POTENTIAL OF OIL PALM LEAVES AS AN ADSORBENT FOR THE REMOVAL OF METHYLENE BLUE FROM AQUEOUS SOLUTION

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Thesis submitted in partial fulfilment of the requirements
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SUPERVISOR’S DECLARATION

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

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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.

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Date : 6 JANUARY 2015

Dedication

I dedicate this to my family, especially for my mother Zaitah binti Mahmud and my father, Mohd Suhaimi bin Embong, that give a lot of support and pray for me to finish my partial thesis research. Love both of you so much.

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ABSTRACT

Coloring effluent from industrial activities may affect environmental and human health and with this concern, many methods have been studied to decolorize such effluent including physical, chemical and biological methods. Among the methods available, adsorption process is the most commonly used to remove dyes because of its low cost, simple design and easy to perform. Adsorption onto activated carbon has been used with great success. However, its high cost sometimes tends to limit its use. Therefore, many low-cost adsorbents have been developed for dye removal such as natural materials, industrial waste and agriculture waste. So, the aim of the present work was to investigate the feasibility of oil palm leaves (OPL), a solid waste, abundantly available in Malaysia, for the adsorption of methylene blue. Batch adsorption studies were conducted to evaluate the effects of adsorbent dosage (0.25-2.0 g/L), pH (2-8), initial concentration (50-400 mg/L), and temperature (30-70 ºC). The experimental data were analyzed by the Langmuir and Freundlich isotherms, and were found to follow the Langmuir isotherm model with coefficients of correlation $R^2 \geq 0.9512$ indicating that the ongoing process is chemical adsorption. 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 oil palm leaves with coefficients of correlation $R^2 \geq 0.998$ for all initial methylene blue concentrations studied. Thermodynamic parameters such as ΔH^o, ΔG^o and ΔS^o clearly indicated that the ongoing process is endothermic, spontaneous, and chemical in nature at 30-50^{o}C, while at 50-70^{o}C, the ongoing process is exothermic, spontaneous, and chemical in nature. The optimum conditions were achieved at 0.5 g/L of adsorbent dosage, pH 6, 400 mg/L initial dye concentration and 50 ^{o}C with maximum adsorption capacity of 694.6 mg/g. The adsorption of MB into the OPL was confirmed by SEM and FTIR for OPL before adsorption and after 50 min adsorption process. The results revealed that the (OPL) could be employed as a low-cost adsorbent for the removal of methylene blue from aqueous solution.

ABSTRAK

Sisa buangan berwarna dari aktiviti-aktiviti perindustrian boleh menjejaskan alam sekitar dan kesihatan manusia dan dengan kesedaran ini, banyak kaedah telah dikaji untuk menyahwarna sisa ini termasuklah kaedah fizikal, kimia dan biologi. Antara kaedah yang sedia ada, proses penjerapan adalah yang paling biasa digunakan untuk membuang pewarna kerana kosnya yang rendah, rekabentuk ringkas dan mudah untuk dilaksanakan. Penjerapan ke atas karbon teraktif telah digunakan dengan jayanya. Namun, kosnya yang tinggi kadang-kadang cenderung untuk menghadkan penggunaannya. Oleh itu, banyak penjerap kos rendah telah diperkenalkan untuk penyingkiran pewarna seperti bahan-bahan semulajadi, sisa perindustrian dan sisa pertanian. Jadi, kajian ini bertujuan untuk menyiasat kebolehan daun kelapa sawit (OPL), iaitu sisa pepejal, yang banyak didapati di Malaysia, untuk menyerap metilena biru. Kajian-kajian penjerapan kelompok telah dijalankan untuk menilai kesan dos bahan penjerap (0.25-2 g/L), pH awal (2-8) , kepekatan awal (50-400 ppm) dan suhu (30-70 ºC). Data kajian telah dianalisis oleh isoterma Langmuir dan Freundlich , dan didapati data mengikuti model isoterma Langmuir dengan pekali korelasi $R^2 \geq 0.9512$ yang menunjukkan bahawa proses berterusan ialah penjerapan kimia. Model kinetik tertib-pseudo-pertama dan model kinetik tertib-pseudo-kedua telah diuji dengan data kajian, dan model kinetik pseudo kadar kedua adalah yang terbaik untuk penjerapan MB oleh daun kelapa sawit dengan pekali korelasi $R^2 \geq 0.998$ untuk semua kepekatan awal yang dikaji. Parameter termodinamik seperti ΔH^o, ΔG^o dan ΔS^o dengan jelas menunjukkan bahawa proses berterusan adalah endoterma, spontan, dan kimia dalam alam semula jadi pada suhu 30-50 ^{o}C, manakala pada suhu 50-70 ^{o}C, proses berterusan adalah eksoterma, spontan dan kimia dalam alam semula jadi. Keadaan optima telah dicapai pada 0.5 g/L dos bahan penjerap, pH 6, 400 mg/L kepekatan awal dan suhu 50 ^{o}C dengan kapasiti penjerapan maksimum 694.6 mg/g. Penjerapan MB ke dalam OPL telah disahkan oleh SEM dan FTIR bagi OPL sebelum dan selepas 50 min proses penjerapan. Hasil kajian menunjukkan bahawa OPL boleh digunakan sebagai bahan penjerap kos rendah untuk penyingkiran metilena biru dari larutan akueus.

