for the adsorption site, which ultimately results in increased uptake rate (Hamdaoui, 2006b, Han et al., 2009).

It was found that, the time required to achieve 50% of adsorbate breakthrough  $\tau$  from the Yoon-Nelson model seemed to agree well with the experimental data ( $\tau_{50\% \text{ exp}}$ ) in the entire column adsorption system, thus indicating Yoon and Nelson model fitted well to the experimental data.

**Table 6.5** Yoon–Nelson parameters at different experimental condition by non linear regression analysis

<i>Yoon-Nelson Parameters</i>	<i>Flow Rate (ml/min)</i>			<i>Initial MB dye Concentration (mg/L)</i>			<i>Bed Height (cm)</i>		
	10	12	15	50	70	100	10	12	15
$K_{YN}$ (min <sup>-1</sup> )	0.020	0.025	0.029	0.019	0.025	0.29	0.029	0.025	0.017
$\tau$ (min)	263.2	217	159.4	269.1	217	158.	183.0	217	282.6
$\tau_{50\% \text{ exp}}$ (min)	260	212	158	255	212	150	165	212	265
$R^2$	0.997	0.997	0.998	0.99	0.997	0.99	0.99	0.997	0.99

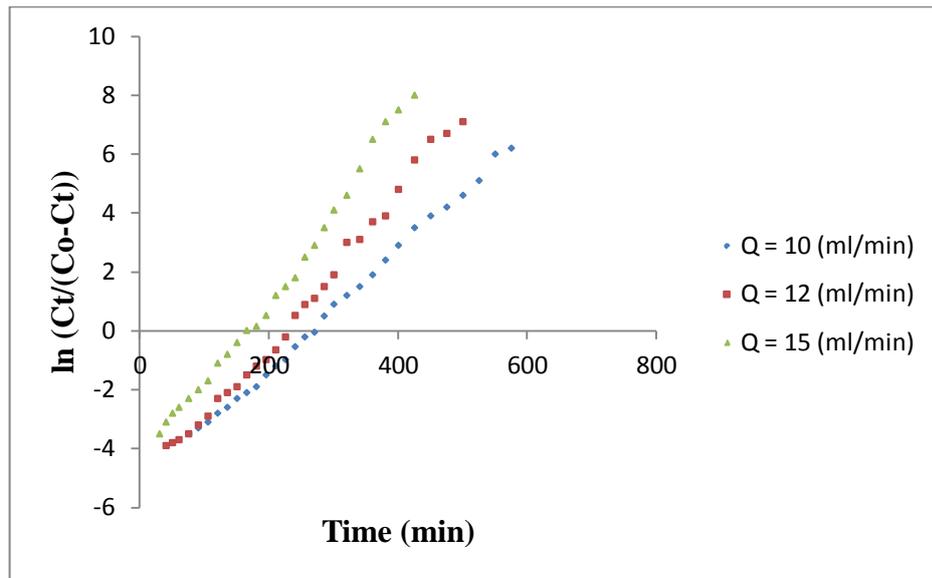


Figure 6.9 Yoon–Nelson kinetic plot for the adsorption of MB on pine cone: Effect of flow rate

(Inlet MB dye concentration = 70 mg/L, bed height = 12 cm, temperature = 25±1°C )

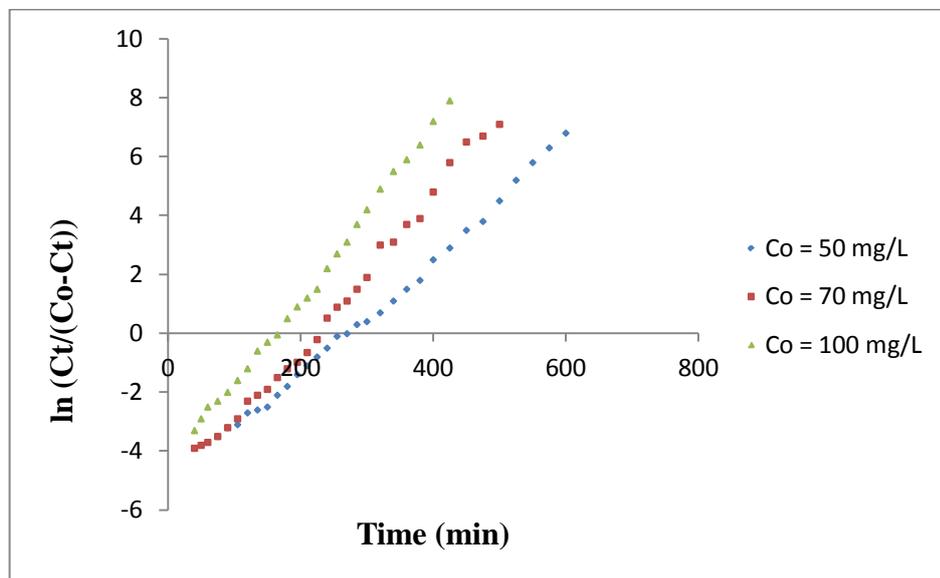


Figure 6.10 Yoon–Nelson kinetic plot for the adsorption of MB on pine cone: Effect of initial dye concentration

(MB dye flow rate = 12 ml/min, bed height = 12 cm, temperature = 25±1°C )

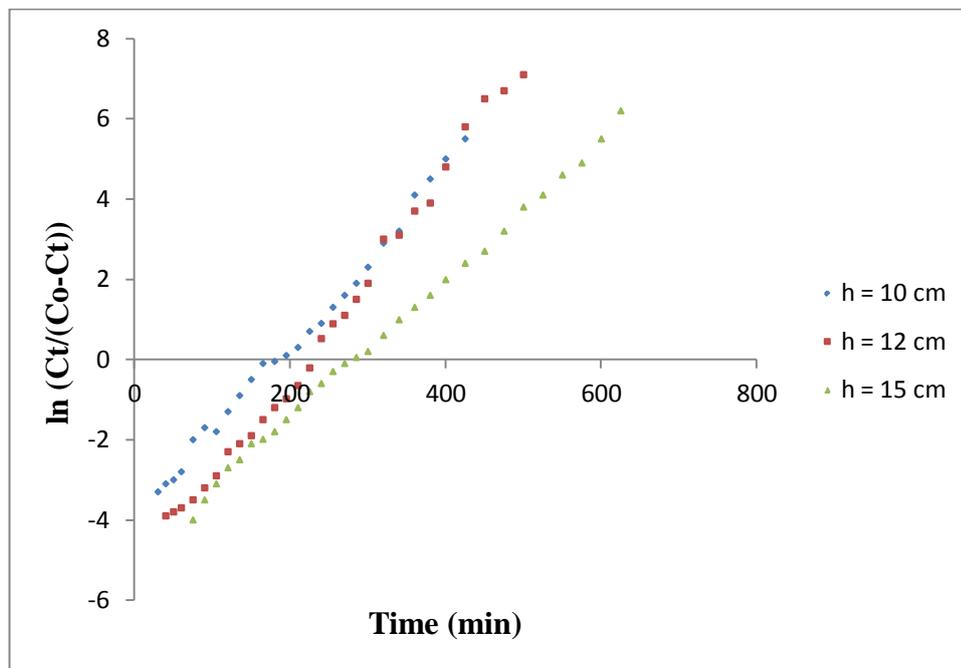


Figure 6.11 Yoon–Nelson kinetic plot for the adsorption of MB on pine cone: Effect of bed height.

(Inlet MB dye concentration = 70 mg/L, MB dye flow rate = 12 ml/min, temperature =  $25 \pm 1$  °C)

### 6.5.4.3 Application of Bed Depth Service Time (BDST) Model

The data obtained from the experimental column studies between MB dye and pine cone also fitted well to the Bed Depth Service Time (BDST) model (see Table 6.6 where  $R^2 > 0.99$ ). The parameters of  $K_o$  and  $N_o$  as calculated from the plots between  $\ln(C_o/C_t - 1)$  versus  $t$  at different experimental conditions (different flow rate, different initial MB dye concentration, and different bed height) are listed in Table (6.6).

As the initial MB dye concentration increased, the value of the volumetric sorption capacity of the bed ( $N_o$ ) increased but the value of the rate constant ( $K_o$ ) decreased. As the bed height increases, the rate constant ( $K_o$ ) decreases while the volumetric sorption capacity of the bed ( $N_o$ ) increases. This is because, the residence time of the fluid inside the column increases, allowing the MB dye molecules to diffuse deeper inside the pine cone (Han et al., 2007a). Thus, the bed capacity changes with bed height. Furthermore, as seen in Table 6.6,  $K_o$  did not change considerably with change in flow rate. These results indicate that the BDST model can be used to predict the adsorption performance at other operation conditions for adsorption of MB dye onto pine cone biomass.

**Table 6.6** Bed Depth Service Time (BDST) parameters at different experimental condition

<i>BDST Parameter s</i>	<i>Flow Rate (ml/min)</i>			<i>Initial MB dye Concentration (mg/L)</i>			<i>Bed Height (cm)</i>		
	10	12	15	50	70	100	10	12	15
$K_o$ (L/ mg min)	0.281	0.285	0.292	0.353	0.285	0.257	0.362	0.285	0.264
$N_o$ (mg/L)	1555.9	1615.2	1673.8	1362.9	1615. 2	1941.4	1551. 2	1615.2	1699.6
$R^2$	0.997	0.997	0.996	0.997	0.995	0.998	0.996	0.994	0.995

## 6.5 Summary

The study of dynamic removal of methylene blue by adsorption onto pine cone biomass in packed bed column was applied. The following outcomes can be made from the fixed bed column breakthrough studies for dye removal:

As the flow rate decreased the breakthrough time increased; this is because the methylene blue MB dye had more contact time with pine cone resulting in higher percentage removal of methylene blue MB at lower flow rate.

- MB removal by pine cone increased with increasing initial MB dye concentration and the highest percent removal of MB dye was obtained with the highest initial dye concentration.
- With the increase in the height of packed bed, the breakthrough time increased, and the total percent removal also increased. This is because more surface of adsorbent are exposed to MB flow.
- The application of Thomas model showed that the value of maximum solid-phase concentration ( $q_0$ ) decreased when the flow rate and the height of the bed increased but increase with increasing initial MB dye concentration. The value of Thomas rate constant ( $K_{Th}$ ) increased with increase flow rate but decreased with increasing initial MB dye concentration and the height of the bed.
- The results from Yoon–Nelson model showed that the time required to achieve 50% adsorbate breakthrough  $\tau$  seemed to agree well with the experimental data ( $\tau_{50\% \text{ exp}}$ ) and also the results showed that the rate constant  $K_{YN}$  increased with both increasing flow rate and initial MB dye concentration but decreased with increasing the bed height.
- From Bed Depth Service Time (BDST) model, the value of the rate constant ( $K_0$ ) decreased when both the bed heights and the initial MB dye concentration increased, but increased with flow rate. However, the value of the volumetric sorption capacity of the bed ( $N_0$ ) increased with increasing flow rate, initial MB dye concentration, and bed heights.
- From the results it can be seen from the regression coefficient  $R^2$ , the value of  $R^2$  is very close for three models (Thomas model, Yoon–Nelson model, and Bed Depth Service Time (BDST) model), and all three models can be applied to account for the experimental data.

