ADSORPTION OF METHYLENE BLUE FROM AQUOUES SOLUTION BY USING IMPRATA CYLINDRICA WASTE

FATIN NADIA BINTI PAUZI

BACHELOR OF CHEMICAL ENGINEERING
UNIVERSITI MALAYSIA PAHANG

Thesis Access Form

No__________________________Location____________________________

Author: Fatin Nadia Binti Pauzi

Title: Adsorption of methylene blue from aquoues solution by using imprata cylindrica waste

Status of access OPEN / RESTRICTED / CONFIDENTIAL

Moratorium period:_____________ years, ending__________/______200____

Conditions of access proved by (CAPITALS): DR HERMA DINA BINTI SETIABUDI

Supervisor (Signature)………………………………………………

Faculty: ………………………………

Author’s Declaration: *I agree the following conditions:*

OPEN access work shall be made available in the Universiti Malaysia Pahang only and not allowed to reproduced for any purpose.

The statement itself shall apply to ***ALL*** *copies:*

This copy has been supplied on the understanding that it is copyright material and that no quotation from the thesis may be published without proper acknowledgement.

Restricted/confidential work: All access and any photocopying shall be strictly subject to written permission from the University Head of Department and any external sponsor, if any.

Author's signature………………………………………Date: ………………………………

users declaration: for signature during any Moratorium period (Not Open work):
I undertake to uphold the above conditions:

Date	Name (CAPITALS)	Signature	Address

ADSORPTION OF METHYLENE BLUE FROM AQUOUES SOLUTION BY USING IMPRATA CYLINDRICA WASTE

FATIN NADIA BINTI PAUZI

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

2015

SUPERVISOR’S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality of the award of the degree of Bachelor of Chemical Engineering (Pure).

Signature :
Name of main supervisor : DR. HERMA DINA BINTI SETIABUDI
Position : SENIOR LECTURER
Date :

STUDENT’S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of another degree.

Signature :
Name : FATIN NADIA BINTI PAUZI
ID Number : KA11145
Date : 6 JANUARY 2015

Dedication

I dedicate this to my family, especially for my mother Zaharah Binti Mahmood and my father, Pauzi bin Ab Ghani, that give a lot of support and pray for me to finish my thesis research. Love both of you so much.

ACKNOWLEDGEMENT

I would like to thank the following people and organizations;

- My supervisor Dr. Herma Dina Binti Setiabudi for his guidance through an effective, well-arranged weekly meeting and also helping me to finish my thesis.
- Laboratory of Faculty of Chemical Resources Engineering to give me a place to run the experiment.

ABSTRACT

Dyes are widely used in many industries, mainly in the textile industries. The effluents containing these dyes are an environmental concern and the disposal of these wastes into receiving water causes damage to the environment and may also be toxic to aquatic life. It is therefore imperative to treat textile effluents due to their toxic and aesthetic impacts on the receiving water bodies (Vadivelan and Kumar, 2005; Hameed and El-Khaiary, 2008). Removal of dyes from wastewater using adsorption process has become one of the most effective and comparable low cost methods for the decolourization of textile wastewater (Mckay et al,1999 ; Khan et al, 2002). Adsorption by using activated carbon is a very effective process, but the high cost of such adsorbents has motivated the search for alternatives and low-cost adsorbents. Agricultural waste is alternative use for wastewater treatment because they are cheap, simple, sludge free and involve small initial cost and investment This work explores the feasibility of Imperata Cylindrica (IC), a solid waste, abundantly available in Malaysia, for the absorption of methylene blue (MB). Batch adsorption studies were conducted to evaluate the effects of adsorbent dosage (0.25-2 g/L), initial pH (2-8), initial concentration (50-400 mg/L), and temperature (30-50 ºC). The optimum conditions were achieved at 1 g/L of adsorbent dosage, pH 6, 400 mg/L initial dye concentration and at 40 ºC, with adsorption capacity of 314.06 mg/g. The adsorption of MB into the surface of IC was confirmed by SEM image for IC before adsorption and after 50 min adsorption process. The experimental data were analyzed by the Langmuir and Freundlich isotherms, and were found to follow the Freundlich isotherm model with coefficients of correlation $R^2 \geq 0.9876$ indicating that the ongoing process is heterogeneous in nature. Pseudo-first-order and pseudo-second-order kinetics models were tested with the experimental data, and pseudo-second-order kinetics was the best for the adsorption of MB by IC with coefficients of correlation $R^2 \geq 0.999$ for all initial MB concentrations studied. Thermodynamic parameters such as ΔH^o, ΔG^o and ΔS^o clearly indicated that the adsorption behaviour of the system is endothermic, feasible and increasing randomness at temperature range of 30-40 ºC, while, at temperature range of 40-50 ºC, the ongoing process is exothermic, feasible and decreasing randomness. The results revealed that IC is potentially low-cost adsorbent for adsorption of MB

ABSTRAK

Pewarna digunakan secara meluas dalam pelbagai industri, terutamanya dalam industri tekstil. Efluen yang mengandungi pewarna ini merupakan satu kebimbangan kepada alam sekitar dan pelupusan bahan buangan ini ke dalam sungai akan menjejaskan alam sekitar dan juga boleh menjadi toksik kepada hidupan akuatik. Oleh itu, adalah penting untuk merawat efluen tekstil kerana kesan toksik dan estetik mereka pada sumber air (Vadivelan dan Kumar, 2005; Hameed dan El-Khaiary, 2008). Penyingkiran pewarna dari air kumbahan menggunakan proses penjerapan telah menjadi salah satu kaedah kos rendah yang paling berkesan dan setanding untuk penyahwarnaan air sisa daripada tekstil industri (Mckay et al, 1999; Khan et al, 2002). Penjerapan dengan menggunakan karbon teraktif adalah salah satu proses yang sangat berkesan, tetapi ia merupakan bahan penyerap kos tinggi dan itu telah mendorong mencari alternatif dan bahan penyerapan kos rendah. Sisa pertanian adalah alternative bahan penyerapan untuk rawatan air sisa kerana mereka adalah murah, mudah, enapcemar percuma dan melibatkan kos yang kecil awal dan pelaburan. Kajian ini dilakukan untuk mengkaji Lalang (IC), iaitu sisa pepejal, yang banyak di dapati di Malaysia, untuk penyerapan metilena biru (MB). Kajian kelompok penjerapan telah dijalankan untuk menilai kesan bahan penyerapan (0,25-2 g / L), pH awal (2-8), kepekatan awal (50-400 mg / L), dan suhu (30-50 ºC). Keadaan optimum telah dicapai pada 1 g/L untuk dos bahan penyerapan, pH 6, 400 mg/L kepekatan awal dan pada suhu 40 ºC, dengan kapasiti penjerapan adalah 314,06 mg/g. Penjerapan MB ke permukaan IC telah disahkan oleh imej SEM bagi IC sebelum penjerapan dan selepas proses penjerapan 50 minit. Data ujikaji dianalisis dengan menggunakan isoterma Langmuir dan Freundlich, dan didapati mengikut model isoterma Freundlich dengan pekali korelasi $R^2 \geq 0.9876$ yang menunjukkan bahawa proses yang berterusan adalah heterogen dalam alam semula jadi. Tertib-pseudo-pertama dan tertib-pseudo-kedua kinetik model telah diuji dengan data uji kaji, dan kinetik tertib-pseudo-kedua adalah yang terbaik untuk penjerapan MB oleh IC dengan pekali korelasi $R^2 \geq 0,999$ untuk semua kepekatan awal MB yang dikaji. Parameter termodinamik seperti ΔH^o, ΔG^o dan ΔS^o jelas menunjukkan bahawa sifat penjerapan sistem adalah endoterma, berlaku dengan mudah dan berlakunya peningkatan rawak pada suhu 30-40 ºC, manakala, pada suhu 40-50 ºC, proses yang berterusan adalah eksoterma , berlaku dengan mudah dan berlakinya pengurangan rawak. Keputusan menunjukkan bahawa IC berpotensi sebagai penyerap kos rendah bagi penjerapan MB.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS

ºC - Degree Celcius
g - Gram
K - Kelvin
L - Litre
mg - Milligram
mL - Millilitre
% - Percent
W - Watt
kJ - KiloJoule
ΔH - Enthalpy
Nm - Nano meter

LIST OF ABBREVIATIONS

MB	Methylene Blue
IC	Imprata Cylindrica
BET	Brunauer-Emmett-Teller

1 INTRODUCTION

1.1 Background

Methylene blue (MB) is the cationic dye which is extensively used in dyeing industry such as dyeing cotton, wool, and silk. MB is a toxic dye and causes several health risks in humans upon exposure, such as nausea, vomiting, eye injury, cyanosis, convulsions, tachycardia, dyspnea and methemoglobinemia (Al-Anber *et al.,* 2011; Dutta *et al.*, 2011; Vucurovic, Razmovski, & Tekic, 2012). Thus, the removal of MB from wastewater becomes environmentally important.

A lot of focuses has been applied to overcome the adverse impact on environment. The numbers of conventional methods are available for colour removals from industrial effluents including ion exchange, adsorption, membrane technology and coagulation (Nigam, 2000). From all this methods, adsorption has become one of the most effective and comparable low cost method for the decolourization of textile wastewater due to its sludge free clean operation and completely removed dyes, even from the diluted solution. (Mckay *et al.,* 1999 ; Khan *et al.,* 2002).

For the adsorbent, there are many types of adsorbent are used to remove dye from wastewater and adsorption by using activated carbon is rapidly becoming a prominent method of treating aqueous effluents and has been used in industrial processes in variety of separation and purification process. Activated carbon has a capability to adsorb many types of dyes with a high adsorption capacity. However, activated carbon is an expensive material and its regeneration for reuse increases the cost (Gong *et al.,* 2009). Therefore, there are growing interest in identifying more low-cost and effective alternatives to activated carbon including algae (Dotto *et al.,* 2012), agricultural waste (Abidin *et al.,* 2011; Rahman *et al.,* 2005), zeolite (Han *et al.,* 2010) and sludge (Ong *et al.,* 2010)

In recent years, various agricultural products and by-products has been investigated to remove dye from aqueous solution including rubber leaf powder (Hanafiah *et al.,* 2006), sago waste (Quek *et al.,* 1998), spent grain (Low *et al.,* 2006), biogas residual slurry (Namasivayam *et al.,* 1992) and rice husk (Guo *et al.,* 2003).

Agricultural waste is an alternative use for wastewater treatment because they are cheap, simple, sludge free and involve small initial cost and investment. Imperata Cylindrica (IC) is one of the agricultural wastes that is abundantly available throughout the year in Malaysia and has been ranked as one of the ten worst weeds of the world. This species is considered a pernicious pest plant due its ability to successfully colonize, spread and subsequently compare and displace desirable vegetation and disrupt ecosystems (Holm *et al.,* 1977). Thus, finding uses for this waste would be profitable from both environmental and economic point of view.

1.2 Motivation

Our earth is the only planet in the universe which has an environment suitable for life and the environment is a major aspect of our life. But now, environmental pollution is the biggest menace to the human race on this planet today. The problem of environmental pollution has become very acute and the most affected environmental pollution is wastewater. Most of the polluted water comes from the industries since industrial expansion, especially from the developed countries. About 25% of worldwide water demand is related to industrial applications (Levine *et al.,* 1995). Since water is vital, it should not be polluted by the discharge of industrial effluents.

There are many sources of water pollution and one of the causes is due to the dye waste. Dyes are widely used in many industries, mainly in the textile industry. Textile dyeing processes are among the most environmentally unfriendly industrial processes by producing clear waste water, there are mass of high concentration and complicated component and refractory organic compounds in dye wastewater, and it is necessary to remove dyes in urgent (Vadivelan and Kumar, 2005; Hameed and El-Khaiary, 2008).