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LIST OF SYMBOLS

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

LIST OF ABBREVIATIONS

MB	Methylene Blue
FTIR	Fourier-Transform Infrared Spectrometer
OPL	Oil Palm Leaves
SEM	Scanning Electron Microscopy

1 INTRODUCTION

1.1 Background

Dyes or coloring are organic compounds, which contain in their molecules color imparting chromophoric groups and acid or basic auxochromic groups responsible for dyeing ability due to the auxochromes, dye molecules can be permanently bonded with fibers or other materials. Chemical engineering aspects of dyes synthesis made essential part in development applied in chemical technology operation and constructions of specialist apparatuses. Besides their traditional use in textile, leather, paper, as well as the paint and varnish industries, dyes have become indispensable in other fields such as microelectronics, medical diagnostics and information recording techniques and they continue to be intensively developed (Hoffmann and Puszynski, 2009).

Dyes is the first contaminant to be recognized in water and has to be removed from wastewater before discharging it into water bodies. In the dyeing section of a textile industry, about 1000 L of water is used for every 1000 kg clothes processed. Discharged of such color effluents imparts color to the receiving water bodies such as rivers and lakes and will interfere with its intended beneficial use (Suraya, 2009). Thus, it is important to remove dyes from receiving water bodies.

Several methods have been used to remove the dye from wastewater such as reduction, precipitation, reverse osmosis dialysis exchange ions and the most popular is the adsorption. Adsorption process has the excellent efficiency in the removal of pollutants besides economical and simple in design, which make it applications, has expanded rapidly (Dabrowski, 2001). Usually, adsorption by activated carbon is widely used to removal dyes. This is because they have high capabilities for various kinds of dyestuffs but sometimes the uses of activated carbon is limited since they have a high costs (Bhatnagar and Jain, 2005).

Therefore, there is a need to find out much economical, effective, viable alternative adsorbent. As for that, natural materials, waste materials from industry or agricultural, and biosorbent can be obtained and employed as an inexpensive adsorbent. Oil palm leaves are usually being leftover or burned at the plantation area. In general, these materials have no economic value and in fact often create a serious problem of disposal. Thus utilizing oil palm leaves as an alternative and low-cost adsorbent would increase the economic value, help to reduce the cost of disposal and consequently can reduce the environmental pollution.

1.2 Motivation and Problem Statement

In the era of globalization, the request for dyes was increased since the industry of dyestuffs, textile, paper, leather, foodstuffs, cosmetics, rubber and plastics was growing rapidly. In our daily lives, dyes are also being used in anywhere like in food, clothing, wood, car, everyday equipments and others (Hoffmann and Puszynski, 2009). Most of the dyes and pigments are considered inert or non as toxic, although some are not totally innocuous. Interest in the environmental behavior of dyes is prompted primarily by concern over their possible toxicity and carcinogenicity, heightened by the fact that many dyes formerly were made of known carcinogens such as benzidine, which may be reformed as a result of metabolism. Methylene blue dyes have been shown to have high partition coefficients and solubility, suggesting significant potential for bioconcentration (Hunger, 2003).

Increasing the use of dyes in the industry indirectly cause environmental pollution, especially water. Textile and dyeing industry are among important sources for the continuous pollution of the aquatic environment. Because they produce approximately 5% of them end up in effluents. The textile and dyeing industries effluents are dumped in the sea, river or lake has bad impact on biological life various organisms in that area. Dyes are undesirable wastewaters because they contain high levels of chemicals, suspended solids, and toxic compounds. Colors that have reacted with metal ions can be highly dangerous toxic to aquatic aquatic flora and fauna and cause many water borne diseases (Vijayakumar *et al*., 2012).