## **CHAPTER 7**

# **CONCLUSIONS AND RECOMMENDATIONS**

## **7.1 Introduction**

This chapter summarizes the overall results and presents some recommendations for future directions. Batch studies show the effectiveness MB dye removal using the prepared raw and treated adsorbents. Also the influences of parameters on the adsorption capacity were reported. The characterizations of raw and modified adsorbents were reported as well. Column study shows that the pine cone powder column can be used in wastewater treatment.

In order to complement the existing data, recommendations for future work include the possibilities of conducting further similar experiments by using new materials.

## **7.2 Conclusions**

This thesis investigates the feasibility of using an agricultural by-product, pine cone and pine leaves, as a low cost adsorbent to remove MB dye contaminate.

In this study, raw pine cone was modified with a different concentration of base solution, also raw pine leaves treated with acid and base solutions, characterized and tested for removal of MB dye from aqueous solution. Thus the summary is based on the results of:

- i) Characterization of prepared adsorbents.
- ii) Batch adsorption study for pine cone materials for MB dye removal.
- iii) Batch adsorption study for pine leaves materials for MB dye removal.
- iv) Column adsorption study for pine cone biomass.

### 7.2.1 Characterization of prepared adsorbents

The characterizations of pine cone and pine leaves were presented in detail in this chapter. The study of characterization helps in understanding adsorption behaviour and mechanisms combined with the biomass and the summary is based on the results of the characterization of prepared raw and treated pine cone and leaves the and outcomes of this chapter are as follows

- The scanning electron microscopy (SEM) of prepared raw materials (pine cone and pine leaves) and modified materials (pine cone and pine leaves) showed the surface morphology of untreated pine materials is different from that of treated pine materials with chemicals was expected to partially remove protective thin wax on pine material surface.
- The FTIR of raw and modified pine materials showed that the two new peaks matching with peaks at about 2901.4 and 2879.56  $\text{cm}^{-1}$  on both PC1 and PC2, and 2921.7 and 2922.6  $\text{cm}^{-1}$  on both PLBT and PLAT, confirmed that the chemical treated was successfully retained on the pine cone surface.
- Surface area was higher for chemically treated pine materials (PC1, PC2, PLBT and PLAT) compared to untreated pine materials (PC and PL), this is due to dissolution of some substances. The increased percentage of surface area for PC1 and PC2 are 62.3% and 23.4%, respectively and those for PLAT and PLBT are 30.7% and 3.4%, respectively.
- The study of zeta potential for raw and modified pine materials showed a decrease of the point of zero charge for modified pine materials compared to unmodified ones. The point of zero charge for activated pine cone PC1 and PC2 are 4.0 and 4.2 respectively, whereas for raw pine cone was 4.7, and the point of zero charge for raw pine leaves was 5.1, whereas for modified pine leaves PLAT and PLBT are 4.3 and 4.5 respectively.
- The study of bulk density for raw and modified pine materials showed that higher bulk densities for treated pine materials. The bulk density for pine cone was 0.272  $\text{gm/cm}^3$ , whereas those for modified pine cone PC1 and PC2 are 0.315 and 0.294  $\text{gm/cm}^3$  respectively, and the bulk density for activated pine leaves PLAT and PLBT are 0.267 and 0.244  $\text{gm/cm}^3$  respectively, whereas for raw pine leaves is 0.216  $\text{gm/cm}^3$ .

## **7.2.2 Batch adsorption study for pine cone materials of MB dye removal**

In this study, the effectiveness of raw and modified biomass pine cone, PC, PC1, PC2 were tested for removal of Methylene Blue MB from aqueous solution and outcome of this chapter are as follows

- The amount of methylene blue dye uptake on raw and basic modified pine cone biomass were found to increase with increase in initial dye concentration, contact time, and solution pH but decreased with increase in, salt concentration and system temperature.
- In batch study, the kinetic experiments revealed that adsorption of dyes were rapid at initial stage followed by a slower phase where equilibrium uptake was achieved.
- The kinetic studies showed that the methylene blue adsorption process followed pseudo-second-order kinetics models.
- Langmuir and Freundlich equations both are applicable to describe the adsorption of methylene blue on raw and basic modified pine cone biomass within this initial dye concentration range. The maximum monolayer adsorption capacity was 129.87 mg/g occurred at pH of 9.02 for an initial dye concentration of 10 ppm by raw pine cone, whereas for base modified pine cone with two different NaOH concentrations were 142.25 mg/g and 139.23 mg/g at the same experimental conditions.
- The constant value, RL (low separation factor), in Langmuir isotherm and Freundlich constant, n, both give an indication of favourable adsorption.
- The thermodynamic analysis indicates that system is spontaneous, exothermic and physical processes in nature.
- A single stage bath adsorber design for the MB adsorption onto pine cone and modified pine cone have been presented based on the Langmuir isotherm model equation.
- Desorption experiments also showed that desorption increased as the pH decreased.

### **7.2.3 Batch adsorption study for pine leaves materials of MB dye removal**

Other type of adsorbents raw and treated pine leaves used to remove MB dye. The activated pine leaves was by chemical treated acid treated (HCl) and base treated (NaOH). The outcome drawn from the batch adsorption experimental study of MB dye removal could be concluded as follows:

- The effectiveness of raw and modified pine leaves, PL, PLAT and PLBT for removal of methylene blue was studied under various experimental conditions such as initial dye concentration, contact time, solution pH, salt concentration and system temperature.
- In batch study, the kinetic experiment revealed that adsorption of dye was rapid at initial stage followed by a slower phase where equilibrium removal was achieved.
- The amount of methylene blue dye adsorption was found to increase with increase in initial dye concentration, contact time, amount of adsorbent, agitation speed, system temperature, and solution pH but decrease with increase in salt concentration.
- It was also observed that the adsorption was pH dependent and the maximum adsorption of 126.58 mg/g occurred at pH of 9.2 for an initial dye concentration of 10 ppm by raw pine leaves, whereas for treated pine leaves the maximum adsorption of 140.84 and 131.58 mg/g for PLAT and PLBT respectively at the same experimental conditions, whereas the maximum monolayer adsorption capacity were 129.87, 142.25 and 139.23 mg/g by raw and treated pine cone PC, PC1, PC2 respectively.
- Overall, the kinetic studies showed that the MB dye adsorption process followed pseudo-second-order kinetics models and the adsorption was controlled by chemisorptions process, and the pine cone study gives the same trend.

- Langmuir model gives a better fit with experimental data, but in the pine cone the Langmuir and Freundlich equations both are applicable to describe the adsorption within the same conditions
- The thermodynamic analysis indicates that system was endothermic and physical processes in nature. In contrast, pine cone study of chapter 4 indicated that adsorption was exothermic.
- A single stage batch adsorber design for the methylene blue MB adsorption onto pine leaves have been presented based on the Langmuir isotherm model equation
- Desorption experiments also showed that desorption of methylene blue decreased as the pH increased.

#### 7.2.4 Column adsorption study for pine cone biomass

The study of dynamic removal of methylene blue by adsorption onto pine cone biomass in packed bed column was applied. The following outcomes can be made from the fixed bed column breakthrough studies for dye removal:

- As the flow rate decreased the breakthrough time increased; this is because the methylene blue MB dye had more contact time with pine cone resulting in higher percentage removal of methylene blue MB at lower flow rate.
- MB removal by pine cone increased with increasing initial MB dye concentration and the highest percent removal of MB dye was obtained with the highest initial dye concentration.
- With the increase in the height of packed bed, the breakthrough time increased, and the total percent removal also increased This is because more surface of adsorbent are exposed to MB flow.
- The application of Thomas model showed that the value of maximum solid-phase concentration ( $q_0$ ) decreased when the flow rate and the height of the bed increased but increase with increasing initial MB dye concentration. The value of Thomas rate constant ( $K_{Th}$ ) increased with increase flow rate but decreased with increasing initial MB dye concentration and the height of the bed.
- The results from Yoon–Nelson model showed that the time required to achieve 50% adsorbate breakthrough  $\tau$  seemed to agree well with the experimental data ( $\tau_{50\% \text{ exp}}$ ) and also the results showed that the rate constant  $K_{YN}$  increased with both increasing flow rate and initial MB dye concentration but decreased with increasing the bed height.
- From Bed Depth Service Time (BDST) model, the value of the rate constant ( $K_0$ ) decreased when both the bed heights and the initial MB dye concentration increased, but increased with flow rate. However, the value of the volumetric sorption capacity of the bed ( $N_0$ ) increased with increasing flow rate, initial MB dye concentration, and bed heights.
- All three models can be applied to account for the experimental data.

### 7.3 Recommendations for Future Research

The applicability of pine tree materials for the removal the methylene blue MB dye was thoroughly studied. The results showed the effectiveness of modified pine tree biomass as an adsorbent material for dye wastewater cleaning. However, some issues need to be addressed in an effort to compliment and improve the current study before considering the real applications. Some of the findings to date and need for future research are as follows:

- Alternative inexpensive materials such as grass, pine tree bark, straw, wheat straw etc should be tested, and the potential of using these adsorbent biomass materials need to be evaluated. Other chemical and physical treatments could also be used. It is interesting to further discover the potential of utilizing different types of treatment as well as other types of biomass.
- As real dye wastewater always consists of more than a single dye and could possibly be mixed with other type of dyes such as cationic and anionic. Therefore much work is necessary to predict the performance of adsorption process for dye removal from real industrial effluents under a wide range of operating conditions.
- Adsorption of dye mechanism on various adsorbents including cellulose biomass materials is very complex and poorly understood. No literature is available to apply the well-developed surface reaction based dye adsorption model to obtain the effect of ionic strength or solution pH on the extent of adsorption.
- It is also evident from literature review that most of the adsorption studies were based on batch adsorption experiments. Few studies reported on the column adsorption experiments results which give more insight into the feasibility of utilising adsorbents on a commercial scale.
- In most of the reported studies, few attempts were made to relate the characterization results with the performance of adsorbents for the removal of dyes from aqueous solution under various physio-chemical conditions.

- Leaching of industrial wastes agricultural solid wastes in water is very important in order to see the dissolution of the various substances present in the wastes. This interference will lead to erroneous results in the adsorption experiments. Therefore, more research work should be performed in this direction.
- In most of the reported studies, few efforts were made to relate the thermodynamic parameters. Therefore, more extensive studies should be performed in this direction.