A lot of focus has been applied to overcome the adverse impact on the environment. To overcome this problem, there are a few of conventional methods that are available for colour removals from industrial effluents. Adsorption method have been choose because it is one of the most effective and comparable low cost methods for the decolourization of textile wastewater due to its sludge free clean operation and completely removed dyes, even from the diluted solution (McKay *et al.,*1999 ; Khan *et al.,* 2002).

1.3 Problem Statement

Recently, rapid advances in technology in the textile and dyeing industry have yielded benefits to society and therefore, the increased use of color rise and it is indirectly increasing environmental pollution, especially water pollution. Since water is vital, it should not be polluted, and if the water is affected with the removal of dyes is an important risk assessment. Since MB can cause several health risks to humans, hence, the removal of MB from waste effluents becomes environmentally important.

There are various methods of dye removal have been studied and developed, including chemical, physico-chemical and biological methods to remove dyes are expensive and inefficient. Among the various methods available, adsorption process is one of the most efficient and cheap methods to remove dye from wastewater, especially if the adsorbent that used is inexpensive and readily available (Karim *et al.,* 2008). Thus, the development of cheap and extensively available resource as an alternative adsorbent is essential for the efficient removal of dyes.

Nowadays, the use of activated carbon is the most popular adsorbent used because of the adsorption capacity of the activated carbon is high. However, activated carbon having a high cost and sometimes tends to limit its use. So, a research about agriculture waste like Imperata Cylindrica that has high potential of adsorption capacity will be carried out. Besides it is abundantly and easy to getting, Imperata Cylindrica creates a serious problem of disposal. Thus, finding uses for this waste would be profitable from both an environmental and economic point of view.

1.4 Objective of the study

The research was conducted to investigate the removal of methylene blue dyes from aqueous solution by using the adsorption method on Imprata Cylindrica as adsorbents.

1.5 Scopes of the study

The scopes of this study were focusing on the:

i. Effect of adsorbent dosage (0.25-2 g/L).
ii. Effect of initial concentration (50-400 mg/L).
iii. Effect of initial pH (4-8).

iv. Effect of initial temperature (30-50 ºC).
v. Kinetic, isotherm and thermodynamic of adsorption.

1.6 Organization of this thesis

The structure of the remainder of the thesis is outlined as follows:

Chapter 2 described about the dyes. Here, a general description of the classification of dye is fully explained, followed by the explanations about the type of dye that have been chosen. This chapter also provides a discussion about the adsorption process, including the explanation about adsorption kinetics, isotherm equation and thermodynamic parameters. Then, an explanation about the absorbent material also will be discussed. The last part of this chapter is the summary about the previous study of removal of dye by using adsorption process by using various of adsorbent focusing on agriculture waste.

Chapter 3 or experimental methodology describes the particulars of the materials and chemical reagents used in the present work and the procedure for adsorption method, kinetic, isotherm and thermodynamic of adsorption.

Chapter 4 explained about the result of research. Discussion for all the scope of study which is the effect of adsorbent dose, initial concentration, initial pH, temperature, and kinetics, isotherm and thermodynamics adsorption are fully described.

2 LITERATURE REVIEW

2.1 Overview

This section discuss about the dyes, adsorption process, adsorbent material and summary about the previous study. A general description of the classification of dye will be fully explained, followed by the explanations about the type of dye that have been chosen. This chapter also provides a discussion about the adsorption process, including the explanation about adsorption kinetics, isotherm equation and thermodynamic parameters. Then, an explanation about the adsorbent material also will be discussed. The last part of this chapter is the summary about the previous study.

2.2 Dye

The earliest written records of the use of dyestuffs were found in China in 2600 BC. Then, the real breakthroughs in the history of dyes came in 1856 when a teenager, William Perkin an 18-year-old student was working on chemical synthesis of natural products. While he was attempting to synthesize quinine, the only cure for malaria, he chanced upon 'Aniline Mauve' dye. "Mauve" or also know as a basic dye was the first synthetic dye stuff (Hunger, 2003).

Dyes are applied everywhere, from Plastic toys for children to that fabrics you wear, from food to wood; hardly there is any industry where dyes are not used commercially. One characteristic of dye is that the dyes must get completely or at least partially soluble in which it is being put to. Dyes also can be toxic, carcinogenic or mutagenic and can pose as a hazard to health.

2.2.1 Classification of Dyes

For thousands of years, plants and animals are the example of natural sources to produce dyes. Until the mid-1800s, dyes were produced individually by harvesting natural fruits, vegetables and other items, boiling them, and submersing fabrics in the dyebath. It was a long and tedious process (Joseph, 1977). But nowadays, for almost every color, it is already packed and easy to obtain.

As discussed in Howard (1986), there are 4 major of dye classes that are discussed and it is shown in the Table 2.1 below. Detail explaination of these dye classes discussed in section 2.2.1.1 , 2.2.1.2, 2.2.1.3 and 2.2.1.4.

Table 2-1: Type of dye classes (Howard, 1986).

Dye Classes	Type of dyes
Dyes containing Anionic Functional Groups	Acid dyes, Direct dyes, Mordant dyes, Reactive dye.
Dyes containing Cationic Groups	Basic dyes.
Dyes requiring Chemical Reaction before Application	Vat dyes, Azoic dyes, Sulfur dyes.
Special Colorant Classes	Disperse dyes, Solvent dyes, Natural dyes.

2.2.1.1 Dyes containing Anionic Functional Groups

In this dye class, it’s containing functional groups that having sodium of sulfonic or carboxylic acids. These functional groups provide water solubility to the dyestuff. The dyes differ in subclassification in their affinity for fibers and/or the presence of special functional groups (Howard, 1986). There are four types of dyes in this class which are acid dyes, direct dyes mordant dyes and reactive dyes.

Table 2-2: Classification of dyes containing Anionic Functional Groups (Hunger, 2003).

Type of dyes	Substrate	Method of Application	Chemical types
Acid	Nylon, wool, silk, paper, inks and leather.	Usually from neutral to acidic bath.	Azo (including premetallized), anthraquinone, tryphenylmethane, azine, xanthene, nitro and nitroso.
Direct	Cotton, rayon, paper, leather and nylon.	Applied from neutral or slightly alkaline baths containing additional electrolyte.	Azo, phthalocyanine, stilbene, and oxazine.
Mordant	Wool, leather and anodized aluminium	Applied in conjunction with Cr salts	Azo and anthraquinone
Reactive	Cotton, wool, silk and nylon.	Reactive site on dye reacts with functional	Azo, anthraquinone, phthalocyanine,

		group on fiber to bind dye covalently under influence of heat and pH (alkaline).	formazan, oxazine, and basic

Acidic dyes are highly water soluble, and have better light fastness than basic dyes. An acid dye is a salt color that comes from the acidic component. These dyes are dyed onto the fibers from acid solution, since positive charge development within the fiber in acid solutions acts as a driving force for dye diffusion and migration into the fiber. It is applied to nylon, wool, silk, and modified acrylics. They are also used to some extent for paper, leather, ink-jet printing, food, and cosmetics (Howard, 1986 and Hunger, 2003).

Direct dyes, or also known as substantive dyes are a special class of dyes which penetrate cellulosic fibers readily and have good affinity for these fibers. It contains one or more also groups that connecting aromatic chromophores, thereby providing a straight chain dye molecule (Howard, 1986). Direct dyes are usually applied with the addition of electrolyte at or near the boil in the machines capable of running at atmospheric pressure. It is used for dyeing of cotton, paper, leather, wool, silk and to some extent to nylon.

According to Howard (1986), Mordant dyes are acid dyes that have special sites other than acid salt anion groups that can react with a metal salt mordant. Mordant dyes are "tailor-made" to chelate with metal ions to form a strong organometallic complex of limited solubility and greater colour fastness.

In 1956, the first reactive dye is introduced commercially by ICI. These dyes form with covalent bonds with –OH, –NH or –SH groups in silk, cotton, nylon and wool. The chemical type of this dye is also, anthraquinone, phthalocyanine, Formosan, oxazine, and basic. To apply these dyes, reactive site on dye must react with functional group of fiber to bind the dye covalently under influence of heat and pH (alkaline) (Hunger, 2003).

2.2.1.2 Dyes containing Cationic Groups (Basic dye)

Basic dye or also known as cationic dyes are applied to a substrate with anionic character where electrostatic attraction is formed. The reason why the basic dye is also known as cationic dye because the chromosphere in basic dye molecules contains a positive charge (Textile Learner website). The substrates of the basic dye are paper, polycrylonitrile, modified nylon, polyester and inks. Some of basic dyes also show biological activity and it can used in medicine as antiseptics.The principal chemical types of basic dyes are diazahemicyanine, triarylmethane, cyanine, hemicyanine, thiazine, oxazine, and acridine (Hunger,2003).

2.2.1.3 Dyes requiring Chemical Reaction before Application

According to Howard (1986), before applying to a fiber, vat and sulfur dyes must be chemically reduced, whereas Azoic or naphthol dyes are formed through reaction of two separate dye components after applied to the fiber. These dyes tend to penetrate the fiber, less than other dyes, and care must be exercised in application to get reasonable fastness properties.

Table 2-3: Classification of Dyes requiring Chemical Reaction before Application (Hunger, 2003).

Type of dyes	**Substrate**	**Method of Application**	**Chemical types**
Vat	Cotton, rayon and wool	Water-insoluble dyes solubilized by reducing with sodium hydrogensulfite, then exhausted on fiber and reoxidized	Anthraquinone (including polycyclic quinines) and indigoids
Azoic	Cotton, rayon, cellulose acetate and polyester	Fiber impregnated with coupling component and treated with a solution of stabilized diazonium salt.	Azo
Sulfur	Cotton and rayon	Aromatic substrate vatted with sodium sulfide and reoxidized to insoluble sulfur-containing products on fiber	Indeterminate structures

According to Hunger (2003), vat dyes are insoluble in water and are applied mainly to cellulosic fibers as soluble lace salts after reduction in an alkaline bath, usually with sodium hydrogensulfite. Vat dyes are a good example of the crossover between dyes and pigments. Vat dyes are large, planar and often containing multi-ring systems, vat dyes come exclusively from the carbonyl class of dyes like indigo.

Azoic or naphthol dyes are formed in situ on the fabric through a coupling reaction of an aromatic alcohol or amine such as naphthol with a diazonium salt. To apply these dyes, fiber will impregnate with coupling component and treated with a solution of stabilized diazonium salt. Chemical type of azoid dyes azo (Hunger, 2003 and Howard, 1986).

For dyeing application, a sulphur dye is one of the best dyes to use. It will dissolve in sodium sulphide solution prior. Sulfur dyes are inexpensive complex reaction mixtures of selected aromatic compounds with sodium polysulfide. Aromatic substrate vatted with sodium sulfide and reoxidized to insoluble sulfur-containing products on fiber. (Hunger, 2003 and Howard, 1986)

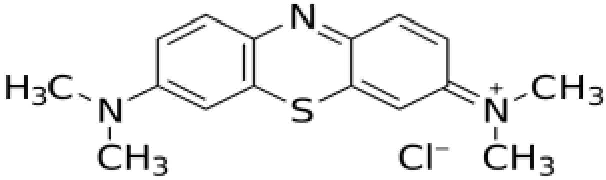
2.2.1.4 Special Colorant Classes

Special colorant classes are the other dye that don't fit logically into the other classification and because of that, it has been included in this class. Disperse dyes are substantially water-insoluble nonionic dyes for application to hyroprophic fiber from aqueous dispersion. It used to a lesser extent on nylon, cellulose acetate and acrylic fibers. The principal chemical types of disperse dyes are azo, anthraquinone, styryl, nitro, and benxodifuranone. Solvent dyes are dyes which are specially formulated then can be applied from solvents other than water. Where for the natural dyes, it is a complex mixture derived from natural sources (Hunger, 2003 and Howard, 1986).