Generally, dyes containing wastewaters can be treated in two ways, which are physical and chemical methods of dye removal (decoloration process) and by means of biodegradation. As for that, various chemical and physical methods have been proposed for the removal of dye from the effluent water. Those techniques are nanofiltration, electrokinetics coagulation, reduction, liquid-liquid extraction, ozonation, biological process and adsorption.

Among those, adsorption has been found to be the superior compared to the others techniques. It is due to its capability for efficiently adsorbing a broad range of adsorbates and its simplicity of design and economical, which make it applications, has expanded rapidly (Dabrowski, 2001). The adsorbents suitable for wastewater treatment plant are dead plant and animal matter called biomass; including charcoals, activated carbon, clays, soils, diatomaceous earth, activated sludge, compost, living plant communities, polymer synthesized from petrochemicals and inorganic salt coagulants.

Usually, adsorption by activated carbon is widely used to removal dyes. This is because they have high capabilities for various kinds of dyestuffs but sometimes the uses of activated carbon is limited since they have a high costs and difficult to regeneration (Bhatnagar and Jain, 2005). This has led many researchers to search for inexpensive and locally available adsorbents so that the process can become economically feasible.

Therefore, agricultural waste has been proposed as an adsorbent because it has the characteristics of ready availability, affordability, eco-friendliness and high uptake capacity for dyes. There are several agricultural waste which are used as adsorbent to removal dyes that have been studied and developed by researchers including palm ash (Abdulbari *et al.*, 2006), oil palm empty fruit bunch (Manase, 2012), mangrove bark (Seey and Nordin, 2002), palm kernel coat (Oladoja and Akinlabi, 2009), Zea mays L (maize) husk (Jalil *et al.*, 2012), coconut husk (Nazirah and Suhaili, 2011) and Acacia nilotica leaves (Prasad and Santhi, 2012).

Malaysia is one of the largest producers and exporters of palm oil in the world. With the increase in the production of palm oil, the amount of wastes generated including oil palm leaves is increasing enormously. One of the significant problems in the oil palm fruit processing is managing of the wastes generated during the processes (Husain, et al, 2003). It has been reported that, in January 2006 itself, the total wastes that include oil palm leaves, oil palm fronds, empty fruit bunch and oil palm shell from the oil palm industries are 3.96 million tons (Suraya, 2009). In addition, oil palm leaves have no economic value and in fact often create a serious problem of disposal. Thus utilizing oil palm leaves as an alternative and low-cost adsorbent would increase the economic value, help to reduce the cost of disposal and consequently can reduce the environmental pollution.

The basic components that included in the oil palm leaves are lignin, cellulose and hemicelluloses with polyphenolic groups (Grassi *et al.*, 2012). These materials are most excellently to removal dyes from the wastewater through sorption mechanisms. Cellulose for example show a potential sorption capacity for various pollutants. Thus, it is expected that the cellulose components in the oil palm leaves will become an active sites for the adsorption of methylene blue from aqueous solution.

1.3 Objective of the study

The research was conducted to investigate the potential of oil palm leaves as an adsorbent for the removal of methylene blue from aqueous solution.

1.4 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 ppm).
iii. Effect of initial pH (2-8).
iv. Effect of initial temperature (30-70 ºC).
v. Kinetic, isotherm and thermodynamic of adsorption.

2 LITERATURE REVIEW

2.1 Dyes

Dyes can be described as colored, ionizing and aromatic organic compounds. Generally, they can be described as a coloured substance that has an affinity to the substrate to which it is being applied. Dyes show the characteristics of intense color, solubility and fastness since they are complex unsaturated aromatic compounds. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber.

The developments of industrial methods of manufacturing fabrics brought about a rapid increase in demand for coloring substances. Besides that, dyes are used everywhere in our daily life like in food, fabrics, car, wood, newspaper, books, plastic products, decorative materials, films, everyday equipment and other. Their importance has grown in almost every area of an economic activity (Hoffmann and Puszynski, 2009).