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# APPENDIX A

Raw data for adsorption of methylene blue MB  
dye onto raw and modified pine cone

Appendix A-1 Effect of Initial Solution pH on adsorption of methylene blue MB dye onto raw and modified pine cone at initial solution pH of 3.1

Time ,t (min)	Raw Pine Cone PC		Modified Pine Cone PC1		Modified Pine Cone PC2	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	8.9795	3.4016	7.4395	6.1816	7.9895	4.8516
10	8.0271	6.5765	6.4871	9.3565	7.0371	8.0265
20	6.9555	10.1482	5.4155	12.9282	5.9655	11.5982
40	6.5303	11.5655	4.9903	14.3455	5.5403	13.0155
60	6.2015	12.6616	4.6615	15.4416	5.2115	14.1116
90	5.7479	14.1734	4.2079	16.9534	4.7579	15.6234
120	5.6345	14.5514	4.0945	17.3314	4.6445	16.0014
150	5.8103	13.9655	3.9703	16.7455	4.5203	16.1155
180	5.9804	13.3986	3.8404	16.1786	4.4504	16.2486
210	5.8443	13.8522	3.79043	16.6322	4.3543	16.3022
240	5.6175	14.6081	3.5775	17.3881	4.2275	16.5581

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Initial dye concentration	10 ppm
Volume of dye solution	50 ml

Appendix A-2 Effect of Initial Solution pH on adsorption of methylene blue MB dye onto raw and modified pine cone at initial solution pH of 5.01

Time ,t (min)	Raw Pine Cone PC		Modified Pine Cone PC1		Modified Pine Cone PC2	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	5.9861	13.3797	4.7661	16.1597	4.9961	14.8297
10	4.512	18.2932	3.292	21.0732	3.522	19.7432
20	3.2761	22.413	2.0561	25.193	2.2861	23.863
40	2.7035	24.3217	1.4835	27.1017	1.7135	25.7717
60	2.6751	24.4162	1.4551	27.1962	1.6851	25.8662
90	1.785	27.3831	1.0112	30.1631	1.595	28.8331
120	1.065	29.7832	0.9785	30.5632	1.2141	29.2332
150	1.9041	26.9863	0.7541	30.7663	1.1235	29.4363
180	1.785	27.3832	0.6265	31.1632	1.0125	30.1833
210	1.9254	26.9485	0.4054	31.7285	0.9854	30.3985
240	1.2124	29.2919	0.3276	32.0719	0.9652	30.7419

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Initial dye concentration	10 ppm
Volume of dye solution	50 ml

Appendix A-3 Effect of Initial Solution pH on adsorption of methylene blue MB dye onto raw and modified pine cone at initial solution pH of 7.06

Time ,t (min)	Raw Pine Cone PC		Modified Pine Cone PC1		Modified Pine Cone PC2	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	5.2263	15.9121	4.4763	17.9121	4.9263	16.4121
10	3.8487	20.5043	3.0987	22.5043	3.5487	21.0043
20	2.7488	24.1705	2.8988	26.1705	3.3488	24.6705
40	1.6093	27.969	0.7593	29.9569	1.2093	28.4569
60	1.3882	28.506	0.6382	30.7106	1.0882	29.2106
90	1.065	29.3832	0.5155	30.9832	0.9655	29.4832
120	0.6965	29.6325	0.4065	31.0116	0.8565	29.5116
150	0.7872	29.8521	0.3372	31.5092	0.7872	30.0092
180	0.8666	30.0021	0.2566	32.1446	0.7066	30.6446
210	0.7192	30.1936	0.3108	32.9436	0.7608	31.4436
240	0.6228	30.2573	0.2712	33.2573	0.7212	31.7573

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Initial dye concentration	10 ppm
Volume of dye solution	50 ml

Appendix A-4 Effect of Initial Solution pH on adsorption of methylene blue MB dye onto raw and modified pine cone at initial solution pH of 9.2

Time, t (min)	Raw Pine Cone PC		Modified Pine Cone PC1		Modified Pine Cone PC2	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	4.5857	16.0278	3.7857	18.3748	4.0857	16.7268
10	3.3441	20.6212	2.3441	22.9647	3.1441	21.3119
20	2.0798	24.2862	2.0798	26.6332	2.5411	24.9852
40	0.9856	28.0847	1.9587	30.4196	2.0125	28.7716
60	0.8156	28.6217	0.7956	31.1733	0.8764	29.5253
90	0.6512	29.4989	0.6712	31.4459	0.7785	29.7979
120	0.3223	29.7482	0.5223	31.4743	0.7452	29.8263
150	0.5037	29.9678	0.4041	31.9719	0.6215	30.3239
180	0.6455	30.1178	0.3513	32.6073	0.5251	30.9593
210	0.5888	30.3093	0.2758	33.4063	0.4785	31.7583
240	0.4017	30.3713	0.2104	33.7112	0.4221	32.0722

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Initial dye concentration	10 ppm
Volume of dye solution	50 ml

Appendix A-5 Effect of Initial dye concentration on adsorption of methylene blue MB dye onto raw and modified pine cone at initial dye conc. of 10 ppm

Time ,t (min)	Raw Pine Cone PC		Modified Pine Cone PC1		Modified Pine Cone PC2	
	$C_t$ (mg/L)	$q_t$ (mg/g)	$C_t$ (mg/L)	$q_t$ (mg/g)	$C_t$ (mg/L)	$q_t$ (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	4.5857	16.0278	3.7857	18.3748	4.0857	16.7268
10	3.3441	20.6212	2.3441	22.9647	3.1441	21.3119
20	2.0798	24.2862	2.0798	26.6332	2.5411	24.9852
40	0.9856	28.0847	1.9587	30.4196	2.0125	28.7716
60	0.8156	28.6217	0.7956	31.1733	0.8764	29.5253
90	0.6512	29.4989	0.6712	31.4459	0.7785	29.7979
120	0.3223	29.7482	0.5223	31.4743	0.7452	29.8263
150	0.5037	29.9678	0.4041	31.9719	0.6215	30.3239
180	0.6455	30.1178	0.3513	32.6073	0.5251	30.9593
210	0.5888	30.3093	0.2758	33.4063	0.4785	31.7583
240	0.4017	30.3713	0.2104	33.7112	0.4221	32.0722

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Solution pH	9.2
Volume of dye solution	50 ml

Appendix A-6 Effect of Initial dye concentration on adsorption of methylene blue MB dye onto raw and modified pine cone at initial dye conc. of 40 ppm

Time ,t (min)	Raw Pine Cone PC		Modified Pine Cone PC1		Modified Pine Cone PC2	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	23.6689	54.4369	53.9661	63.2781	42.7305	58.7568
10	21.9907	60.0308	51.1833	68.872	39.9477	64.3507
20	17.9541	73.4862	46.1035	82.3274	34.8679	77.8061
40	14.0536	86.488	39.3569	95.3292	28.1213	90.8079
60	13.5547	88.151	38.4044	96.9922	27.1688	92.4709
90	11.6044	93.6519	34.9121	102.4931	23.6765	97.9718
120	10.3344	95.8851	33.6421	104.7263	22.4065	100.205
150	11.5137	96.5543	32.4359	105.3955	21.2003	100.8742
180	11.6951	96.9495	31.5471	105.7907	20.3115	101.2694
210	11.5591	97.8031	29.7533	106.6443	18.5177	102.123
240	10.5159	98.2803	27.4044	107.1215	16.1688	102.6002

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Solution pH	9.2
Volume of dye solution	50 ml

Appendix A-7      Effect of Initial dye concentration on adsorption of methylene blue MB dye onto raw and modified pine cone at initial dye conc. of 70 ppm

Time ,t (min)	Raw Pine Cone PC		Modified Pine Cone PC1		Modified Pine Cone PC2	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	53.9661	54.2154	51.2154	62.7139	52.4254	58.4783
10	51.1833	62.7224	46.4333	71.2209	47.6433	66.9853
20	46.1035	79.6955	41.3535	88.1945	42.5635	83.9584
40	39.3569	102.1436	34.6069	110.6421	35.8169	106.4065
60	38.4044	105.3184	33.6544	113.8169	34.8644	109.5813
90	35.5471	114.8431	30.7971	123.3416	32.0071	119.1056
120	34.9121	116.9596	30.1621	125.4581	31.3721	121.2225
150	34.7533	117.4888	30.0033	125.9873	31.2133	121.7517
180	34.4359	118.5471	29.6859	127.0456	30.8959	122.8541
210	34.0139	119.5699	29.2639	128.0684	30.4739	123.8328
240	33.6421	120.1928	28.8921	128.6913	30.1021	124.4557

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Solution pH	9.2
Volume of dye solution	50 ml

Appendix A-8      Effect of Initial dye concentration on adsorption of methylene blue MB dye onto raw and modified pine cone at initial dye conc. of 90 ppm

Time ,t (min)	Raw Pine Cone PC		Modified Pine Cone PC1		Modified Pine Cone PC2	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	75.2976	49.008	72.2135	58.8204	73.7135	54.3503
10	73.3587	55.4709	69.2154	65.2833	70.7154	60.8132
20	70.9095	63.6348	65.2143	73.4472	66.7143	68.9771
40	61.0107	96.6308	58.5452	106.4432	60.0452	101.9731
60	59.5821	101.3931	54.2135	111.2055	55.7135	106.7354
90	57.0308	109.8972	53.7245	119.7096	55.2245	115.2395
120	55.4185	113.9382	52.1021	123.7506	53.6021	119.2805
150	54.2144	115.6185	50.2351	125.4309	51.7351	120.9608
180	54.0135	117.2988	48.2351	127.1112	49.7351	122.6411
210	53.8561	119.5462	47.561	129.3586	49.061	124.8885
240	53.1529	122.8234	46.2315	132.6358	47.7315	128.1657

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Solution pH	9.2
Volume of dye solution	50 ml

Appendix A-9 Effect of inorganic Monovalent Salt Concentration on adsorption of methylene blue MB dye onto raw and modified pine cone at initial NaCl concentrations of 50 mg L<sup>-1</sup>

Time ,t (min)	Raw Pine Cone PC		Modified Pine Cone PC1		Modified Pine Cone PC2	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	6.4906	11.6979	5.5621	14.1979	6.0831	13.3979
10	5.1356	16.2144	3.9853	18.7144	4.5063	17.9144
20	3.843	20.5232	2.9856	23.0232	3.5066	22.2232
40	3.2648	22.4508	2.4565	24.9508	2.9775	24.1508
60	2.5617	24.7941	1.8121	27.2941	2.3331	26.4941
90	2.3576	25.4744	1.6542	27.9744	2.1752	27.1744
120	2.1762	26.0792	1.4568	28.5792	1.9778	27.7792
150	1.9948	26.6839	1.2658	29.1839	1.7868	28.3839
180	1.8021	27.3265	1.1101	29.8265	1.6311	29.0265
210	1.4392	28.5359	0.9754	31.0359	1.4964	30.2359
240	1.1557	29.7461	0.9542	32.8363	1.4752	30.5548

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Solution pH	9.2
Volume of dye solution	50 ml
Initial dye Concentration	10 ppm

Appendix A-10 Effect of inorganic Monovalent Salt Concentration on adsorption of methylene blue MB dye onto raw and modified pine cone at initial NaCl concentrations of 100 mg L<sup>-1</sup>