2.2.2 *Methylene Blue (MB)*

Methylene Blue (MB) was first prepared by Cora in 1876 as an aniline-derived dye for textiles. With molecular formula $C_{16}H_{18}N_3SCl$, ethylene blue is a heterocyclic aromatic chemical compound that has many uses in different fields. The properties of methylene blue, which are listed in Table 2.4 below, were obtained from Chemical Book websites.

Table 2-4: Properties of Methylene Blue (Chemical Book, 2010)

<table>
<tr><th colspan="2">Methylene Blue</th></tr>
<tr><td colspan="2"></td></tr>
<tr><td colspan="2"></td></tr>
<tr><td colspan="2"></td></tr>
<tr><td>IUPAC Name</td><td>3,7-bis(Dimethylamino)-phenothiazin-5-ium chloride</td></tr>
<tr><td>Molecular formula</td><td>$C_{16}H_{18}N_3SCl$</td></tr>
<tr><td>Molar mass</td><td>319.85 g/mol</td></tr>
<tr><td>Density</td><td>1.0 g/mL at 20°C</td></tr>
<tr><td>Melting point</td><td>190°C</td></tr>
<tr><td>Boiling point</td><td>Decomposes</td></tr>
<tr><td>Solubility in water</td><td>Slightly soluble</td></tr>
</table>

Methylene blue also known as Basic Blue 9. This dye is under the Basic dye and is a dark green crystalline solid. It can categorize as phenothiazine family. When MB is dissolved in water, a basic aniline dye which is a deep blue solution is formed and it is used as a bacteriological stain. The common application of methylene blue is uses for therapeutic. It is a treatment of methemoglobinemia, antidote for cyanide poisoning, urinary antiseptic and also for treatment of manic-depressive psychosis. MB also will be used as a dye as bacteriologic stain, indicator dye, surgical and medical marking and temporary hair colorant (Anber *et al.*, 2011).

Production of MB is a cationic thiaznic dye that is deep blue in the oxidized state while it is colourless in it reduces dorm. MB+ is a sensitizer that has been used for a variety of applications including energy conversion and photodynamic therapy (PDT). Acute exposure to MB has been found to cause increased heart rate, dyanosis, vomiting, shock, Heinz body formation, jaundice and tissue necrosis in humans (Dutta *et al.*, 2011).

2.3 Adsorption

Adsorption is a physical process that involves the transfer of solutes from the liquid phase to the surface of a solid matrix. A process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), then it forming a molecular or atomic film (the adsorbate) is known as adsorption process. The simple way to understand the adsorption process is by the use of solids for removing substances from either gaseous or liquid solutions. The history of carbon adsorption in the purification of water dates back to ancient times (Cheremisinoff, 2002). Adsorption techniques have been proven successful in removing colours organics (Erdem *et al.*, 2004).

Heinrich Kayser which is a German physicist was the person that introduced the term of adsorption in 1881. He postulated that the basic feature of an adsorption process is a surface accumulation of material (Gupta and Suhas, 2009). A liquid solute accumulates on the surface of a solid adsorbent and then will forming a molecular or atomic film. Application for adsorption process is chemical processing, air pollution control and water treatment. Generally the factors like concentration of dyes, initial pH and temperature of the effluent, affect the decolourisation process (Gupta and Suhas, 2009).

Adsorption is a consequence of surface energy with is similar to the surface tension. In a bulk material, all the bonding requirements like ionic, covalent or metallic of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus, it is energetically favourable for them to bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption (Gupta and Suhas, 2009; Anjaneyulu *et al.*, 2005).

Physisorption or also known as physical adsorption is a type of adsorption in which the adsorbate adheres to the surface only through weak intermolecular interactions, where chemisorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond. The table below shows the differences between physisorption and chemisorption.

Table 2-5: Diffentation between Physisorption and chemisorptions (eMedicalprep, 2011)

Characteristic	**Physisorption**	**Chemisorption**
Temperature	Low : always under the critical temperature of the adsorbate	High
Type of interaction	Intermolecular forces (van der Waals forces)	Strong; covalent bond between adsorbate and surface.
Enthalpy	$\Delta H < 20$ KJ/mol	$\Delta H \approx 400$ KJ/mol
Adsorption take place	Multilayer	Monolayer
Activation energy	Low	High

The combination between physical and chemical adsorption are the most adsorption phenomena that happen and thus, it is generally difficult to distinguish between physical and chemical and adsorption. Because of that, adsorption process has been demonstrated to be widely effective for removing dissolved organic substances from wastewaters and it’s also as an economically feasible process that produces a high quality product.

The calculation of the percentage of dye adsorbed by the adsorbent is calculated by using an equation:

$$\% d = \frac{(C_o - C_t)}{C_o} \times 100 \tag{2.1}$$

Where $\% d$ is the percentage of dye adsorbed; C_o and C_t are respectively the initial and liquid-phase concentration of the dye solution at any time t (mg/L)

For the amount of dye adsorbent in each time interval is calculated by the following mass balance equation:

$$q_t = (C_o - C_t)\frac{V}{m} \tag{2.2}$$

Where q_t the amount of is dye the adsorbent weight of adsorbent at any time t (mg/g); C_o and C_t are respectively initial and liquid-phase concentrations of the dye solution at any time t (mg/L); V is the volume of the dye solution (L); and m is the mass of the adsorbent used (g).

2.3.1 Adsorption Kinetics

Adsorption kinetics, which describes the adsorbent adsorption rate, is an important characteristic in evaluating the efficiency of adsorption. A study of the kinetics of adsorption is desirable as it provides information about the mechanism of adsorption, which is important for the efficiency of the process (Jain *et al.,* 2003). It describes the solute uptake rate which controls the residence time of adsorbate uptake at the solid–solution interface (Nacera *et al.,* 2006).

In order to investigate the controlling mechanisms of adsorption process, the pseudo-first-order (Ho and McKay, 1998) and pseudo-second-order (Gürses *et al.,* 2006; Alkan *et al.,* 2008) will use to test the experiment data.

2.3.1.1 *The Pseudo-First-Order Model*

Lagergren was presented the pseudo-first-order model and then it is expressed as by Gürses *et al.,* 2006. The pseudo-first-order model is used to predict the dye adsorption kinetics. When absorption is preceded by diffusion through a boundary, the kinetic in most systems follows the pseudo-first-order equation. The pseudo-first-order kinetics model is given as:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \tag{2.3}$$

Where q_e and q_t are the amount of dye (mg/g) adsorbed on the clay at equilibrium, and at time t, respectively and k_1 is the rate constant (min^{-1}).

Integrating and applying the boundary condition, t = 0 and q_t = 0 to $t = t$ and q_e $= q_t$. Equation 2.3 takes the form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{2.4}$$

The rate constant, k_1 was obtained from slope of the linear plots of $\log(q_e - q_t)$ against t .

2.3.1.2 *Pseudo-Second-Order Model*

Pseudo-second-order equation (Ho, 1995) predicts the behavior over the whole range of adsorption with chemisorption being the rate controlling step. By Gürses *et al.*, (2006) and Alkan *et al.,* (2008), the pseudo-second-order model is described as given:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{2.5}$$

Where k_2 is the rate constance of pseudo-second-order sorption (g/mg min). Then the equation 2.5 will be integrated and applying the boundary condition $t = 0$ and $q_t = 0$ to $t = t$ and $q_e = q_t$ and it will be becomes:

$$q_t = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}} \tag{2.6}$$

Equation 2.6 will be rearranged to obtain a linear form:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{2.7}$$

If second-order kinetics is applicable, the plot of $1/(q_e - q_t)$ against t of equation 2.7 should give a linear relationship from which the value $1/q_e$ and k_2 can be determined.

2.3.2 Isotherm Equation

Isotherm are usually used to describe the adsorption, where the amount of adsorbate on the adsorbent as a function of its pressure or concentration at constant temperature. For more understanding about the adsorption method, equilibrium isotherms are very important to know. The equilibrium state will be achieved if the rate at which molecules adsorb onto a surface is equal to the rate at which they desorb. No change can be observed at equilibrium, in the concentration of the solute on the solid surface or in the bulk solution. Different adsorption isotherms can be calculated by using Langmuir isotherm equations and Freundlich isotherm equation.

2.3.2.1 Langmuir Isotherm Equation

In 1918, Irving Langmuir was the first to derive a scientifically based adsorption isotherm and retained his name (Fraissard *et al.,* 1997). The central assumption of the Langmuir model is that adsorption takes place on a homogeneous adsorbent surface of identifying sites that are equally available and energetically equivalent, with each site carrying equal numbers of molecules and no interaction between adsorbate molecules.

The equation of Langmuir isotherm is:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_a} + \frac{C_e}{q_{\max}} \tag{2.8}$$

From the equation 2.8, C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount adsorbed at equilibrium (mg/g), q_{max} (mg/g) and K_a (L/mg) are the Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively. These constants can be evaluated from the intercept and the slope of the linear plot of experimental data of C_e/q_e versus C_e, respectively.

By Kannan and Sundaram, (2001), the essence of the Langmuir isotherm can be expressed by means of a dimensionless constant separation factor or equilibrium parameter R_L and the equation is:

$$R_L = \frac{1}{1 + K_a C_o} \tag{2.9}$$

Co is the initial concentration (mg/L), and Ka is the Langmuir constant (L/mg). The value of the separation factor R_L, indicates the nature of the adsorption process as given below:

Table 2-6: Nature of the Adsorption Process (Inbaraj *et al.*, 2009)

R_L value	Nature of adsorption process
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

2.3.2.2 Freundlich Isotherm Equation

Freundlich and Küster was the person that published the Freundlich Isotherm equation and it is the first mathematical fit to an isotherm and it also a purely empirical formula for gaseous adsorbates. The isotherm assumes that adsorbent surface sites have a spectrum of different binding energies (Almeida *et al.*, 2009). The concentration of adsorbate on the adsorbent surface increases as the adsorbent concentration increases (Wang and Zhu, 2005).

Equation 2.10 is the Freundlich isotherm equation:

$$q_e = K_f C_e^{1/n} \tag{2.10}$$

Then form into linear form:

$$\log q_e = (1/n)\log C_e + \log K_f \tag{2.11}$$

Where *1/n* is the adsorption intensity, K_f represents the adsorption capacity related to Freundlich isotherm. These constants can be evaluated from the intercept and the slope of the linear plot of $\log q_e$ versus $\log C_e$.

2.3.3 Thermodynamic Parameters

For more understanding about the effect of temperature on adsorption, the thermodynamic parameters are must know (Seki and Yurdakoç, 2006). The equation that used is the Gibbs free energy:

$$\Delta G^o = -RT \ln K_D \tag{2.12}$$

By Lakshmi *et al.,* (2009), Gibbs free energy change of the adsorption process is related to the equilibrium constant by the classical Van't Hoff equation. Equation 2.12 also related to the entropy change and heat of adsorption temperature as an equation:

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{2.13}$$

The combination of the equation 2.12 and 2.13 then will get:

$$\ln K_D = \frac{-\Delta G^o}{RT} = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{R}\frac{1}{T} \tag{2.14}$$

Where ΔG_o is the free energy change (kJ/mol), ΔH_o is the change in enthalpy (kJ/mol), ΔS_o is the entropy change (J/mol K), T is the absolute temperature (K) and *R* is the universal gas constant (0.314 x10^{-3} kJ/mol K); and $K_D = (q_e/C_e)$ is a single point or linear sorption distribution coefficient.