2.1.1 Classification of Dyes

Dyes are classified based on the fiber to which they may be used and the chemical properties of each coloring. Before dyes are categorized, it must be noticed that each class has a particular dye chemistry, structure and how the particular bond. Dyes can react chemically or physically with the substrates that make up firm bonds in the process. Dyes are divided into nine types, namely dyes azoic dyes, acid dyes, basic dyes, direct dyes, reactive dyes, mordant dyes, solvents dyes, sulfur dyes and vat dyes (Christie, 2007).

Azoic dyes are dispersed in water and are used for most synthetic fibers. Since most of the other classes of dye quickly deficiency in red dye, these coloring is used mainly for the bright red colors in dyeing and printing. They are used to rarely on nylon, cellulose, cellulose acetate, and acrylic fibers but used to mostly on polyester. Azoic dyes, with fixation rates of 80 to 90 percent requiring an additional factor likes carriers of coloring, pressure, and heat to penetrate the synthetic fibers (Snowden, 1995).

Acid dyes are a very bigger and substantial group of dyestuff. These type was covered in brief by (Hendrickx and Boardman, 1995) which are the acid dyes containing sulfonic groups. They attach to organic fibers under acidic condition. Usually, these colorings are used in dyeing nylon, silk and wool but it rarely used for dyeing cotton besides paper, leather, ink-jet printing, food, and cosmetics.

Basic dyes are water-soluble and resulting colored cations in solution. For this reason, they are often referred to as the cationic dye (Hunger, 2003). Dyes are coloring derived from the first synthetic coal-tar derivatives. Without the help from mordant and agent, basic dyes originally used to color the wool, silk, linen, hemp and others. But, by using mordant like tannis acid, basic dyes have been used on cotton and rayon. These dyes give attractive colors with exceptional fastness to acrylic fibers. Today, the basic colouring no longer be used for any level of cotton or linen and seldom on wool but by the reasons of they are cheap, they are used for hemp, jute and similar fibers. Now, basic dyes used are focused on acrylics (Hoffmann and Puszynski, 2009).

Direct dyes are water-soluble anionic dyes because it consist sulfonic acid group that has a high linking for cellulosic fibers. These dyes have been used from a neutral or slightly alkaline, which consists of additional electrolyte. By looking the aspect of easiest to use and the low-priced in their beginning and operation charge, direct dyes are most suitable coloring even there are tradeoffs in the dyes' shade range and wet fastness (Corbman, 1975). Direct dyes generally were applied on cotton, linen, rayon, wool, silk and nylon.

Reactive dyes are successfully used on coloring cotton, wool, silk, and nylon. Reactive dyes form a covalent bond with the fiber under influence of heat and pH (alkaline). Reactive dyes have more advantages than direct dyes since their chemical structures are much clear, their absorption spectra show thinner absorption bands and the dyeing are much brighter. These dyes are made from azo, triphendioxazine, phthalocyanine, formazan, and anthraquinone (Christie, 2007).

Mordant are known as metal salt. Although other metallic salt mordants available, alum still used for ancient dyes. Mordant dyes are applied in conjunction with chromium salts like sodium or potassium. Some acid dyes that have the capability to form complexes with metal ions needed mordant as fixing agents to upgrade the color fastness. Dyeing consists in prep adding of the substrate with metal salts and then applying dyes forming insoluble complexes with the metals, which are anthraquinone, nitroso, xanthene, oxazine, triphenylmethane and azo dyes (Hoffmann and Puszynski, 2009). Commonly, these dyes are used for wool, leather, and anodized aluminium.

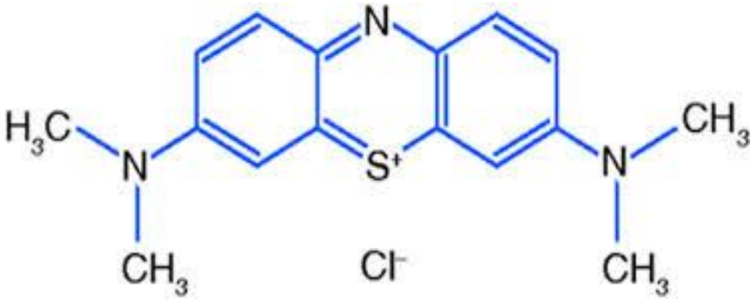
Solvent dyes are good used for dyeing plastics, gasoline, varnishes, lacquers, stains, inks, fats, oils, and waxes. Method applications for solvent dyes are dissolution in the substrate. The principal chemical classed are azo, triphenylmethane, anthraquinone, and phthalocyanine (Hunger, 2003).