Time ,t (min)	Raw Pine Cone PC		Modified Pine Cone PC1		Modified Pine Cone PC2	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	7.4148	8.6174	6.5418	11.6467	6.7918	10.9467
10	6.2242	12.8604	5.1868	16.1632	5.4368	15.4632
20	5.0109	16.6302	3.8942	20.472	4.1442	19.772
40	4.3533	18.8224	3.316	22.3996	3.566	21.6996
60	3.4915	21.6949	2.6129	24.7429	2.8629	24.0429
90	2.7828	24.057	2.4088	25.4232	2.6588	24.7232
120	1.7794	27.4021	2.2274	26.028	2.4774	25.328
150	2.2896	25.7012	2.046	26.6327	2.296	25.9327
180	2.2045	25.9847	1.8533	27.2753	2.1033	26.5753
210	1.9551	26.8163	1.4904	28.4847	1.7404	27.7847
240	1.7851	29.1591	1.2069	32.2592	1.4569	30.0652

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Solution pH	9.2
Volume of dye solution	50 ml
Initial dye Concentration	10 ppm

Appendix A-11 Effect of inorganic Monovalent Salt Concentration on adsorption of methylene blue MB dye onto raw and modified pine cone at initial NaCl concentrations of 150 mg L<sup>-1</sup>

Time ,t (min)	Raw Pine Cone PC		Modified Pine Cone PC1		Modified Pine Cone PC2	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	7.5111	8.2962	6.5874	10.5467	6.9074	9.3967
10	6.3262	12.2459	5.2143	15.0632	5.5343	13.9132
20	5.0676	16.4412	4.2351	19.372	4.5551	18.222
40	4.4497	18.5011	3.3214	21.2996	3.6414	20.1496
60	3.6899	21.0334	2.9852	23.6429	3.3052	22.4929
90	2.7999	24.0004	2.7563	24.3232	3.0763	23.1732
120	2.6524	24.4917	2.5142	24.928	2.8342	23.778
150	2.5164	24.9453	2.3521	25.5327	2.6721	24.3827
180	2.2386	25.8713	2.1241	26.1753	2.4441	25.0253
210	2.0855	27.3816	1.8421	28.3847	2.1621	27.2347
240	1.8927	29.0832	1.7845	31.8942	2.1045	29.8893

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Solution pH	9.2
Volume of dye solution	50 ml
Initial dye Concentration	10 ppm

Appendix A-12 Effect of inorganic Monovalent Salt Concentration on adsorption of methylene blue MB dye onto raw and modified pine cone at initial NaCl concentrations of 200 mg L<sup>-1</sup>

Time ,t (min)	Raw Pine Cone PC		Modified Pine Cone PC1		Modified Pine Cone PC2	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	8.0157	6.6143	7.1258	8.5924	7.7758	7.6254
10	6.7684	10.7718	6.1212	12.7499	6.7712	11.7829
20	5.6345	14.5514	5.0231	16.5295	5.6731	15.5625
40	5.0676	16.4412	4.2314	18.4193	4.8814	17.4523
60	4.3532	18.8224	3.2145	20.8005	3.8645	19.8335
90	3.4802	21.7327	3.0214	23.7108	3.6714	22.7438
120	3.2534	22.4886	2.8986	24.4667	3.5486	23.4997
150	3.1457	22.8476	2.8412	24.8257	3.4912	23.8587
180	2.8225	24.9248	2.5521	26.9029	3.2021	25.9359
210	2.5958	26.6808	2.2154	28.6589	2.8654	27.6919
240	2.4654	28.5554	2.0215	30.6551	2.6715	29.1552

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Solution pH	9.2
Volume of dye solution	50 ml
Initial dye Concentration	10 ppm

Appendix A-13      Effect of temperature on adsorption of methylene blue MB dye onto raw and modified pine cone at 30 °C

Time, t (min)	Raw Pine Cone PC		Modified Pine Cone PC1		Modified Pine Cone PC2	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	4.5857	16.0278	3.7857	18.3748	4.0857	16.7268
10	3.3441	20.6212	2.3441	22.9647	3.1441	21.3119
20	2.0798	24.2862	2.0798	26.6332	2.5411	24.9852
40	0.9856	28.0847	1.9587	30.4196	2.0125	28.7716
60	0.8156	28.6217	0.7956	31.1733	0.8764	29.5253
90	0.6512	29.4989	0.6712	31.4459	0.7785	29.7979
120	0.3223	29.7482	0.5223	31.4743	0.7452	29.8263
150	0.5037	29.9678	0.4041	31.9719	0.6215	30.3239
180	0.6455	30.1178	0.3513	32.6073	0.5251	30.9593
210	0.5888	30.3093	0.2758	33.4063	0.4785	31.7583
240	0.4017	30.3713	0.2104	33.7112	0.4221	32.0722

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Initial dye Concentration	10 ppm
Solution pH	9.2
Volume of dye solution	50 ml

Appendix A-14 Effect of temperature on adsorption of methylene blue MB dye onto raw and modified pine cone at 40 °C

Time, t (min)	Raw Pine Cone PC		Modified Pine Cone PC1		Modified Pine Cone PC2	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	4.5803	15.7428	4.4957	18.2278	4.5277	17.2278
10	3.3387	20.3362	3.2541	22.8212	3.2861	21.8212
20	2.0744	24.0012	1.9898	26.4862	2.0218	25.4862
40	0.9802	27.7997	0.8956	30.2847	0.9276	29.2847
60	0.8102	28.3367	0.7256	30.8217	0.7576	29.8217
90	0.6458	29.2139	0.5612	31.6989	0.5932	30.6989
120	0.3169	29.4632	0.2323	31.9482	0.2643	30.9482
150	0.4983	29.6828	0.4137	32.1678	0.4457	31.1678
180	0.6401	29.8328	0.5555	32.3178	0.5875	31.3178
210	0.5834	30.0243	0.4988	32.5093	0.5308	31.5093
240	0.3963	30.0863	0.3117	32.5833	0.3437	31.5183

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Initial dye Concentration	10 ppm
Solution pH	9.2
Volume of dye solution	50 ml

Appendix A-15      Effect of temperature on adsorption of methylene blue MB dye onto raw and modified pine cone at 50 °C

Time ,t (min)	Raw Pine Cone PC		Modified Pine Cone PC1		Modified Pine Cone PC2	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	4.5814	15.1567	4.5068	16.6779	4.5298	16.1279
10	3.3398	19.7501	3.2652	21.2713	3.2882	20.7213
20	2.0755	23.4151	2.0009	24.9363	2.0239	24.3863
40	0.9813	27.2136	0.9067	28.7348	0.9297	28.1848
60	0.8113	27.7506	0.7367	29.2718	0.7597	28.7218
90	0.6469	28.6278	0.5723	30.149	0.5953	29.599
120	0.3183	28.8771	0.2434	30.3983	0.2664	29.8483
150	0.4994	29.0967	0.4248	30.6179	0.4478	30.0679
180	0.6412	29.2467	0.5666	30.7679	0.5896	30.2179
210	0.5845	29.4382	0.5099	30.9594	0.5329	30.4094
240	0.3974	29.5098	0.3228	31.0251	0.3458	30.4695

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Initial dye Concentration	10 ppm
Solution pH	9.2
Volume of dye solution	50 ml

Appendix A-16      Effect of temperature on adsorption of methylene blue MB dye onto raw and modified pine cone at 60 °C

Time, t (min)	Raw Pine Cone PC		Modified Pine Cone PC1		Modified Pine Cone PC2	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	4.5826	15.0279	4.5081	16.1678	4.5312	15.7778
10	3.341	19.6213	3.2665	20.7612	3.2896	20.3712
20	2.0767	23.2863	2.0022	24.4262	2.0253	24.0362
40	0.9825	27.0848	0.908	28.2247	0.9311	27.8347
60	0.8125	27.6218	0.738	28.7617	0.7611	28.3717
90	0.6481	28.499	0.5736	29.6389	0.5967	29.2489
120	0.3192	28.7483	0.2447	29.8882	0.2678	29.4982
150	0.5006	28.9679	0.4261	30.1078	0.4492	29.7178
180	0.6424	29.1179	0.5679	30.2578	0.591	29.8678
210	0.5857	29.3094	0.5112	30.4493	0.5343	30.0593
240	0.3986	29.3521	0.3241	30.5184	0.3472	30.1142

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Initial dye Concentration	10 ppm
Solution pH	9.2
Volume of dye solution	50 ml

Appendix A-17      Effect of adsorbent doses on adsorption of methylene blue MB dye onto raw and modified pine cone at 10 mg

Time, t (min)	Raw Pine Cone PC		Modified Pine Cone PC1		Modified Pine Cone PC2	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	5.2264	15.9121	4.7264	19.1642	4.9264	17.3642
10	3.8487	20.5043	3.3487	23.7564	3.5487	21.9564
20	2.3916	25.3611	1.8916	28.6132	2.0916	26.8132
40	1.6093	27.9691	1.1093	31.2211	1.3093	29.4211
60	1.3995	28.6682	0.8995	31.9203	1.0995	30.1203
90	1.165	28.9223	0.665	32.1721	0.865	30.3721
120	0.9708	29.1512	0.4708	32.4021	0.6708	30.6021
150	0.8272	29.5245	0.3272	32.7721	0.5272	30.9721
180	0.7509	29.8143	0.2509	33.0621	0.4509	31.2621
210	0.7192	30.0102	0.2192	33.2621	0.4192	31.4621
240	0.6285	30.3525	0.1285	33.6221	0.3285	31.8251

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	30 °C
Initial dye Concentration	10 ppm
Solution pH	9.2
Volume of dye solution	50 ml

Appendix A-18      Effect of adsorbent doses on adsorption of methylene blue MB dye onto raw and modified pine cone at 15 mg

Time, t (min)	Raw Pine Cone PC		Modified Pine Cone PC1		Modified Pine Cone PC2	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	4.9259	16.9137	4.6759	20.2089	4.7959	18.4589
10	3.5482	21.5059	3.2982	24.8011	3.4182	23.0511
20	2.4483	25.1721	2.1983	28.4673	2.3183	26.7173
40	1.3088	26.5435	1.0588	29.8387	1.1788	28.0887
60	1.0989	27.8924	0.8489	31.1876	0.9689	29.4376
90	0.8434	28.985	0.5934	32.2802	0.7134	30.5302
120	0.7311	28.5325	0.4811	31.8277	0.6011	30.0777
150	0.6491	29.2221	0.3991	32.5173	0.5191	30.7673
180	0.5511	29.5432	0.3011	32.8384	0.4211	31.0884
210	0.4867	29.8859	0.2367	33.1811	0.3567	31.4311
240	0.4277	30.0123	0.1777	33.3075	0.2977	31.5525

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	30 °C
Initial dye Concentration	10 ppm
Solution pH	7.05
Volume of dye solution	50 ml

Appendix A-19 Effect of adsorbent doses on adsorption of methylene blue MB dye onto raw and modified pine cone at 20 mg