Then, enthalpy change (kJ/mol) which is ΔH_o can be determined from the slope of the linear Van't Hoff plot, i.e. *ln KD* versus *(1/T),* using the equation:

$$\Delta H^o = \left[R \frac{d \ln K_D}{d(1/T)} \right] \tag{2.15}$$

From equation 2.15, ΔH^o is the corresponds to the isosteric heat of adsorption with zero surface coverage (i.e. $q_e = 0$). ΔH^o value provides a direct measure of strength of bonding between the adsorbate and adsorbent surface. KD at $q_e = 0$ was obtained from the intercept of the $ln\ (q_e/C_e)$ versus qe graph.

2.4 Adsorbent Material

2.4.1 Introduction of Adsorbent

Adsorbent is a material that usually porous in nature and with a high surface area that have the ability to extract certain substances (gases, liquids, or solids) by causing them to adhere to its surface without changing the physical properties of the adsorbent. There are many types of adsorbent that have been tested on the possibility to lower dye concentrations of aqueous solutions and can used to remove dye from wastewater such as activated carbon (Malik, 2004), chitin (McKay *et al.*, 2003), peat (Brown *et al.*, 2000) and others. Among all the adsorbent, activated carbon is the popular adsorbent and has the capacity to absorb many types of dyes with a high adsorption capacity (Gong *et al.*, 2009). However, activated carbon suffers from high cost production and regeneration.

Because of this, there are many studies is attempting to use alternative low-cost adsorbent to substitute the most expensive, commercially available activated carbons. Alternative adsorbent from biosorbents, agricultural waste and industrial by-products are used to find the new alternative low-cost adsorbent. In this study, I attempt to use Imprata Cylindrica as low-cost adsorbent for removal of methylene blue.

2.4.2 Imprata Cylindrica

Imprata cylindrical is an agricultural waste and also known as a 'lalang' that is abundant in Malaysia. Agricultural waste is an alternative use for wastewater treatment because they are cheap, simple, sludge free and involve small initial cost and investment. In this study, an attempt to use Imperata Cylindrica, as low cost adsorbent for removal of methylene blue from aqueous solution has been made. Imprata Cylindrica has been ranked as one of the ten worst weeds of the world. This species is considered a pernicious pest plant due its ability to successfully colonize, spread and subsequently compare and displace desirable vegetation and disrupt ecosystems (Holm *et al.,* 1977). To overcome this problem, Imprata Cylindrica will use as adsorbent that would minimize the total amount of waste and it is a step towards a more ‘‘earth-friendly’’ process.

2.5 Previous studies

Adsorption has become one of the most effective and comparable low cost methods for the decolourization of textile wastewater due to its sludge free clean operation and completely removed dyes, even from the diluted solution (McKay *et al.,* 1999; Khan *et al.,* 2002). Adsorption by using activated carbon is rapidly becoming a prominent method of treating aqueous effluents and has been used in industrial processes in variety of separation and purification process. However, activated carbon is an expensive material and its regeneration for reuse increases the cost (Gong *et al.,* 2009).

Therefore, these are growing interest in identifying more low-cost and effective alternatives to activated carbon. For the example the removal of methylene blue from aqueous solutions by wheat brant by Hamdaoui and Chiha (2007), adsorption of methylene blue from aqueous solution onto NaOH-modified to reject tea by Nasuha & Hameed (2011), the removal of dye colours from aqueous solutions by adsorption on low-cost materials by McKay *et al.,* (1999), batch study of liquid-phase adsorption of lead ions using Lalang (Imprata Cylindrica) leaf powder by Zakaria, H (2007), etc. Besides that, some of growing interest in identifying more low-cost and effective alternatives to activated carbon including algae (Dotto *et al.,* 2012), agro-industrial waste (Abidin *et al.,* 2011; Rahman *et al.,* 2005), zeolite (Han *et al.,* 2010) and sludge (Ong *et al.,* 2010).

In recent years, various agricultural products and by-products has been investigated to remove dye from aqueous solution including rubber leaf powder (Hanafiah *et al.,* 2006), sago waste (Quek *et al.,* 1998), spent grain (Low *et al.,* 2006), biogas residual slurry (Namasivayam *et al.,* 1992) and rice husk (Guo *et al.,* 2003). Agricultural waste is an alternative use for wastewater treatment because they are cheap, simple, sludge free and involve small initial cost and investment.

In 2007, Zakaria had investigated the ability of Imprata Cylindrica (IC) as low cost adsorbent for the removal of lead ions. The adsorption process was found to follow

Langmuir model and the adsorption capacity was found to be 5.89 mg/g at pH 4. As pH increased, more adsorbent surface would be exposed and carried negative charges with subsequent attraction of lead ions. It also found that the Pb^{2+} adsorption was found to be dependent on inital lead concentration, pH, temperature and adsorbent dosage. So, this this studies indicated that the IC leaf powder can be used as low cost adsorbent for adsorption process because it has higher adsorption rate.

Jalil *et al.*, (2012) studies about the utilization of bivalve shell-treated Zea mays L. (maize) husk leaf as a low-cost biosorbent for enhanced adsorption of malachite green. From the result obtain, the use of 25 g/L shell-treated Zea mays L. husk leaf resulted complete removal of 200 mg/L of malachite green with the maximum adsorption capacity of 81.5 mg/g after 30 min of contact time at pH 6 and 323 K. Hence, it proved that the bivalve shell-treated Zea mays L .husk leaf can be used to effectively remove malachite green from aqueous media and it also can minimize the wastes. Besides that, pretreatment of the raw Zea mays L. husk with bivalve shell effectively enhanced its electronegativity, which led to an increased adsorption capacity.

Studies about the adsorption by using grass become more significant and in 2008b, Hameed do a research about Grass waste: A novel sorbent for the removal of basic dye from aqueous solution. From the result obtain, the adsorption isotherm was found to follow the Langmuir model and the kinetic data were found to follow the pseudo-second-order kinetic model. The maximum adsorption capacity obtained was 457.64 mg/g at 30 ºC and it revealed that the grass waste sorbent was an effective adsorbent for the methylene blue. Besides that, the grass waste adsorbent also a low-cost adsorbent. Since IC is almost similar properties with grass, it is expected that IC have a great potential for removal dyes.

3 MATERIALS AND METHODS

3.1 Overview

In this chapter, the explanation about chemical and material used, preparation of adsorbent and dye solution, and methodology for the adsorption process will be explained.

3.2 Chemical

The Imperata Cylindrica (IC) used was collected around Universiti Malaysia Pahang, Pahang, Malaysia. The methylene blue (MB) used in this study was purchased from Merck (M) Sdn. Bhd, Malaysia with C.I.52015, purity of 99%, chemical formula of $C_{16}H_{18}N_3SCl$ and molecular weight of319.85 g/mol. The maximum wavelength of this dye is 668 nm.

3.3 Imprata Cylindrica Preparation

Imprata Cylindrica that used in this study was obtained around Universiti Malaysia Pahang. IC were chopped into pieces that were 1–2 cm in length, and then the pieces were soaked in water overnight to remove any impurities adhering to the surface before the pieces were oven-dried at 80 ºC for 24 h. The pieces were crushed and sieved to a consistent size of 355–600 µm, and then the powder was oven-dried at 100 ºC overnight until the weights were constant. Finally, the powder was kept in a glass bottle to use as an adsorbent.

3.4 Characterization of IC

The morphological features and surface characteristics of the samples were obtained from Scanning Electron Microscopy (Zeiss Evo 50). The sample was put on the carbon tape on the aluminium stub and coated with gold for electron reflection. The sample was then vacuumed for 5-10 minutes before analysis.

3.5 Procedures

A batch adsorption method was applied to carry out the adsorption process. The sample of dye solution was prepared by dissolving accurately weighted MB in 1 L distillated water. The dye solution pH was adjusted with 0.1 M Sodium Hydroxide (NaOH) and 0.1 M hydrochloric acid (HCl) solution using pH meter. Then it were carried out in a series of Erlenmeyer flasks of 250 mL containing 200 mL dye solution and specific amount of Imprata Cylindrica. The mixture is stir at a rate of 300 rpm to reach equilibrium. The samples were then withdrawn at appropriate time intervals and centrifuged at 3500 rpm for 15 min. All samples were centrifuged prior to analysis to minimize interference of adsorbent with the analysis. The dye concentrations in the supernatant were analyzed using UV/vis spectrophotometer at 668 nm. Each experiment was carried out in triplicate and an average value will be determined. The initial dye concentration in the test solution and the adsorbent dosage were varied to investigate their effect on the adsorption kinetics. The effect of pH is observed by studying the adsorption of dye over the pH range from 2 to 8. The pH of the dye solution was adjusted by using NaOH or HCl solution and a pH meter. The sorption studies were carried out at different temperatures (30-50 ºC). This is used to determine the effects of temperature on the thermodynamic parameters and for the effect of the concentration of the adsorbate, range from 50-200 ppm were studied. For the characterization of the Imprata Cylindrica, Scanning Electron Microscopy (SEM) will be used. This characterization process was done before and after the experiment.

3.6 Adsorption kinetic

For interpretation of adsorption kinetics, the aqueous samples were withdrawn at different time intervals and the concentrations of MB were similarly measured. The amount of adsorption at time *t*, q_t (mg/g) was calculated by:

$$q_e = \frac{(C_o - C_e)}{W} \times V \tag{3.1}$$

where C_o and C_e (mg/L) are the liquid-phase concentration of dye at initial and equilibrium, respectively. V (L) is the volume of the solution and W (g) is the mass of adsorbent used.

The MB removal percentage can be calculated as follows,

$$\text{Removal } (\%) = \left(\frac{C_o - C_t}{C_t} \right) \times 10 \tag{3.2}$$

where C_t (mg/L) is the liquid-phase concentrations of dye at any time.

For evaluating the adsorption kinetics of MB, the pseudo-first-order (Lagergren, 1898) and pseudo-second-order (Ho and McKay, 1999) kinetic models were used to fit the experimental data. The pseudo-first-order and pseudo–second-order models are expressed as follows:

Pseudo-first-order equation: $$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{3.3}$$

Pseudo-second-order equation: $$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{3.4}$$

where q_e (mg/g) is the amount of adsorbate adsorbed at equilibrium, q_t (mg/g) is the amount of adsorbate at time t, k_1 (1/min) is the rate constant of pseudo-second-order adsorption, k_2 (g/mg.min) is the rate constant of pseudo-second-order adsorption.

3.7 Adsorption isoterm

Adsorption isotherm is essential for practical design of the adsorption systems (Foo and Hameed, 2010) and it is basically important to describe how solutes interact with adsorbents, and is critical in optimizing the use of adsorbents. Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1906) models are the several isotherm equations available for analyzing experiment sorption equilibrium parameter. The linearized forms of these two isotherms are expressed as below.

The Langmuir isotherm: $$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \tag{3.5}$$

where q_m (mg/g) is the maximum adsorption capacity in monolayer adsorption, K_a (L/mg) is the adsorption equilibrium constant related to free energy adsorption and C_e (mg/L) is the MB concentration at equilibrium. The essential characteristics of the

Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by equation 3.6 (Inbaraj *et al.*, 2009):

$$R_L = \frac{1}{(1 + K_L C_O)} \tag{3.6}$$

where K_L (L/mg) is Langmuir constant and C_0 (mg/L) is the highest initial concentration of adsorbate.

The Freundlich isotherm: $q_e = K_F C_e^{1/n}$ (3.7)

where K_F is the Freundlich adsorbent capacity and n is the heterogeneity factor.

3.8 Thermodynamic Studies

Thermodynamic parameters such as change in standard free energy (ΔG^o), change in standard enthalpy (ΔH^o), and change in standard entropy (ΔS^o), are calculated using following equations (Smith and Van Ness, 1987).

$$\Delta G^o = -RT \ln K_D \tag{3.8}$$

$$\ln K_D = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{3.9}$$

where R is the ideal gas constant (8.314 J/mol K), T is the absolute temperature in Kelvin, K_D (L/mg) is the Langmuir isotherm constant. The values of ΔH^o and ΔS^o were determined from the slope and intercept of the Van't Hoff plot of $ln\ K_D$ versus 1/T, respectively. The calculated values of ΔH^o, ΔS^o and ΔG^o are listed in Table 4 for temperature range of 30-40 ^{o}C and 40-50 ^{o}C.