Sulfur dyes are used for cotton, linen, and rayon but these dyes have given not brightly colored on the materials. These dyes act as reducing agent when dyes are applied for cotton from an alkaline reducing bath with sodium sulfide. Solvent dyes are very small group of dyes compared with the other types of dyes. These dyes are excellent wash fastness properties and the low cost making this class important dyeing in term of the economy although they are a small group of dyes. Nevertheless, they are not very suitable in term of environmental condition (Hunger, 2003). These dyes followed the method application of aromatic substrate vatted with sodium sulfide and deoxidized to insoluble sulfur-containing products on fiber.

The term vat comes from the old indigo method dyeing in a vat: indigo had to be reduced to light form (Michael, 1990). Vat dyes are water insoluble. Usually these dyes are treated with alkaline reducing agents, commonly with sodium hydrogensulfite before they are applied to cellulosic fibers as leuco salts. Anthraquinone (including polycyclic quinones) and indigoids are the principle chemical in making of vat dyes. Generally, these dyes are applied on cotton, linen, rayon, wool, silk, but they are rarely used on nylon.

2.1.2 Methylene Blue dye (MB)

Table 2.1: Properties of Methylene Blue (MB) (PubChem website)

Methylene Blue (MB)


	
Chemical formula	$C_{16}H_{18}ClN_3S$
IUPAC name	(7-dimethylaminophenothiazin-3- ylidene)- dimethyl- azanium chloride, Methylthioninium chloride
Other names	Methylthioninium chloride, Basic blue 9, Chromosmon, Swiss Blue, Methylene Blue N, 61-73-4
Molecular Mass	319.85 g/mole
Melting Point	100-110 ^{o}C
Vapor Pressure	1.30×10^{-7} mmgH
Solubility in Water	43 600 mg/L
Soluble in Organic	Soluble in glacial acetic acid and glycerol, insoluble in xylene and oleic acid, in ethanol 2%, and in acetone 0.5%.
Nature	Powder form
CAS No.	61-73-4

Among the various classes of dyes, basic dyes are the brightest class of soluble dyes used by the textile industry, as their tinctorial value is very high. Methylene blue is a basic dye by nature. MB is a basic dye which is widely used in textile, trace, biological laboratory purpose. MB is a blue dye used to dye wool, silk and tannin mordant cotton (Christie, 2007).

A MB can cause eye bum, and if swallowed, its causes irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhea. It may also cause methemoglobinemia, cyanosis, convulsions and dyspnea if inhaled (Senthilkumaar *et al.*, 2005). It is also can cause formation of toxic carcinogenic breakdown products.

2.2 Adsorption

Adsorption is the process that substances accumulates at the interface of two phase like gas-liquid, gas-solid, liquid-liquid or liquid-solid interface (Grassi *et al.*, 2012). Adsorbent and adsordate are the mainly component that include in adsorption process.

Adsorbate is the substance being adsorbed on the surface of adsorbent whereas adsorbent is adsorbing materials or the substance that accumulates on the surface of a solid or a liquid. The constituents of adsorbates and adsorbents will specify their properties.

Attraction force between adsorbate and adsorbent occur when the force attractions Van der Waal are weak or chemical bonds have strong attraction force. Adsorption can be divided into two types according to the attraction force between two components, adsorbate and adsorbent. The types of adsorption are physisorption and chemisorptions. Table 2.2 below show the differences between physisorption and chemisorptions.

Table 2.2 : Differences between physisorption and chemisorptions (Butt *et al.*, 2003 and Myers, 1999)

Physisorption	Chemisorption
• Involves van der Waals force between adsorbate and adsorbent.	• Involves formation of chemical bonds between adsorbate and adsorbent
• Low enthalpy of adsorption	• High enthapy of adsorption
• May formed multi-molecular layer	• Monolayer is formed
• Reversible process	• Irreversible process
• A general phenomenon, occurs in any solid/fluid or solid/gas system.	• A highly specific process
• Perturbation of the electronic states of adsorbent and adsorbate is minimal	• Changes in the electronic states may be detectable by suitable physical means.
• Typical binding energy is about • 10–100 meV.	• Typical forms bonding with • energy of 1–10 eV
• No activation energy is invovled	• Often involves activation energy
• Equilibrium can be achieved • quickly	• May take a longer time to • achieve equilibrium

Generally, the process that involve in adsorption is energy release. In nature, the most adsorption process is exothermic. Since adsorption process are spontaneous, so its free energy change and entropy change is negative value because during the adsorbate get linked to the surface of the adsorbent, the adsorbate molecules lose their translation freedom (Butt *et al.*, 2003).