Time, t (min)	Raw Pine Cone PC		Modified Pine Cone PC1		Modified Pine Cone PC2	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	4.8522	17.1593	4.5572	20.5386	4.7097	18.5416
10	3.4745	21.7516	3.1795	25.1309	3.332	23.1339
20	2.3747	25.4178	2.0797	28.7971	2.2322	26.8001
40	1.2351	26.3254	0.9401	29.7047	1.0926	27.7077
60	1.0253	26.9965	0.7303	30.3758	0.8828	28.3788
90	0.9981	27.5412	0.7031	30.9205	0.8556	28.9235
120	0.8243	27.9985	0.5293	31.3778	0.6818	29.3808
150	0.7867	28.5245	0.4917	31.9038	0.6442	29.9068
180	0.6058	28.9541	0.3108	32.3334	0.4633	30.3364
210	0.5413	29.1163	0.2463	32.4956	0.3988	30.4986
240	0.4749	29.2315	0.1799	32.6108	0.3324	30.6138

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	30 °C
Initial dye Concentration	10 ppm
Solution pH	9.2
Volume of dye solution	50 ml

Appendix A-20 Effect of adsorbent doses on adsorption of methylene blue MB dye onto raw and modified pine cone at 30 mg

Time, t (min)	Raw Pine Cone PC		Modified Pine Cone PC1		Modified Pine Cone PC2	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	4.8068	17.3105	4.5103	18.6886	4.5857	17.92171
10	3.4235	21.9216	3.127	23.2997	3.2024	22.53281
20	2.3236	23.8542	2.0271	25.2323	2.1025	24.46541
40	1.8841	24.8654	1.5876	26.2435	1.663	25.47661
60	1.5686	25.3214	1.2721	26.6995	1.3475	25.93261
90	0.9944	25.9865	0.6979	27.3646	0.7733	26.59771
120	0.7976	26.5323	0.5011	27.9104	0.5765	27.14351
150	0.6564	27.5145	0.3599	28.8926	0.4353	28.12571
180	0.5888	27.9852	0.2923	29.3633	0.3677	28.59641
210	0.5504	28.2315	0.2539	29.6096	0.3293	28.84271
240	0.4652	28.6142	0.1687	29.9923	0.2441	29.22541

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	30 °C
Initial dye Concentration	10 ppm
Solution pH	9.2
Volume of dye solution	50 ml

Appendix A-21 Effect of Agitation Speed on adsorption of methylene blue MB dye onto raw and modified pine cone at 100 rpm

Time, t (min)	Raw Pine Cone PC		Modified Pine Cone PC1		Modified Pine Cone PC2	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	7.1426	9.5245	6.6294	12.7469	6.8005	11.2769
10	5.1723	16.0254	4.6591	19.2478	4.8302	17.7778
20	4.0755	19.7484	3.5623	22.9708	3.7334	21.5008
40	3.2987	22.3374	2.7855	25.5598	2.9566	24.0898
60	2.6298	24.5474	2.1166	27.7698	2.2877	26.2998
90	2.2216	25.9281	1.7084	29.1505	1.8795	27.6805
120	1.8428	27.8572	1.3296	31.0796	1.5007	29.6096
150	1.5583	28.1391	1.0451	31.3615	1.2162	29.8915
180	1.4922	28.2257	0.9792	31.4481	1.1501	29.9781
210	1.4502	28.5658	0.9372	31.7882	1.1081	30.3182
240	1.4131	29.1125	0.8999	32.3349	1.0712	30.8649

Experimental Conditions

Adsorbent dosage	15 gm
Experimental temperature	30 °C
Initial dye Concentration	10 ppm
Solution pH	9.2
Volume of dye solution	50 ml

Appendix A-22 Effect of Agitation Speed on adsorption of methylene blue MB dye onto raw and modified pine cone at 150 rpm

Time, t (min)	Raw Pine Cone PC		Modified Pine Cone PC1		Modified Pine Cone PC2	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	3.9564	20.1452	3.7153	23.2176	3.8138	21.7465
10	2.7488	24.1705	2.5077	27.2429	2.6062	25.7718
20	1.6092	27.969	1.3681	31.0414	1.4666	29.5703
40	1.3995	28.6682	1.1584	31.7406	1.2569	30.2695
60	1.1265	28.9832	0.8854	32.0556	0.9839	30.5845
90	0.9666	29.2144	0.7255	32.2868	0.8242	30.8157
120	0.8167	29.7854	0.5756	32.8578	0.6741	31.3867
150	0.7867	29.9856	0.5456	33.0582	0.6441	31.5869
180	0.6521	30.2856	0.4112	33.3582	0.5095	31.8869
210	0.5187	30.4446	0.2776	33.5171	0.3761	32.0459
240	0.4311	30.6123	0.1912	33.6847	0.2885	32.2136

Experimental Conditions

Adsorbent dosage	15 gm
Experimental temperature	30 °C
Initial dye Concentration	10 ppm
Solution pH	9.2
Volume of dye solution	50 ml

Appendix A-23 Effect of Agitation Speed on adsorption of methylene blue MB dye onto raw and modified pine cone at 200 rpm

Time, t (min)	Raw Pine Cone PC		Modified Pine Cone PC1		Modified Pine Cone PC2	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	3.3951	22.0161	3.1812	24.6724	3.28989	23.6385
10	2.2953	25.6823	2.0812	28.3386	2.19009	27.3047
20	1.3371	27.8761	1.1231	30.5324	1.23189	29.4985
40	1.2635	28.5425	1.0494	31.1988	1.15829	30.1649
60	1.1331	28.9865	0.9194	31.6428	1.02789	30.6089
90	0.9078	29.4213	0.6937	32.0776	0.80259	31.0437
120	0.8767	29.8563	0.6626	32.5126	0.77149	31.4787
150	0.7337	30.4123	0.5196	33.0686	0.62849	32.0347
180	0.6244	30.6891	0.4103	33.3454	0.51919	32.3115
210	0.5511	30.9985	0.3371	33.6548	0.44589	32.6209
240	0.4639	31.2231	0.2498	33.8794	0.35869	32.8455

Experimental Conditions

Adsorbent dosage	15 gm
Experimental temperature	30 °C
Initial dye Concentration	10 ppm
Solution pH	9.2
Volume of dye solution	50 ml

# Appendix B

Raw data for adsorption of methylene blue MB  
dye onto raw and modified pine leaves

Appendix B-1 Effect of Initial Solution pH on adsorption of methylene blue MB Dye onto raw and treated pine leaves at initial solution pH of 3.1

Time, t (min)	Raw Pine Leaves PL		Base Modified Pine Leaves PLBT		Aced Modified Pine Leaves PLAT	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	9.0929	3.0236	8.18166	4.0448	6.5715	8.3964
10	8.7697	4.1008	7.85846	5.1225	6.2483	9.4732
20	8.4806	5.0646	7.56936	6.0858	5.9592	10.4374
40	8.2481	5.8394	7.33686	6.8606	5.7267	11.2118
60	8.1744	6.0851	7.26316	7.1063	5.6537	11.4575
90	7.9477	6.8411	7.03646	7.8623	5.4263	12.2135
120	7.8683	7.1056	6.95706	8.1268	5.3469	12.4787
150	7.5451	8.1828	6.63386	9.2045	5.0237	13.5552
180	7.3694	8.7686	6.45816	9.7898	4.8484	14.1412
210	7.6755	7.7481	6.76426	8.7693	5.1541	13.1205
240	7.4884	8.3718	6.57716	9.3931	4.9672	13.7442

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Initial dye concentration	10 ppm
Volume of dye solution	50 ml

Appendix B-2 Effect of Initial Solution pH on adsorption of methylene blue MB Dye onto raw and treated pine leaves at initial solution pH of 5.01

Time, t (min)	Raw Pine Leaves PL		Base Modified Pine Leaves PLBT		Aced Modified Pine Leaves PLAT	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	6.3035	12.3215	5.8515	14.3217	5.3357	16.3498
10	5.4248	15.2507	4.9728	17.2502	4.4563	19.2797
20	4.6367	17.8774	4.1847	19.8765	3.6682	21.9053
40	4.2455	19.1814	3.7935	21.1809	3.2777	23.2097
60	3.8146	20.6177	3.3626	22.6172	2.8461	24.6464
90	3.3555	22.1484	2.9035	24.1479	2.387	26.1767
120	3.2988	22.3374	2.8468	24.3369	2.3303	26.3657
150	3.2364	22.5453	2.7844	24.5448	2.2679	26.5736
180	2.8282	23.9059	2.3762	25.9054	1.8597	27.9342
210	2.9586	23.4713	2.5066	25.4708	1.9901	27.4996
240	2.8565	23.8114	2.4045	25.8109	1.8882	27.8397

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Initial dye concentration	10 ppm
Volume of dye solution	50 ml

Appendix B-3 Effect of Initial Solution pH on adsorption of methylene blue MB dye onto raw and treated pine leaves at initial solution pH of 7.06

Time ,t (min)	Raw Pine Leaves PL		Base Modified Pine Leaves PLBT		Acid Modified Pine Leaves PLAT	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	5.3907	15.3641	4.9407	18.3642	4.5807	21.1498
10	4.7898	17.3672	4.3398	20.3671	3.9798	23.1529
20	4.1492	19.5027	3.6992	22.5026	3.3392	25.2884
40	4.2059	19.3137	3.7559	22.3136	3.3959	25.0994
60	3.4802	21.7326	3.0302	24.7325	2.6702	27.5183
90	3.2457	22.8476	2.7957	25.8475	2.4357	28.6333
120	3.0153	23.2823	2.5653	26.2822	2.2053	29.0684
150	2.8055	23.6115	2.3555	26.6114	1.9955	29.3972
180	2.6921	23.7512	2.2421	26.7511	1.8821	29.5369
210	2.5885	23.8382	2.1385	26.8381	1.7785	29.6239
240	2.4168	23.9437	1.9668	26.9436	1.6068	29.7294

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Initial dye concentration	10 ppm
Volume of dye solution	50 ml

Appendix B-4 Effect of Initial Solution pH on adsorption of methylene blue MB dye onto raw and treated pine leaves at initial solution pH of 9.2

Time ,t (min)	Raw Pine Leaves PL		Base Modified Pine Leaves PLBT		Aced Modified Pine Leaves PLAT	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	4.8862	17.0459	4.6762	17.7458	3.8362	21.951
10	4.5801	18.0665	4.3701	18.7664	3.5301	22.9716
20	3.3895	22.0351	3.1795	22.7355	2.3395	26.9402
40	2.6751	24.4162	2.4651	25.1161	1.6251	29.3213
60	2.4881	25.0398	2.2781	25.7397	1.4381	29.9449
90	2.1479	26.1737	1.9379	26.8736	1.0979	31.0788
120	2.0855	26.3816	1.8755	27.0815	1.0355	31.2867
150	2.0458	26.5139	1.8358	27.2138	0.9958	31.4194
180	1.9268	26.9107	1.7168	27.6106	0.8768	31.8158
210	1.9891	26.7028	1.7791	27.4027	0.9391	31.6079
240	1.9551	26.8162	1.7451	27.5161	0.9051	31.7213