3.9 Process Flow Diagram

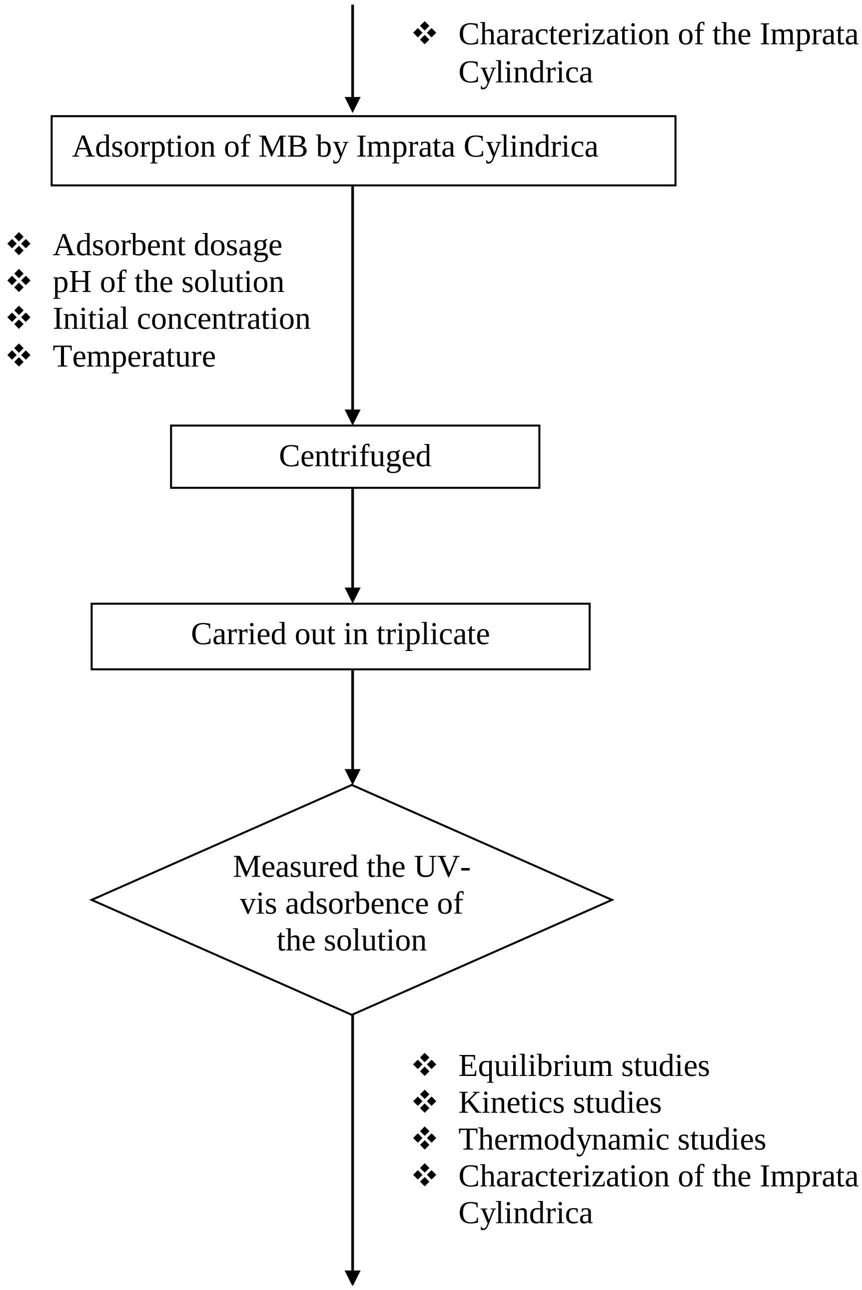


Figure 3-1: Process Flow Diagram

4 RESULTS AND DISCUSSION

4.1 Overview

In this section, a discussion of the results will be described in detail and it will be covered all the scopes that have been presented in chapter 1.

4.2 Effect of adsorbent dosage

In order to investigated the effect of adsorbent dose (g/L) on dye adsorption, the experiments were conducted at initial dye concentration of 100 mg/L, 30 °C and pH 6, while the amount of adsorbent added was varied (0.25-2 g/L). Figure 4-1 shows the effect of adsorbent dosage on the percentage removal of MB. At equilibrium time, the percentage removal increased from 68.28% to 89.27% for an increase in amount of IC from 0.25 to 1 g/L and the remained nearly constant over the dosage of 1 to 2g/L. The increase in percentage colour removal was due to the increase in the available sorption surface and sites (Hameed, 2008b). Similar results had been reported for the removal of methylene blue using grass waste (Hameed, 2008b), removal of cationic dye from aqueous solution using jackfruit peel (Hameed, 2008a) and removal of basic dye from aqueous medium using pumpkin seed hull (Hameed and El-Khaiary, 2008a).On the basis of the results obtained, 1 g/L of the IC leaf powder was used for the further experiment.

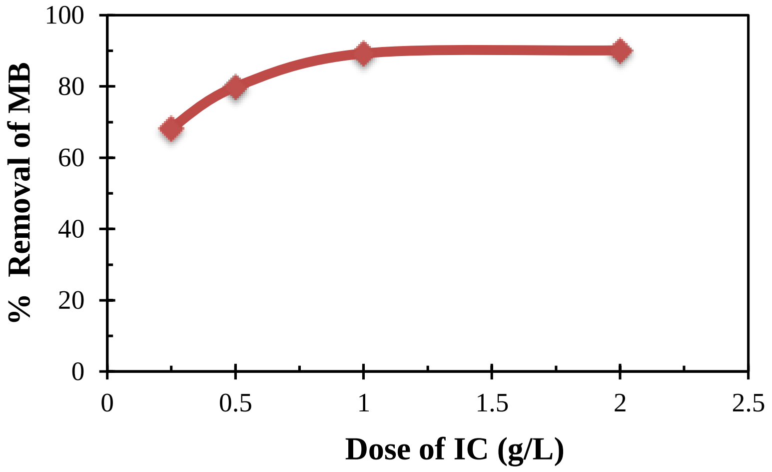


Figure 4-1: Effect of adsorbent dosage on the adsorption of MB on IC leaf powder (T = 30 °C, C_o = 100 mg/L, pH = 6)

4.3 Effect of initial pH

The important role of the pH dye solution is in the absorption process particularly on its capacity. It influenced not only the surface charge of the absorbent but also the degree of ionization of the absorbent in the solution but also the dissociation of functional groups on the active sites of the adsorbent (Dülger *et al.,* 2013). Therefore, the effects of the initial pH of MB solution were examined over a pH range of 2-8, and the results are presented in Figure 4-2.

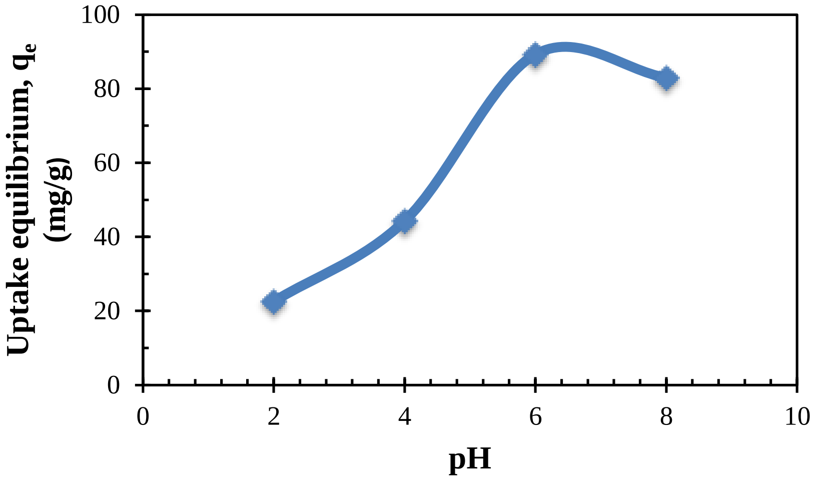


Figure 4-2: Effect of pH on methylene blue adsorption onto IC leaf powder (T = 30 °C, C_o = 100 mg/L, adsorbent dosage = 1g/L)

It was observed that the adsorption of MB onto IC increased with increasing pH and decreased after reached the maximum at pH 6. Low adsorption rate of MB on the IC at low pH may be because the surface charge become positively charged, thus making (H^+) ions compete effectively with dye cations causing a decrease in the amount of dye adsorbed. When the pH increased (pH 2 to pH 6), the positive charge on the solution interface decreased and the adsorbent surface appeared to be negatively charged (Hameed, 2008a). Thus, it resulted to a rapid increase in MB uptake from 40 to 85 mg/g at pH 4 to 6.However, at pH higher than pH 6, a slight decrease in MB uptake was observed due to the surface of the IC became negatively charged and electrostatically adsorbed the positively charged MB cations (Çelekli *et al.,* 2009). Therefore, pH 6 was determined to be the optimum pH value in this study. A similar behaviour was reported for methylene blue adsorption on grass waste (Hameed, 2008) and malachite green adsorption on rice straw-derived char ((Hameed and El-Khaiary, 2008b). Since the adsorption process was higher at pH 6, further experiments were carried out at this pH.

4.4 Effect of initial concentration

The initial dye concentration has an important influence on the adsorption capacity of MB. It provides an important driving force to overcome all mass transfer resistances of all molecules between the aqueous and solid phases (Hameed *et al.*, 2008). Figure 4-3 shows the effect of initial concentration on adsorption of MB onto IC.

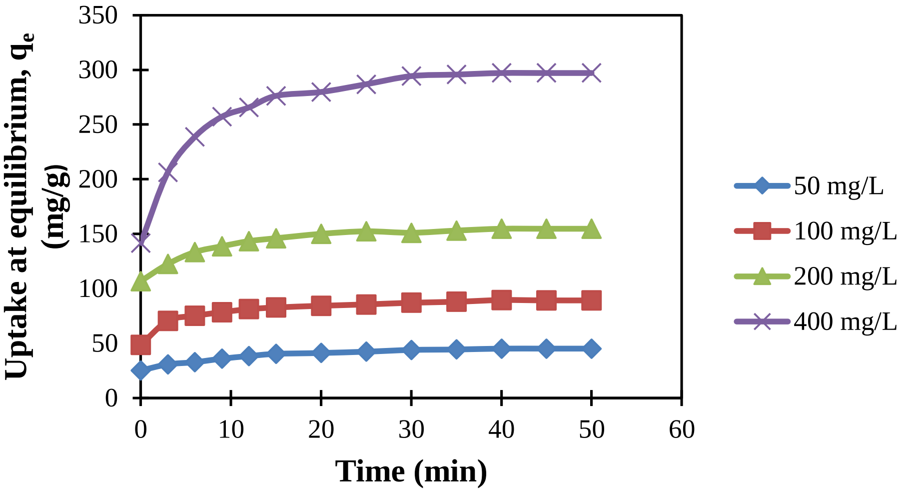


Figure 4-3: Effect of concentration on methylene blue adsorption onto IC leaf powder (T = 30 °C, pH = 6, adsorbent dosage = 1 g/L)

It was observed that dye uptake was rapid for the first 10 min, and then after processed at a slower rate and finally attained saturation. The result indicates that an increase in initial MB concentration leads to increase in the adsorption of MB on IC. The equilibrium adsorption increases from 33.2 to 294.96 mg/g, with increase in the initial MB concentration from 50 to 400 mg/L. This is because, when the initial concentration increased, the mass transfer driving force would become larger, hence resulting in higher MB adsorption. The adsorption of MB on IC was found to reach equilibrium in less than 20 min for MB solutions with lower initial concentration (50–200 mg/L), while at higher initial MB concentration (400mg/L), the time necessary to reach equilibrium was 30 min. However, in order to make sure that the full equilibrium was attained the experimental data were measured at 50 min. Similar results had been reported in the removal of methylene blue using grass waste (Hameed, 2008b) and removal of cationic dye from aqueous solution using jackfruit peel (Hameed,2008a). Since the adsorption process was higher at concentration 400 mg/L, further experiments were carried out at this concentration.

4.5 Effect of temperature

Temperature presents a notable effect on the adsorption process that is explained by means of thermodynamic parameters (Hu *et al.*, 2010).To observe the effect of temperature, the adsorption studies were performed at five different temperatures 30, 35, 40, 45 and 50°C while the adsorbent dosage, pH and concentration were constant at 0.2 g, pH 6 and 400 mg/L, respectively. Figure 4-4 shows that, at equilibrium, the amounts of MB adsorbed were around 297 mg/g, 305 mg/g and 317 mg/g at temperature 30 °C, 35 °C and 40 °C, respectively. Whereas at temperature 45 and 50 °C, the MB adsorbed were decreased around 308 mg/g and 295 mg/g. It was also observed that the maximum adsorption occurred at 40 °C. At a higher temperature, there will be a slight decrease of the surface coverage that maybe because of increase of dye penetration inside micro pores at higher temperatures or the creation of new active site as increase surface area. Similar results had been reported in study of carbon as a low cost adsorbent for treatment of methylene blue containing wastewater (Wang *et al.*, 2005).

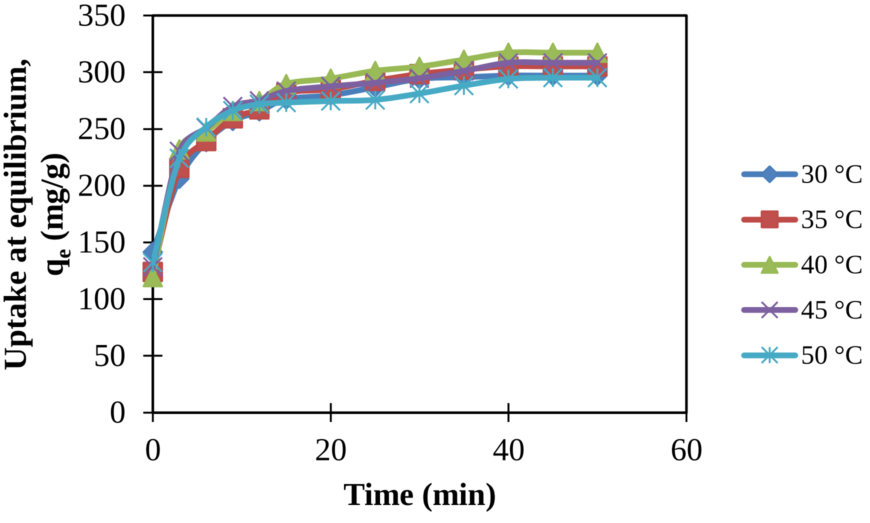


Figure 4-4: Effect of temperature on methylene blue adsorption onto IC leaf powder (C_o = 400 mg/L, pH = 6, adsorbent dosage = 0.2 g/L).

4.6 Adsorption kinetics

The dynamics and mechanism of adsorption process can be explained by evaluating the kinetic data (Silva *et al.,* 2011). Adsorption kinetic describes the controlling mechanism of adsorption processes which in turn governs the mass transfer and equilibrium time (Mestre *et al.,* 2011). Investigation of adsorption kinetics is important in the treatment of aqueous effluents because the adsorption kinetics provide valuable information regarding the mechanism of the adsorption process. For evaluating the adsorption kinetics of MB, the pseudo-first-order (Lagergren, 1898) and pseudo-second-order (Ho and McKay, 1999) kinetic models were used to fit the experimental data and it is already discussed in chapter 2.

From Figure 4-5 (a), the straight-line plots of $log\ (q_e - q_t)$ for the adsorption of MB onto IC have also been rested to obtain the rate parameter. The k_1, $q_{e,cal}$ and correlation coefficients R^2 under different MB concentrations were calculated from these plots and are listed in Table 1. The correlation coefficients R^2 listed in Table 1 for the first-order kinetic models were ≥ 0.9298. The value of R^2 indicated that the pseudo-first-order model data do not fall on straight lines for most initial concentrations resulting that this model is less appropriate. It also was found that the calculated q_e values do not agree with the experimental q_e values. Then, the experimental kinetic data were further analyzed using the pseudo-second-order model.

Figure 4-5 (b) show the plotting of t/q_t against t for different initial MB concentration, a straight line was obtained in all cases and using equation 3.4, the second-order rate constant (k_2) and q_e values were determined from the plots and are list in Table 4-1. The values of correlation coefficient, R^2 were very high which is above 0.999 for all concentrations studied, which were higher than the R^2 values obtained for the pseudo-first order model. It is important to note that for the pseudo-first-order model, the correlation coefficient obtained in this study, $R^2 \leq 0.9744$ at different initial MB concentrations, which is lower as compared to the correlation coefficient obtained from the pseudo-second-order model. Moreover, from Table 4-1, it can be seen that the experimental values of $q_{e,exp}$ are not in good agreement with the theoretical values calculated ($q_{e,cal}$) from the pseudo-first-order equation. Therefore, it can be concluded that the pseudo-second-order kinetic model provided a better correlation for the adsorption of MB on IC at different initial MB concentrations compared to the pseudo-first order model. Similar phenomenon has been observed in the adsorption of methylene blue by hazelnut shells and wood sawdust (Ferrero, 2007) and activated carbon prepared from rattan sawdust (Mittal *et al.*, 2007).

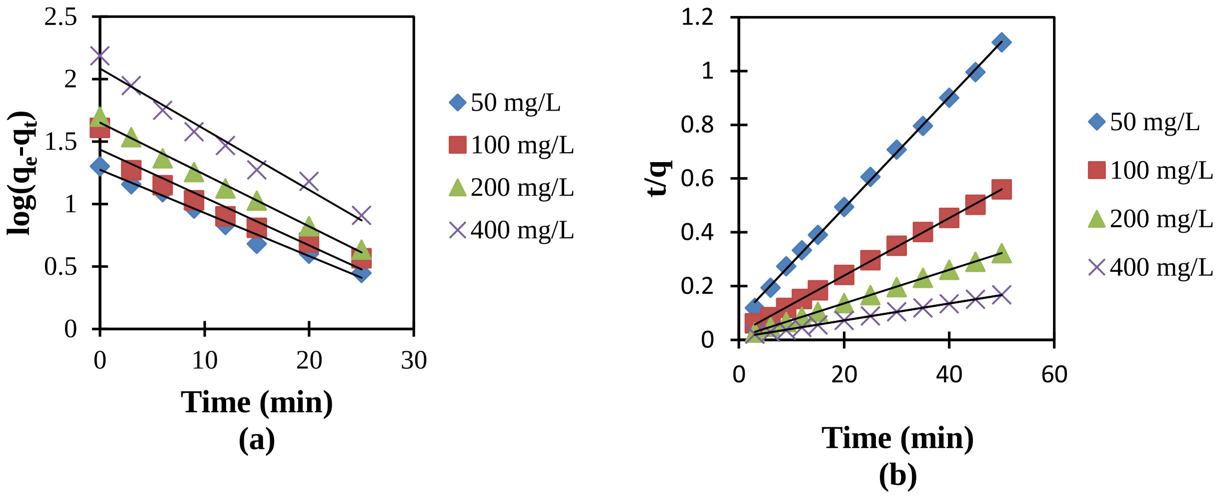


Figure 4-5: (a) Pseudo-first-order kinetic and (b) Pseudo-second-order kinetic for adsorption for adsorption of MB on IC leaf powder

Table 4-1: Comparison of the pseudo-first-order and pseudo-second-order

Conc. (mg/L)	**Experimental**	**Pseudo first order**			**Pseudo second order**		
	q_e (mg/g)	**q_e (mg/g)**	**k_1 (1/min)**	**R^2**	**q_e (mg/g)**	**k_2 (1/min)**	**R^2**
50	45.2	18.74995	0.079454	0.9844	48.54369	0.005399	0.999
100	89.26380368	27.20195	0.088205	0.9298	93.45794	0.004455	0.9997
200	154.7420965	44.8229	0.095805	0.9939	161.2903	0.003527	0.9999
400	297.0822281	121.283	0.111926	0.9744	322.5806	0.000971	0.9997

4.7 Adsorption Isotherm

Adsorption isotherm is an essential data source for practical design and fundamental understanding of the carbonaceous adsorbents. The parameters obtained from different isotherm models are important for optimization of the adsorption mechanism pathways and expression of the surface properties of adsorbents (Foo and Hameed, 2010). Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1906) models are the several isotherm equations available for analyzing experiment sorption equilibrium parameter and all the equation are presented in the chapter 2.

The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface (Langmuir, 1916). A basic assumption is that sorption takes place at specific homogeneous sites within the adsorbent. Once a dye molecule occupies a site, no further adsorption can take place at that site. From Table 4-1, it shows that the value of correlation coefficient R^2 decreased as the temperature is increased which shows that the adsorption of MB not fitted well with Langmuir isotherm model. The values of R_L for the studied system were found to be 0.1019-0.1412 and which confirmed that the IC is favourable for adsorption of MB dye under conditions used in this study.

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems and the characteristic Freundlich parameters (K_F and $1/n$) calculated from the intercept and slope of the linear plot log q_e versus log C_e and the value of correlation coefficient R^2 are presented in Table 4-2. It shows that the Freundlich model is the best fit model for the adsorption isotherm data at all the temperature ranges studied suggesting multilayer adsorption between the MB and IC surface. This also suggests the heterogeneous nature of the IC involving physisorption. The Freundlich K_F value decreases from 19.82 to 11.88 with increasing temperature from 30 to 50 °C. The higher n values also suggest that IC adsorption on is favorable.

Table 4-2: Langmuir isotherm and Freundlich isotherm parameter for adsorption of MB on IC leaf powder

T (°C)	**Langmuir Isotherm**				**Freundlich Isotherm**		
	q_{max} (mg/g)	**K_a (L/mg)**	**R^2**	**R_L**	**K_f (mg/g)**	**N**	**R^2**
30	400.0000	0.1135	0.8707	0.1019	19.8243	1.7470	0.9761
35	556.4123	0.1137	0.9012	0.1235	17.4327	1.6376	0.9775
40	526.3158	0.1141	0.9236	0.1305	15.1739	1.4446	0.9795
45	503.4449	0.1149	0.9287	0.1351	13.3746	1.3284	0.9824
50	491.3781	0.1153	0.9302	0.1412	11.8884	1.1165	0.9876

4.8 Thermodynamic Studies

Adsorption thermodynamic is an important tool elucidating the adsorption behaviour of an isolated system. Temperature presents a notable effect on the adsorption process that is explained by means of thermodynamic parameters (Hu *et al.*, 2010). The thermodynamic parameters were evaluated to investigate the nature of the adsorption. Thermodynamic parameters such as change in standard free energy (ΔG^o), change in standard enthalpy (ΔH^o), and change in standard entropy (ΔS^o), are calculated using equations 2.12 and 2.14 and are listed in Table 4-3 for temperature range of 30-40 ^oC and 40-50 ^oC.