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Initial dye concentration	10 ppm
Volume of dye solution	50 ml

Appendix B-5 Effect of Initial dye concentration on adsorption of methylene blue MB dye onto raw and modified pine leaves at initial dye conc. of 10 ppm

Time ,t (min)	Raw Pine Leaves PL		Base Modified Pine Leaves PLBT		Aced Modified Pine Leaves PLAT	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	4.8862	17.0459	4.6762	17.7458	3.8362	21.951
10	4.5801	18.0665	4.3701	18.7664	3.5301	22.9716
20	3.3895	22.0351	3.1795	22.7355	2.3395	26.9402
40	2.6751	24.4162	2.4651	25.1161	1.6251	29.3213
60	2.4881	25.0398	2.2781	25.7397	1.4381	29.9449
90	2.1479	26.1737	1.9379	26.8736	1.0979	31.0788
120	2.0855	26.3816	1.8755	27.0815	1.0355	31.2867
150	2.0458	26.5139	1.8358	27.2138	0.9958	31.4194
180	1.9268	26.9107	1.7168	27.6106	0.8768	31.8158
210	1.9891	26.7028	1.7791	27.4027	0.9391	31.6079
240	1.9551	26.8162	1.7451	27.5161	0.9051	31.7213

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Solution pH	9.2
Volume of dye solution	50 ml

Appendix B-6 Effect of Initial dye concentration on adsorption of methylene blue MB dye onto raw and modified pine leaves at initial dye conc. of 40 ppm

Time ,t (min)	Raw Pine Leaves PL		Base Modified Pine Leaves PLBT		Aced Modified Pine Leaves PLAT	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	25.1202	49.5991	23.6202	54.4825	18.8002	68.9497
10	23.3968	55.3441	21.8968	60.2275	17.0768	74.6947
20	22.1268	59.5772	20.6268	64.4606	15.8068	78.9278
40	18.7705	70.7648	17.2705	75.6482	12.4505	90.1154
60	17.1831	76.0563	15.6831	80.9397	10.8631	95.4069
90	15.641	81.1965	14.1414	86.0799	9.3214	100.5471
120	13.0558	89.8141	11.5558	94.6975	6.7358	109.1647
150	10.4705	98.4315	8.9705	103.3149	4.1505	117.7821
180	9.8355	100.5481	8.3355	105.4315	3.5155	119.8987
210	10.5159	98.2803	9.0159	103.1637	4.1959	117.6309
240	9.8809	100.3969	8.3809	105.2803	3.5609	119.7475

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Solution pH	9.2
Volume of dye solution	50 ml

Appendix B-7 Effect of Initial dye concentration on adsorption of methylene blue MB dye onto raw and modified pine leaves at initial dye conc. of 70 ppm

Time ,t (min)	Raw Pine Leaves PL		Base Modified Pine Leaves PLBT		Aced Modified Pine Leaves PLAT	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	58.0886	39.7046	56.0886	45.6731	53.0886	67.1099
10	48.0084	73.3052	46.0084	79.2737	43.0084	100.7105
20	40.7856	97.3813	38.7856	103.3498	35.7856	124.7866
40	38.9601	103.4665	36.9601	109.435	33.9601	130.8718
60	36.8964	110.3453	34.8964	116.3138	31.8964	137.7506
90	36.0233	113.2556	34.0233	119.2241	31.0233	140.6609
120	35.7058	114.3139	33.7058	120.2824	30.7058	141.7192
150	35.4677	115.1076	33.4677	121.0761	30.4677	142.5129
180	35.3089	115.6368	33.3089	121.6053	30.3089	143.0421
210	35.3883	115.3722	33.3883	121.3407	30.3883	142.7775
240	35.2296	115.9014	33.2296	121.8699	30.2296	143.3067

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Solution pH	9.2
Volume of dye solution	50 ml

Appendix B-8 Effect of Initial dye concentration on adsorption of methylene blue MB dye onto raw and modified pine leaves at initial dye conc. of 90 ppm

Time ,t (min)	Raw Pine Leaves PL		Base Modified Pine Leaves PLBT		Aced Modified Pine Leaves PLAT	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	78.3591	38.8029	70.1446	48.8644	64.1272	65.4265
10	65.7057	80.9832	57.4905	91.0447	51.4731	107.6068
20	60.6025	97.9914	52.3887	108.0529	46.3706	124.6155
40	58.0513	106.4955	49.8368	116.557	43.8194	133.1191
60	56.3165	112.2783	48.1025	122.3398	42.0846	138.9019
90	54.9898	116.7004	46.7753	126.7619	40.7579	143.3244
120	54.2755	119.0816	46.0614	129.1431	40.0436	145.7052
150	54.1734	119.4217	45.9589	129.4832	39.9415	146.0453
180	53.6632	121.1226	45.4487	131.1841	39.4313	147.7462
210	54.0714	119.7619	45.8569	129.8234	39.8395	146.3855
240	54.0714	119.7619	45.8569	129.8234	39.8395	146.3855

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Solution pH	9.2
Volume of dye solution	50 ml

Appendix B-9 Effect of inorganic Monovalent Salt Concentration on adsorption of methylene blue MB dye onto raw and modified pine leaves at initial NaCl concentrations of 50 mg L<sup>-1</sup>

Time ,t (min)	Raw Pine Leaves PL		Base Modified Pine Leaves PLBT		Aced Modified Pine Leaves PLAT	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	6.8478	10.5073	6.0978	12.9342	4.9478	16.934
10	6.2808	12.3971	5.5308	14.8247	4.3808	18.8238
20	5.4758	15.0806	4.7258	17.5075	3.5758	21.5073
40	4.6991	17.6696	3.9491	20.0965	2.7991	24.0963
60	4.1832	19.3893	3.4332	21.8162	2.2832	25.8165
90	3.8431	20.5232	3.0931	22.9501	1.9431	26.9499
120	3.4859	21.7138	2.7359	24.1407	1.5859	28.1405
150	3.6503	21.4657	2.9003	23.8926	1.7503	27.8924
180	3.8771	20.4098	3.1271	22.8367	1.9771	26.8365
210	3.3668	22.1106	2.6168	24.5375	1.4668	28.5373
240	3.3044	22.3185	2.5544	24.7454	1.4044	28.7452

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Solution pH	9.2
Volume of dye solution	50 ml
Initial dye Concentration	10 ppm

Appendix B-10 Effect of inorganic Monovalent Salt Concentration on adsorption of methylene blue MB dye onto raw and modified pine leaves at initial NaCl concentrations of 100 mg L<sup>-1</sup>

Time ,t (min)	Raw Pine Leaves PL		Base Modified Pine Leaves PLBT		Aced Modified Pine Leaves PLAT	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	7.0519	9.8269	6.3391	12.0925	4.7649	17.0152
10	6.3149	12.2836	5.6021	14.5492	4.0279	19.4719
20	6.2015	12.6616	5.4887	14.9272	3.9145	19.8499
40	4.9882	16.7058	4.2754	18.9714	2.7012	23.8941
60	4.4893	18.3688	3.7765	20.6344	2.2023	25.5571
90	3.9167	20.2775	3.2039	22.5431	1.6297	27.4658
120	3.7636	20.7878	3.0508	23.0534	1.4766	27.9761
150	3.7523	20.8255	3.0395	23.0911	1.4653	28.0138
180	3.7296	20.9011	3.0168	23.1667	1.4426	28.0894
210	3.7183	20.9389	3.0055	23.2045	1.4313	28.1272
240	3.9526	19.9428	3.2398	22.2084	1.6656	27.1311

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Solution pH	9.2
Volume of dye solution	50 ml
Initial dye Concentration	10 ppm

Appendix B-11 Effect of inorganic Monovalent Salt Concentration on adsorption of methylene blue MB dye onto raw and modified pine leaves at initial NaCl concentrations of 150 mg L<sup>-1</sup>

Time ,t (min)	Raw Pine Leaves PL		Base Modified Pine Leaves PLBT		Aced Modified Pine Leaves PLAT	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	7.5168	8.2773	6.6979	11.5444	5.0879	16.2686
10	6.9385	10.2049	6.1196	13.472	4.5096	18.1962
20	6.3375	12.2081	5.5186	15.4752	3.9086	20.1994
40	5.6345	14.5514	4.8156	17.8185	3.2056	22.5427
60	5.1234	16.2522	4.3045	19.5193	2.6945	24.2435
90	4.5007	18.3311	3.6818	21.5982	2.0718	26.3224
120	4.4099	18.6334	3.5914	21.9005	1.9814	26.6247
150	4.2796	18.0681	3.4607	21.3352	1.8507	26.0594
180	4.0358	17.8807	3.2169	21.1478	1.6069	25.8724
210	4.1038	17.6538	3.2849	20.9209	1.6749	25.6451
240	4.0131	17.9413	3.1942	21.2084	1.5842	25.9326

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Solution pH	9.2
Volume of dye solution	50 ml
Initial dye Concentration	10 ppm

Appendix B-12 Effect of inorganic Monovalent Salt Concentration on adsorption of methylene blue MB dye onto raw and modified pine leaves at initial NaCl concentrations of 200 mg L<sup>-1</sup>

Time ,t (min)	Raw Pine Leaves PL		Base Modified Pine Leaves PLBT		Aced Modified Pine Leaves PLAT	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	7.7719	7.4269	7.0521	9.6413	6.1242	13.1624
10	7.3411	8.8631	6.6213	11.0775	5.6934	14.5986
20	6.8251	10.5828	6.1053	12.7972	5.1774	16.3183
40	6.7684	10.7718	6.0486	12.9862	5.1207	16.5073
60	5.4134	15.2884	4.6936	17.5028	3.7657	21.0239
90	4.7728	16.4239	4.0534	18.6383	3.1251	22.1594
120	4.6764	16.7452	3.9566	18.9596	3.0287	22.4807
150	4.5007	17.3311	3.7809	19.5455	2.8535	23.0666
180	4.2002	18.3326	3.4804	20.547	2.5525	24.0681
210	4.1172	16.2759	3.3974	18.4903	2.4695	22.0114
240	4.1888	16.3404	3.4694	18.5548	2.5411	22.0759

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Experimental temperature	30 °C
Solution pH	9.2
Volume of dye solution	50 ml
Initial dye Concentration	10 ppm

Appendix B-13 Effect of temperature on adsorption of methylene blue MB dye onto raw and modified pine leaves at 30 °C