Table 4-3: Thermodynamic parameters for the adsorption of MB onto IC leaf powder

Temp (^{o}C)	**ΔH^o (kJ/mol)**	**ΔS^o (J/mol.K)**	**ΔG^o (kJ/mol)**
30-40	22.40	85.60	-2.64
40-50	-25.90	-71.50	-3.50

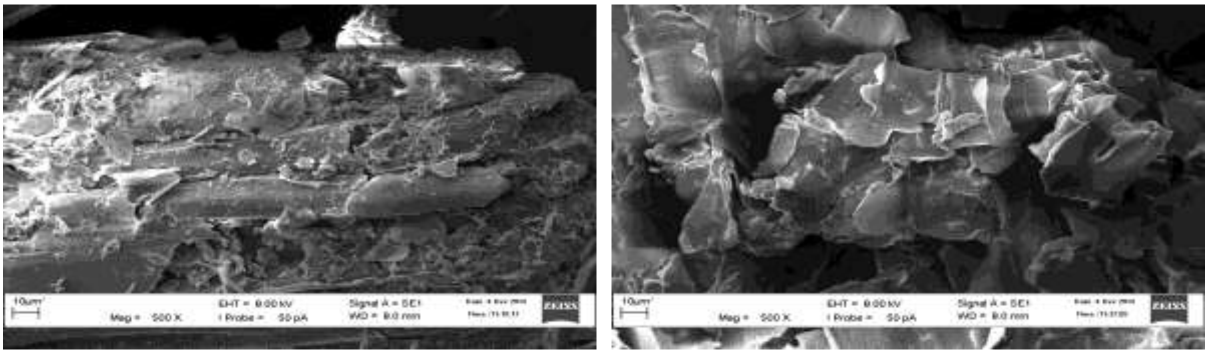
At temperature range of 30-40 ^oC, the positive value of ΔH^o (22.4 kJ/mol) indicated the endothermic nature of the adsorption process and the magnitude (22.4 kJ/mol) was in the heat range of physisorption (<40 kJ/mol) (Wang *et al.*, 2010). This endothermic process was due to the increase in temperature that enhanced the diffusion rate of adsorbate molecules across the external boundary layer and in the internal pores of adsorbent particle. Moreover, the magnitude of ΔH^o (22.4 kJ/mol) was in the heat range of physisorption (< 40 kJ/mol) (Wang *et al.*, 2010) consistent with the results obtained in isotherm studies. The positive value of ΔS^o (85.6 kJ/mol.K) corresponded to an increase in randomness at their solid-solution interface during the adsorption process. While, the negative value of ΔG^o (-2.64 kJ/mol) indicated the feasibility of the process and the spontaneous nature of the adsorption with a high preference of MB onto the IC.

However at temperature range of 40-50 ^oC, all the thermodynamic parameters are the negative value. The negative value of ΔH^o (-25.90 kJ/mol) represents exothermic nature of the adsorption interaction. Increasing temperature showed a dramatic decrease of adsorption capacity. This exothermic process was attributed to the weakening of adsorptive forces between the binding sites and the dye species, and between the adjacent dye molecules on the adsorbed phase. The negative value of ΔS^o (-71.50 kJ/mol.K) corresponded to a decreasing in randomness at their solid-solution interface during the adsorption process. Same as temperature between 30-40 ^{o}C, the negative value of ΔG^{o} (-2.64 kJ/mol) indicated the feasibility of the process and the spontaneous nature of the adsorption with a high preference of MB onto the IC. With all the negative values at this range of temperature give a clear evidence that the interaction between MB and IC was weak.

In general, the calculated values of thermodynamic parameters such as ΔH^{o}, ΔG^{o} and ΔS^{o} clearly indicated that the adsorption behaviour of the system is endothermic, feasible and increasing randomness at temperature range of 30-40 ^{o}C, while, at temperature range of 40-50 ^{o}C, the ongoing process is exothermic, feasible and decreasing randomness. Similar finding was reported by Nasuha and Hameed (2011) and Safa and Bhatti (2011) where MB dye was adsorbed on tea waste and rice husk, respectively.

4.9 SEM analysis of IC

Scanning Electron Microscopy was used to study the morphology and structure of IC surface before adsorption and after 50 min adsorption process. Figure 4-6 (a) and (b) shows SEM images for IC adsorbent before adsorption and after 24 hour adsorption process, respectively. From Figure 4-6 (a), it is clear that, IC has a rough surface with a heterogeneous pores and cavities. This indicates that there is a good possibility for MB dye to be trapped and adsorbed into the surface. Whereas in Figure 4-6 (b) depicting the surfaces of particles after adsorption, it is clearly seen that the caves, pores and surfaces of adsorbent were covered by dye and consequently the surface has become rough and corroded.



(a) (b)

Figure 4-6: SEM micrograph of (a) Imperata Cylindrica before adsorption process (b) Imperata Cylindrica after 50 min of adsorption process

5 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This study was mainly focused to establish the feasibility of using Imperata Cylindrica as a low cost adsorbent for removal of methylene blue. Based on the result, the Imperata Cylindrica leaf powder has a rapid absorption rate and good adsorption capacity of methylene blue. The optimum conditions for MB removal from aqueous solution by IC were achieved at 1 g/L of adsorbent dosage, pH 6, 400 mg/L initial dye concentration and at 40 ºC, with adsorption capacity of 314.06 mg/g. The Equilibrium data were analyzed using the Langmuir and Freundlich isotherms. The data were better described by the Freundlich isotherm model with coefficients of correlation $R^2 \geq 0.9795$, indicating that the ongoing process is heterogeneous in nature. Kinetic data were adequately fitted by the pseudo-second order kinetic model. The thermodynamic studies provided evidence for the feasibility, spontaneity and endothermic nature of the adsorption process, which is controlled by a physisorption process at temperature range of 30-40 ºC, while, at temperature range of 40-50 ºC, the ongoing process is exothermic, feasible and decreasing randomness. These results may be useful in considering preservation strategies for wastewater treatment focusing in dye wastewater by using Imperata Cylindrica.

5.2 Recommendation

From the result, it show that Imperata Cylindrica have the high capacity for removing methylene blue from aqueous solution. To improve the result of experiment, there are some investigations that can study to improve the effectiveness of adsorption capacity. One of that is by mixing the adsorbent with egg shell powder. Egg shell powder has a substantially larger capacity to remove the reactive dye by adsorption. It has been proved in the investigation of Sorption on eggshell waste—A review on ultrastructure, biomineralization and other applications (Guru and Dash, 2014) and Biosorption of Cr(III) ions by eggshells (Chojnacka, 2005). So, it is suggested to mixing the adsorbent with egg shell powder to getting the higher adsorption capacity. Apart from that, there are other investigate that can be carried out to improve the result:

- Investigate in detail the morphological characteristics of oil palm leave by using Brunauer-Emmett-Teller (BET),
- Used the real wastewater sample from the industries to see the efficiency of the natural sorbent in removing dye.
- Chemical modification of Imperata Cylindrica to enhance its adsorption capacity.

6 REFERENCES

Anber, Z. A., Al-Anber, M. A., Matouq, M., Al-Ayed, O., and Omari, N. M., 2011. Defatted Jojoba for the removal of methylene blue from aqueous solution: Thermodynamic and kinetic studies. *Desalination*. **276**(1-3): 169–174.

Abidin, M.A.Z., Jalil, A.A., Triwahyono, S., Adam, S.H., and Kamarudin, N.H.N., 2011. Recovery of gold (III) from an aqueous solution onto a durio zibethinus husk. *Biochemical Engineering Journal*. **54**(2): 124–131.

Abdulbari, Ahmad, A., Hameed, B. H., and Aziz, N., 2006. Basic Dye Removal from Synthetic Wastewater by Adsorption on Palm Ash. Proceedings of the 1st International Conference on Natural Resources Engineering and Technology, **2006**: 372-383.

Anjaneyulu, Y., Chary, N.S., and Raj, D.S.S., 2005. Decolourization of industrial effluents-available methods and emerging technologies-a review. *Reviews in Environmental Science and Bio/Technology*. **4**: 245-273.

Alkan, M., Doğan, M., Turhan, Y., Demirbaş, Ö., and Turan, P., 2008. Adsorption kinetics and mechanism of maxilon blue 5G dye on sepiolite from aqueous solutions. *Chemical Engineering Journal.* **139**(2): 213–223.

Almeida, C.A.P., Debacher, N.A., Downs, A.J., Cottet, L., and Mello C.A.D., 2009. Removal of methylene blue from colored effluents by adsorption on montmorillonite clay. *Journal of Colloid and Interface Science.* **332**(1): 46-53.

A. Mittal, A. Malviya, D. Kaur, J. Mittal, and L. Kurup, 2007. Studies on the adsorption kinetics and isotherms for the removal and recovery of methyl orange from wastewaters using waste materials, *Journal of Hazardous Materials.* **148**(1-2): 229–240.

B. H. Hameed, D. K. Mahmoud, and A. L. Ahmad, 2008. Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: Coconut (Cocos nucifera) bunch waste. *Journal of Hazardous Materials.* **158**(1): 65-72.

B. H. Hameed, 2008a. Removal of cationic dye from aqueous solution using jackfruit peel as non-conventional low-cost adsorbent. *Journal of Hazardous Materials.* **162**(1): 344-350.

B. H. Hameed, 2008b. Grass waste : A novel sorbent for the removal of basic dye from aqueous solution. *Journal of Hazardous Materials..*, **166**(1): 233–238.

B. H. Hameed and M. I. El-Khaiary, 2008a. Removal of basic dye from aqueous medium using a novel agricultural waste material: pumpkin seed hull. *Journal of Hazardous Materials.* **155**(3): 601-609.

B.H. Hameed and M.I. El-Khaiary, 2008b. Kinetics and equilibrium studies of malachite green adsorption on rice straw-derived char. *Journal of Hazardous Materials..* **153**(1-2): 701–708.

Brown, P. A., Gill, S. A., and Allen, S.J., 2000. Metal removal from wastewater using peat. *Journal of Water Research.* **34**(16): 3907-3916.

Çelekli, A., Yavuzatmaca, M., and Bozkurt, H., 2009. Kinetic and equilibrium studies on the adsorption of reactive red 120 from aqueous solution on Spirogyra majuscula. *Chemical Engineering Journal*. **152**(1): 139–145

Cheremisinoff, N.P., 2002. Handbook of Water and Wastewater Treatment Technologies. Butterworth-Heinemann, Boston.

Chemical Book, 2010. Methylene Blue (Online). http://www.chemicalbook.com/ (3 April 2014)

Dotto, G.L., Lima, E.C., and Pinto, L.A.A., 2012. Biosorption of food dyes onto Spirulinaplatensis nanoparticles: equilibrium, isotherm and thermodynamic analysis. *Journal of Bioresource Technology.* **103**(1): 123–130.

Dutta, S., Bhattacharyya, A., Ganguly, A., Gupta, S., and Basu, S., 2011. Application of response surface methodology for preparation of low-cost adsorbent from citrus fruit peel and for removal of methylene blue. *Desalination,* **275**: 26– 36.

Erdem, E., Çölgeçen, G., and Donat., R., 2005. The removal of textile dyes by diatomite earth. *Journal of Colloid and Interface Science.* **282**(2): 314-319.

eMedicalprep, 2011. Study Material, Chemistry, Surface Chemistry, Comparisons-Physisorption and Chemisorptions (Online). http://www.emedicalprep.com/study-material/chemistry/comparision-phsisorption-chemisorption.html (5 April 2014).

Fraissard, J.P., and Conner, C.W., 1997. Physical Adsorption: Experiment, Theory and Applications. Spinger-Verlag.

F. Ferrero,2007. Dye removal by low cost adsorbents: hazelnut shells in comparison with wood sawdust. *Journal of Hazardous Materials.* **142**(1-2): 144–152.

Freundlich, H.M.F., 1906. Über die adsorption in lösungen. Z. *Physical Chemistry Journal.* **57**: 385–470

Foo, K.Y., and Hameed, B.H., 2010. Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal*. **156**(1): 2–10.

Gong, R., Feng, M., Zhao, J., Cai, W., and Liu, L., 2009. Functionalization of sawdust with monosodium glutamate for enhancing its malachite green removal capacity. *Journal of Bioresource Technology.* **100**(2): 975–978.

Guo, Y., Yang, S., Fu, W., Qi, J., Li, R., and Wang, Z., 2003. Adsorption of malachitegreen on micro and mesoporous rice husk based activated carbon. *Journal of Dyes & Pigments*. **56**(3): 219-229.

Gupta, V.K., and Suhas, 2009. Application of low-cost adsorbents for dye removal: a review. *Journal of Environmental Management*. **90**(8): 2313-2342.

Gürses, A., Dogar, Ç., Yalçin, M., Açikyildiz, M., and Karaca , S., 2006. The adsorption kinetics of the cationic dye, methylene blue, onto clay. *Journal Hazardous Material.* **131**(1-3): 217–228.

Hamdaoui O. and Chiha M., 2007. Removal of Methylene Blue from Aqueous Solutions by Wheat Bran. *Acta Chimica Slovenica Journal*.**54:** 407–418.

Hanafiah, M.A.K.M., W.S.W. Ngah, S.C. Ibrahim, H. Zakaria and W.A.H.W. Ilias, 2006. Kinetics and thermodynamic study of lead adsorption from aqueous solution onto rubber (Hevea brasiliensis) leaf powder. *Journal of Applied Science.* **6**(13): 2762-2767.

Ho, Y.S., and McKay, G., 1998. Sorption of dyes from aqueous solution by peat. *Chemical Engineering Journal*. **70**(2): 115-124.

Ho, Y.S., and McKay, G., 1999. Pseudo-second order model for sorption processes. *Journal of Process Biochemistry*. **34**(5): 451–465.

Holm, L.G., D.L. Plucknett, J.V. Pancho and J.P. Herberger, 1977. The World's Worst Weeds: *Distribution and Biology, University Press of Hawaii, Honolulu, Hawaii, USA.*, pp. 609.

Howard L. Needles, 1986. Textile Fibers, Dyes, Finishes, and Processes. Noyes Publications.

Hu, Z., Chen, H., Ji, F., and Yuan, S., 2010. Removal of Congo Red from aqueous solution by cattail root. *Journal of Hazardous Material.* **173**(1-3): 292–297.

Hunger, K., 2003. Industrial Dyes. Chemistry, Properties, Applications. WILLEY-VCH Verlag GmbH & Co. KgaA, Weinheim.

I. Langmuir, 1916. The constitution and fundamental properties of solids and liquids,

Journal of the American Chemical Society. **38**(11): 2221–2295.

Jalil, A.A., Triwahyono, S., Yaakob, M.R., Azmi, Z.Z., Sapawe, N., and Kamarudin, N.H.N.,2012. Utilization of bivalve shell-treated Zea mays L. (maize) husk leaf as a low cost biosorbent for enhanced adsorption of malachite green. *Journal of Process Biochemistry.* **120**: 218-224.

Jain, A.K., Gupta, V.K., Bhatnagar, A., and Suhas, 2003. Utilization of industrial waste products as adsorbents for the removal of dyes. *Journal of Hazardous Materials..* **101**(1): 31–42.

Joseph, M. L., 1977. Introductory Textile Science. New York: Holt, Rinehart, and Winston.

Karim, A.B., Mounir, B., Hachkar, M., Bakasse, M., and Yaacoubi, A., 2008. Removal of basic red 46 dye from aqueous solution by adsorption onto Moroccan clay. *Journal of Hazardous Materials.* **168**(1): 304-309.

Kannan, N., and Sundaram, M., 2001. Kinetics and mechanisms of removal of methylene blue by adsorption on various carbons — a comparative study. *Dyes Pigments* **51**(1), 25–40.

Lagergren, S., 1898. About the theory of so-called adsorption of soluble substances. **24**(1): 1–39.

Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*. **40**(9): 1361–1403.

Lakshmi, U.R., Srivastava, V.C., Mall, I.D., Dilip H. and Lataye, D.H., 2009. Rice husk ash as an effective adsorbent: Evaluation of adsorptive characteristics for Indigo Carmine dye. *Journal of Environmental Management.* **90**(2): 710-720.

Levine, A. D and Asano, T., 1995. *Wastewater Reuse*. Water quality International.

Low, K.S., C.K. Lee and S.C. Liew, 2000. Sorption of cadmium and lead from aqueous solutions by spent grain. *Journal of Process Biochemistry.* **36**(1-2): 59-64.

Malik, P. K., 2004. Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics. *Journal of Hazardous Material.* **113**(1-3): 81-88.

M.A.K. Megat Hanafiah, W.S. Wan Ngah , H. Zakaria and S.C. Ibrahim , 2007. Batch Study of Liquid-Phase Adsorption of Lead Ions Using Lalang (*Imperata cylindrica*) Leaf Powder. *Journal of Biological Sciences,* **7**(2): 222-230.

Mckay, G, J.F. Porter, and G.R. Prasad, 1999. The removal of dye coloures from aqueous solutions by adsorption on low-cost materials, *Water, Air and Soil Pollution Journal.* **114**(3-4): 423–438.

Mckay, G, Blair, H. S., and Prasad, J. R., 2003. Adsorption of dyes on chitin. I. Equilibrium studies. *Journal of Applied Polymer Science.* **27**(8): 3043–3057.

Mestre, A.S., Bexiga, A.S., Proença, M., Andrade, M., Pinto, M.L., Matos, I., Fonseca, I.M., and Carvalho, A.P., 2011. Activated carbons from sisal waste by chemical activation with K2CO3: kinetics of paracetamol and ibuprofen removal from aqueous solution. *Journal of Bioresource Technology.* **102**(17): 8253–8260.

Nigam P, 2000. Physical removal of textile dyes from effluents and solid-state fermentation of dye-adsorbed agricultural residues. *Journal of Bioresource Technology.* **72**(3): 219-226.

Namasivayam, C., and Yamuna, R.C., 1992. Removal of Rhodamine B by biogas slurry from aqueous solutions. *Water, Air and Soil Pollution Journal.* **65**(1-2),101-109.

Nasuha, N., and Hameed, B. H., 2011. Adsorption of methylene blue from aqueous solution onto NaOH-modified rejected tea. *Chemical Engineering Journal*. **166**(2): 783–786.

Nacera, Y., and Aicha, B., 2006. Equilibrium and kinetic modelling of methylene blue biosorption by pretreated dead *streptomyces rimosus*: Effect of temperature. *Chemical Engineering Journal.* **119**(2-3): 121–125.

Öznur Dülger, Fatma Turak, Kadir Turhan, and Mahmure Özgür, 2013. Sumac Leaves as a Novel Low-Cost Adsorbent for Removal of Basic Dye from Aqueous Solution. *International Scholarly Research Notices Analytical Chemistry*. **2013** (2013).

Patil, S., S. Renukdas, and N. Patel, 2011. Removal of methylene blue, a basic dye from aqueous solutions by adsorption using teak tree (Tectona grandis) bark powder. *International Journal of Environmental Sciences*. **1**(5): 711-726.

Quek, S.Y., D.A.J. Waste and C.F. Forster, 1990. The use of sago waste for the soption of lead and copper. *Journal of Water SA.* **24**(3): 251-256.

Safa, Y., and Bhatti, H. N., 2011. Kinetic and thermodynamic modeling for the removal of Direct Red-31 and Direct Orange-26 dyes from aqueous solutions by rice husk. *Desalination.* **272**(1-3), 313–322.

Seki, Y., and Yurdakoç¸ K., 2006. Adsorption of Promethazine hydrochloride with KSF Montmorillonite. *Adsorption.* **12**(1): 89–100.

Shukla, A., Y.H. Zhang, P. Dubey, J.L. Margrave and S.S. Shukla, 2002. The role of sawdust in the removal of unwated materials from water. *Journal of Hazardous Materials.,* **95**(1-2): 137-152.

Silva, L. G., Ruggiero, R., Gontijo, P. M., Pinto, R. B., Royer, B.,and Lima, E. C., 2011. Adsorption of Brilliant Red 2BE dye from water solutions by a chemically modified sugarcane bagasse lignin. *Chemical Engineering Journal.* **168**(2): 620–628.

Uddin, Md. Tamez; Rukanuzzaman, Md.; Khan, Md. Maksudur Rahman; Islam, and Md. Akhtarul , 2008. Jackfruit (Artocarpus heterophyllus) leaf powder: An effective adsorbent for removal of methylene blue from aqueous solutions. *Indian Journal of Chemical Technolody,* **16**(2): 142-149.

Vadivelan, V., and Kumar K. V., 2005. Equilibrium, kinetics, mechanism and process design for the sorption of Methylene Blue onto rice husk. *Journal of Colloid and Interface Science.* **286**(1): 90-100.

Vucurovic, V. M., Razmovski, R. N., and Tekic, M. N., 2012. Methylene blue (cationic dye) adsorption onto sugar beet pulp: Equilibrium isotherm and kinetic studies. *Journal of Taiwan Institute of Chemical Engineers.* **43**(1): 108– 111.

Vucurovic, V. M., Razmovski, R. N., and Tekic, M. N., 2012. Methylene blue (cationic dye) adsorption onto sugar beet pulp: Equilibrium isotherm and kinetic studies. *Journal of Taiwan Institute of Chemical Engineers.***43**(1): 108– 111.

V. Vadivelan, K. V. Kumar, 2005. Equilibrium, kinetics, mechanism andprocess design for the sorption of Methylene Blue onto rice husk. *Journal of Colloid and Interface Science.* **286**(1): 90-100.

Wang, S., Zhu, Z.H., 2005. Sonochemical treatment of fly ash for dye removal from wastewater. *Journal of Hazardous Materials.azardous material.* **126**(1-3): 91-95.

Wang, Y., Gong, C., Sun, J., Gao, H., Zheng, S., Wu, S., 2010. Separation of ethanol / water azeotrope using compound starch-based adsorbents. *Journal of Bioresource Technology*. **101**(15): 6170-6176.

7 APPENDICES

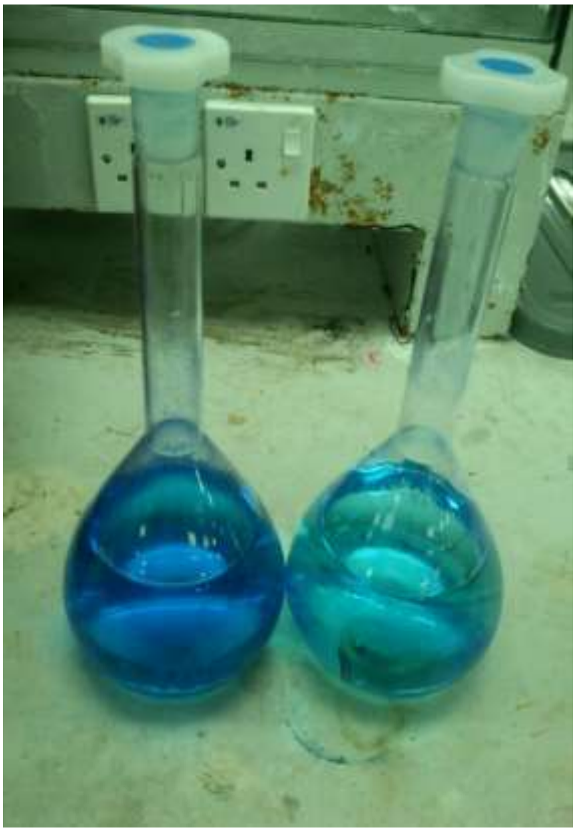


Figure 7-1: Methylene blue solution


Figure 7-2: Adsorption process

Figure 7-3: Imprata Cylindrica before and after adsorption process

Figure 7-4: Scanning Electron Microscope (Zess Evo 50)