Time ,t (min)	Raw Pine Leaves PL		Base Modified Pine Leaves PLBT		Aced Modified Pine Leaves PLAT	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	4.8862	17.0459	4.6762	17.7458	3.8362	21.951
10	4.5801	18.0665	4.3701	18.7664	3.5301	22.9716
20	3.3895	22.0351	3.1795	22.7355	2.3395	26.9402
40	2.6751	24.4162	2.4651	25.1161	1.6251	29.3213
60	2.4881	25.0398	2.2781	25.7397	1.4381	29.9449
90	2.1479	26.1737	1.9379	26.8736	1.0979	31.0788
120	2.0855	26.3816	1.8755	27.0815	1.0355	31.2867
150	2.0458	26.5139	1.8358	27.2138	0.9958	31.4194
180	1.9268	26.9107	1.7168	27.6106	0.8768	31.8158
210	1.9891	26.7028	1.7791	27.4027	0.9391	31.6079
240	1.9551	26.8162	1.7451	27.5161	0.9051	31.7213

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Initial dye Concentration	10 ppm
Solution pH	9.2
Volume of dye solution	50 ml

Appendix B-14 Effect of temperature on adsorption of methylene blue MB dye onto raw and modified pine leaves at 40 °C

Time ,t (min)	Raw Pine Leaves PL		Base Modified Pine Leaves PLBT		Aced Modified Pine Leaves PLAT	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	5.7706	14.0979	5.0206	16.5106	4.4506	20.838
10	4.2852	19.0491	3.5352	21.4618	2.9652	25.7892
20	2.6865	24.3784	1.9365	26.7911	0.9213	31.1185
40	2.4767	25.0776	1.7267	27.4903	0.9012	31.8177
60	1.7113	27.6288	0.9613	30.0415	0.8423	34.3689
90	0.9913	28.0289	0.9521	30.4416	0.8212	34.7694
120	0.9289	28.2368	0.9321	30.6495	0.8121	34.9769
150	0.8779	28.4068	0.9563	30.8195	0.8014	35.1469
180	0.3979	29.0699	0.9123	31.4826	0.7951	35.8141
210	0.3584	29.8053	0.8632	32.2184	0.7745	36.5454
240	0.4187	28.3376	0.9856	30.7503	0.7995	35.0777

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Initial dye Concentration	10 ppm
Solution pH	9.2
Volume of dye solution	50 ml

Appendix B-15 Effect of temperature on adsorption of methylene blue MB dye onto raw and modified pine leaves at 50 °C

Time ,t (min)	Raw Pine Leaves PL		Base Modified Pine Leaves PLBT		Aced Modified Pine Leaves PLAT	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	5.6506	14.3512	5.3506	17.0015	5.3006	22.0148
10	4.1652	19.6742	3.8652	22.3245	3.8152	27.3378
20	2.5665	24.5862	2.2665	27.2365	2.2165	32.2498
40	2.3567	25.1942	2.0567	27.8445	2.0067	32.8578
60	1.5913	28.3214	1.2913	30.9717	1.2413	35.9854
90	0.8713	28.0865	0.5713	30.7368	0.5213	35.7501
120	0.8541	28.4213	0.5541	31.0716	0.5041	36.0849
150	0.8214	28.9865	0.5214	31.6368	0.4714	36.6501
180	0.5412	29.0984	0.2412	31.7487	0.1912	36.7624
210	0.3215	29.9862	0.2251	32.6365	0.1524	37.6498
240	0.4122	29.3652	0.2012	32.0155	0.1654	37.0288

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Initial dye Concentration	10 ppm
Solution pH	9.2
Volume of dye solution	50 ml

Appendix B-16      Effect of temperature on adsorption of methylene blue MB dye onto raw and modified pine leaves at 60 °C

Time ,t (min)	Raw Pine Leaves PL		Base Modified Pine Leaves PLBT		Aced Modified Pine Leaves PLAT	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	5.5665	14.7782	5.4636	17.9867	5.3936	24.1105
10	3.9961	20.0129	3.8932	23.2214	3.8232	29.3452
20	2.5504	24.8319	2.4475	28.0404	2.3775	34.1642
40	2.3803	25.3989	2.2774	28.6074	2.2074	34.7312
60	1.2238	29.2541	1.1209	32.4626	1.0509	38.5864
90	0.9516	29.1612	0.8487	32.3697	0.7787	38.4935
120	0.8212	30.5958	0.7183	33.8043	0.6483	39.9281
150	0.5831	31.3895	0.4802	34.5987	0.4102	40.7218
180	0.3627	31.1266	0.2591	34.3351	0.1891	40.4589
210	0.3904	30.0321	0.2875	33.2406	0.2175	39.3644
240	0.3117	30.2966	0.2081	33.5051	0.1381	39.6289

Experimental Conditions

Shaking speed	150 rpm
Adsorbent dosage	15 mg
Initial dye Concentration	10 ppm
Solution pH	9.2
Volume of dye solution	50 ml

Appendix B-17 Effect of adsorbent doses on adsorption of methylene blue MB dye onto raw and modified pine leaves at 10 mg

Time, t (min)	Raw Pine Leaves PL		Base Modified Pine Leaves PLBT		Aced Modified Pine Leaves PLAT	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	5.1697	16.1011	4.8697	17.4142	3.8697	21.0136
10	4.8862	17.0459	4.5862	18.359	3.5862	21.9584
20	3.4688	21.7705	3.1688	23.0836	2.1688	26.683
40	2.8679	23.7736	2.5679	25.0867	1.5679	28.6861
60	1.9891	26.7028	1.4856	28.0159	0.6891	31.6153
90	1.7083	26.9722	1.5956	28.2853	0.4083	31.8847
120	1.5212	27.0012	1.5998	28.3143	0.2212	31.9137
150	1.5121	27.1025	1.5684	28.4156	0.2121	32.015
180	1.4856	28.0121	1.4521	29.3252	0.1856	32.9246
210	1.5956	27.5412	1.4875	28.8543	0.2956	32.4537
240	1.5998	27.2112	1.4254	28.5243	0.2998	32.1237

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	30 °C
Initial dye Concentration	10 ppm
Solution pH	9.2
Volume of dye solution	50 ml

Appendix B-18 Effect of adsorbent doses on adsorption of methylene blue MB dye onto raw and modified pine leaves at 15 mg

Time ,t (min)	Raw Pine Leaves PL		Base Modified Pine Leaves PLBT		Aced Modified Pine Leaves PLAT	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	4.8862	17.0459	4.6762	17.7458	3.8362	21.951
10	4.5801	18.0665	4.3701	18.7664	3.5301	22.9716
20	3.3895	22.0351	3.1795	22.7355	2.3395	26.9402
40	2.6751	24.4162	2.4651	25.1161	1.6251	29.3213
60	2.4881	25.0398	2.2781	25.7397	1.4381	29.9449
90	2.1479	26.1737	1.9379	26.8736	1.0979	31.0788
120	2.0855	26.3816	1.8755	27.0815	1.0355	31.2867
150	2.0458	26.5139	1.8358	27.2138	0.9958	31.4194
180	1.9268	26.9107	1.7168	27.6106	0.8768	31.8158
210	1.9891	26.7028	1.7791	27.4027	0.9391	31.6079
240	1.9551	26.1162	1.7451	27.8161	0.9051	31.1213

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	30 °C
Initial dye Concentration	10 ppm
Solution pH	9.05
Volume of dye solution	50 ml

Appendix B-19 Effect of adsorbent doses on adsorption of methylene blue MB dye onto raw and modified pine leaves at 20 mg

Time, t (min)	Raw Pine Leaves PL		Base Modified Pine Leaves PLBT		Aced Modified Pine Leaves PLAT	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	5.4403	8.9447	5.2903	12.0526	5.0903	16.3656
10	4.8393	10.9479	4.6893	14.0558	4.4893	18.3688
20	3.6261	14.7091	3.4761	17.817	3.2761	22.13
40	3.0081	17.052	2.8581	20.1599	2.6581	24.4729
60	2.8542	19.9812	2.7541	23.0891	1.7793	27.4021
90	2.3125	20.778	2.5412	23.8859	0.9403	28.1989
120	2.3254	21.9859	2.3214	25.0938	0.8779	29.4068
150	2.5412	22.158	2.3251	25.2659	0.8269	29.5789
180	2.1245	23.46	2.2145	26.5679	0.4357	30.8809
210	2.4512	22.1387	2.3512	25.2466	0.5321	29.5596
240	2.5421	22.2135	2.3514	25.3214	0.4527	29.6344

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	30 °C
Initial dye Concentration	10 ppm
Solution pH	9.2
Volume of dye solution	50 ml

Appendix B-20 Effect of adsorbent doses on adsorption of methylene blue MB dye onto raw and modified pine leaves at 30 mg

Time, t (min)	Raw Pine Leaves PL		Base Modified Pine Leaves PLBT		Aced Modified Pine Leaves PLAT	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	6.0965	6.8839	5.8265	10.2141	5.5765	14.5846
10	4.5161	8.8871	4.2461	12.2173	3.9961	16.5878
20	3.0904	12.6483	2.8204	15.9785	2.5704	20.349
40	2.9003	14.9912	2.6303	18.3214	2.3803	22.6919
60	1.7438	17.9204	1.4738	21.2506	1.2238	25.6211
90	1.4716	18.7172	1.2016	22.0474	0.9516	26.4179
120	1.3412	19.9251	1.0712	23.2553	0.8212	27.6258
150	1.1031	20.0972	0.8331	23.4274	0.5831	27.7979
180	0.8842	21.3992	0.6142	24.7294	0.3642	29.0999
210	0.9104	20.0779	0.6404	23.4081	0.3904	27.7786
240	0.8511	20.1527	0.5811	23.4829	0.3311	27.8534

Experimental Conditions

Shaking speed	150 rpm
Experimental temperature	30 °C
Initial dye Concentration	10 ppm
Solution pH	9.2
Volume of dye solution	50 ml

Appendix B-21 Effect of Agitation Speed on adsorption of methylene blue MB dye onto raw and modified pine leaves at 100 rpm

Time, t (min)	Raw Pine Leaves PL		Base Modified Pine Leaves PLBT		Aced Modified Pine Leaves PLAT	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	7.7719	7.4269	5.5471	12.2168	3.9501	17.6584
10	7.3411	8.8631	5.1163	13.6534	3.5193	19.0942
20	6.8251	10.5828	4.6003	15.3727	3.0033	20.8139
40	6.7684	10.7718	4.5436	15.5617	2.9466	21.0029
60	5.4134	15.2884	3.1886	20.0783	1.5916	25.5195
90	4.7728	15.4239	2.5484	20.2138	0.9514	25.6554
120	4.6764	15.7452	2.4516	20.5351	0.8546	25.9763
150	4.5007	15.8311	2.2759	20.6214	0.6789	26.0622
180	4.2002	13.3326	1.9754	18.1225	0.3784	23.5637
210	4.1172	16.0759	1.8924	20.8658	0.2954	26.3074
240	4.1888	15.9823	1.9645	20.7722	0.3674	26.2134

Experimental Conditions

Adsorbent dosage	15 gm
Experimental temperature	30 °C
Initial dye Concentration	10 ppm
Solution pH	9.2
Volume of dye solution	50 ml

Appendix B-22 Effect of Agitation Speed on adsorption of methylene blue MB dye onto raw and modified pine leaves at 150 rpm

Time ,t (min)	Raw Pine Leaves PL		Base Modified Pine Leaves PLBT		Aced Modified Pine Leaves PLAT	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	4.8862	17.0459	4.6762	17.7458	3.8362	21.951
10	4.5801	18.0665	4.3701	18.7664	3.5301	22.9716
20	3.3895	22.0351	3.1795	22.7355	2.3395	26.9402
40	2.6751	24.4162	2.4651	25.1161	1.6251	29.3213
60	2.4881	25.0398	2.2781	25.7397	1.4381	29.9449
90	2.1479	26.1737	1.9379	26.8736	1.0979	31.0788
120	2.0855	26.3816	1.8755	27.0815	1.0355	31.2867
150	2.0458	26.5139	1.8358	27.2138	0.9958	31.4194
180	1.9268	26.9107	1.7168	27.6106	0.8768	31.8158
210	1.9891	26.7028	1.7791	27.4027	0.9391	31.6079
240	1.9551	26.8162	1.7451	27.5161	0.9051	31.7213

Experimental Conditions

Adsorbent dosage	15 gm
Experimental temperature	30 °C
Initial dye Concentration	10 ppm
Solution pH	9.2
Volume of dye solution	50 ml

Appendix B-23 Effect of Agitation Speed on adsorption of methylene blue MB dye onto raw and modified pine leaves at 200 rpm

Time ,t (min)	Raw Pine Leaves PL		Base Modified Pine Leaves PLBT		Aced Modified Pine Leaves PLAT	
	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)	C <sub>t</sub> (mg/L)	q <sub>t</sub> (mg/g)
0	0.0	0.0	0.0	0.0	0.0	0.0
5	6.3587	11.8365	5.0669	13.8672	4.372	16.8759
10	5.9034	15.2381	4.6116	17.2688	3.9167	20.2775
20	4.0176	21.1914	2.7258	23.2217	2.0309	26.2304
40	3.4826	23.3075	2.1908	25.3382	1.4959	28.3469
60	3.3522	23.7422	2.0604	25.7729	1.3655	28.7816
90	2.9383	25.1218	1.6465	27.1525	0.9516	30.1612
120	2.7569	25.7265	1.4651	27.7572	0.7702	30.7659
150	2.5812	26.3123	1.2894	28.343	0.5945	31.3517
180	2.3601	27.0494	1.0683	29.0801	0.3734	32.0888
210	2.4734	26.6714	1.1816	28.7021	0.4867	31.7108
240	2.3771	27.9527	1.0853	29.9834	0.3904	32.9921

Experimental Conditions

Adsorbent dosage	15 gm
Experimental temperature	30 °C
Initial dye Concentration	10 ppm
Solution pH	9.2
Volume of dye solution	50 ml

# Appendix C

Adsorption of methylene blue MB dye onto raw  
pine cone powder (Packed Bed Column)



Appendix C-2      Effect of Flow Rate on adsorption of methylene blue MB dye onto raw pine cone at 12 ml/min (Packed Bed Column)

Time ,t (min)	C <sub>t</sub> (mg/L)	C <sub>t</sub> /C <sub>0</sub>	Time ,t (min)	C <sub>t</sub> (mg/L)	C <sub>t</sub> /C <sub>0</sub>
5	0	0	210	34.664	0.4952
10	0	0	225	39.361	0.5623
15	0	0	240	40.469	0.5777
20	0	0	255	44.464	0.6352
25	0	0	270	47.684	0.6812
30	0	0	285	49.105	0.7015
40	0.231	0.0033	300	52.185	0.7455
50	0.308	0.0044	320	56.203	0.8029
60	0.567	0.0081	340	59.486	0.8498
75	0.987	0.0141	360	61.593	0.8799
90	1.477	0.0211	380	64.652	0.9236
105	3.577	0.0511	400	65.877	0.9411
120	4.963	0.0709	425	67.907	0.9701
135	6.986	0.0998	450	68.796	0.9828
150	9.786	0.1398	475	69.283	0.9898
165	18.277	0.2611	500	69.363	0.9909
180	25.907	0.3701	525	70	1
195	28.777	0.4111			

Experimental Conditions

Column bed Height	12 cm
Experimental temperature	30 °C
Initial dye Concentration	70 ppm

Appendix C-3      Effect of Flow Rate on adsorption of methylene blue MB dye onto raw pine cone at 15 ml/min (Packed Bed Column)

Time ,t (min)	C <sub>t</sub> (mg/L)	C <sub>t</sub> /C <sub>0</sub>	Time ,t (min)	C <sub>t</sub> (mg/L)	C <sub>t</sub> /C <sub>0</sub>
5	0	0	180	39.487	0.5641
10	0	0	195	42.945	0.6135
15	0	0	210	46.823	0.6689
20	0	0	225	48.776	0.6968
25	0	0	240	50.554	0.7222
30	0.259	0.0037	255	53.585	0.7655
40	0.777	0.0111	270	56.847	0.8121
50	1.687	0.0241	285	59.948	0.8564
60	3.108	0.0444	300	62.216	0.8888
75	3.606	0.0658	320	65.562	0.9366
90	7.707	0.1101	340	67.116	0.9588
105	13.993	0.1999	360	67.893	0.9699
120	20.293	0.2899	380	68.439	0.9777
135	26.978	0.3854	400	68.516	0.9788
150	31.983	0.4569	425	69.223	0.9889
165	37.247	0.5321	445	70	1

Experimental Conditions

Column bed Height	12 cm
Experimental temperature	30 °C
Initial dye Concentration	70 ppm

Appendix C-4      Effect of initial Dye concentration on adsorption of methylene blue MB dye onto raw pine cone at 50 ppm (Packed Column)

Time ,t (min)	C <sub>t</sub> (mg/L)	C <sub>t</sub> /C <sub>o</sub>	Time ,t (min)	C <sub>t</sub> (mg/L)	C <sub>t</sub> /C <sub>o</sub>
5	0	0	240	20.625	0.4125
10	0	0	255	24.76	0.4952
15	0	0	270	26.705	0.5341
20	0	0	285	29.94	0.5988
25	0	0	300	31.055	0.6211
30	0	0	320	34.27	0.6854
40	0	0	340	35.625	0.7125
50	0	0	360	37.775	0.7555
60	0	0	380	41.005	0.8201
75	0.275	0.0055	400	43.055	0.8611
90	0.855	0.0171	425	45.005	0.9001
105	1.29	0.0258	450	46.44	0.9288
120	1.505	0.0301	475	47.105	0.9421
135	1.69	0.0338	500	48.495	0.9699
150	2.705	0.0541	525	48.695	0.9739
165	5.105	0.1021	550	49.275	0.9855
180	6.23	0.1246	575	49.345	0.9869
195	9.495	0.1899	600	49.585	0.9917
210	11.28	0.2256	620	50	1
225	16.38	0.3276			

Experimental Conditions

Column bed Height	12 cm
Experimental temperature	30 °C
Flow Rate	12 ml/min





Appendix C-7      Effect of Column Bed Height on adsorption of methylene blue  
MB dye onto raw pine cone at 10 cm (Packed Bed Column)

Time ,t (min)	C <sub>t</sub> (mg/L)	C <sub>t</sub> /C <sub>o</sub>	Time ,t (min)	C <sub>t</sub> (mg/L)	C <sub>t</sub> /C <sub>o</sub>
5	0	0	180	38.969	0.5567
10	0	0	195	43.254	0.6179
15	0	0	210	47.219	0.6746
20	0	0	225	49.126	0.7018
25	0	0	240	51.225	0.7318
30	0.298	0.0043	255	54.231	0.7747
40	0.801	0.0114	270	57.108	0.8158
50	1.712	0.0244	285	60.186	0.8598
60	3.214	0.0459	300	63.142	0.9021
75	3.712	0.0531	320	66.228	0.9461
90	7.698	0.1099	340	67.852	0.9693
105	14.215	0.2031	360	68.208	0.9744
120	21.365	0.3052	380	68.858	0.9837
135	27.568	0.3938	400	69.189	0.9884
150	32.658	0.4665	425	69.953	0.9993
165	36.985	0.5283	455	70	1

Experimental Conditions

Initial dye Concentration	70 ppm
Experimental temperature	30 °C
Flow Rate	12 ml/min

Appendix C-8      Effect of Column Bed Height on adsorption of methylene blue  
MB dye onto raw pine cone at 12 cm (Packed Bed Column)

Time ,t (min)	C <sub>t</sub> (mg/L)	C <sub>t</sub> /C <sub>0</sub>	Time ,t (min)	C <sub>t</sub> (mg/L)	C <sub>t</sub> /C <sub>0</sub>
5	0	0	210	34.664	0.4952
10	0	0	225	39.361	0.5623
15	0	0	240	40.439	0.5777
20	0	0	255	44.464	0.6352
25	0	0	270	47.684	0.6812
30	0	0	285	49.105	0.7015
40	0.231	0.0033	300	52.185	0.7455
50	0.308	0.0044	320	56.203	0.8029
60	0.567	0.0081	340	59.486	0.8498
75	0.987	0.0141	360	61.593	0.8799
90	1.477	0.0211	380	64.652	0.9236
105	3.577	0.0511	400	65.877	0.9411
120	4.963	0.0709	425	67.907	0.9701
135	6.986	0.0998	450	68.796	0.9828
150	9.786	0.1398	475	69.286	0.9898
165	18.277	0.2611	500	69.363	0.9909
180	25.907	0.3701	525	70	1
195	28.777	0.4111			

Experimental Conditions

Initial dye Concentration                      70 ppm  
 Experimental temperature                      30 °C  
 Flow Rate    12 ml/min

Appendix C-9      Effect of Column Bed Height on adsorption of methylene blue  
MB dye onto raw pine cone at 15 cm (Packed Bed Column)

Time ,t (min)	C <sub>t</sub> (mg/L)	C <sub>t</sub> /C <sub>0</sub>	Time ,t (min)	C <sub>t</sub> (mg/L)	C <sub>t</sub> /C <sub>0</sub>
5	0	0	240	27.923	0.3989
10	0	0	255	34.013	0.4859
15	0	0	270	38.206	0.5458
20	0	0	285	43.806	0.6258
25	0	0	300	45.206	0.6458
30	0	0	320	48.384	0.6912
40	0	0	340	50.806	0.7258
50	0	0	360	53.886	0.7698
60	0	0	380	58.135	0.8305
75	0.462	0.0066	400	61.488	0.8784
90	1.309	0.0189	425	63.847	0.9121
105	1.946	0.0278	450	65.275	0.9325
120	2.261	0.0323	475	66.878	0.9554
135	2.436	0.0348	500	67.907	0.9701
150	4.109	0.0587	525	68.586	0.9798
165	7.756	0.1108	550	69.146	0.9878
180	9.492	0.1356	575	69.307	0.9901
195	12.523	0.1789	600	69.657	0.9951
210	16.275	0.2325	625	69.888	0.9984
225	22.386	0.3198	650	70	1

Experimental Conditions

Initial dye Concentration	70 ppm
Experimental temperature	30 °C
Flow Rate	12 ml/min