Adsorption is widely used in industrial applications and useful most natural physical, biology and chemical systems. Lately, applications for adsorption have expanded rapidly especially for wastewater treatment besides for activated charcoal and synthetic resins. Their efficiency in the removal of pollutants, economical and simple in design makes the adsorption process become famous.

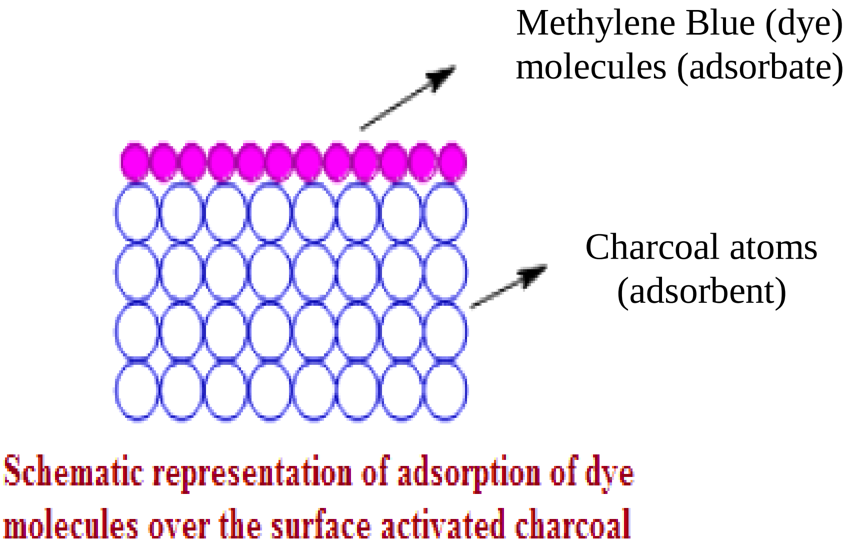


Figure 2.1 : Schematic representation of adsorption mechanism (Kumar, 2012)

2.2.1 Adsorption Kinetics

Several kinetic models have been proposed in order to examine the controlling mechanism of adsorbate adsorbed by adsorbents. Usually, the controlling mechanisms that have been examined are mass transfer, diffusion control and chemical reaction. In practical operation, analysis of adsorption rates is very essential especially in terms of system design (Wu, 2002). The simple kinetic analyses of adsorption are the pseudo-first-order model and the pseudo-second-order model.

2.2.1.1 Pseudo-First-Order Model

Lagergren's first order rate equation or also known as pseudo-first-order model is the earliest known predict dye adsorption kinetics. According to (Lagergren, 1898), the pseudo first order equation is expressed by the following equation:

$$\frac{dq}{dt} = k_1^{'}(q_e - q_t) \qquad (1)$$

Where q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g), q_t the amount of solute adsorbed at any time (mg/g) and k_1 is the adsorption constant (min^{-1}).

Integrating equation above for the boundary conditions $t = 10$ to $t = t$ and $q_t = q_t$ gives:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{2}$$

In order to obtain the rate constants k_1, the slope of the linear plots of log ($q_e - q_t$) against t be calculated.

2.2.1.2 Pseudo-Second-Order Model

Ho and Mckay (Ho and Mckay, 1998) proposed a second order model for the sorption of divalent metal ions onto peat particles based on the adsorption capacity of the adsorbents. These models were proposed with the goal of differentiating the kinetics of a second-order rate expression based on the adsorbent concentration. The models that are based on the solute concentration and represent a pseudo-second-order rate expression.

The pseudo-second-order kinetic equation is described as:

$$\frac{dq}{dt} = k_2 (q_e - q_t)^2 \tag{3}$$

Where k_2 is the rate constant of pseudo-second-order adsorption (g/mg min). Integrating equation above for the boundary conditions $t = 0$ to $t = t$ and $q_t = q_t$ gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{4}$$

or equivalently

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

Where k_2 and q_e can be obtained from the intercept and slope of the plot of t/q_t verses t (Wu, 2001).

2.2.2 Isotherm Equation

Adsorption isotherms or also known as equilibrium data explain how adsorption occurs between adsorbate and adsorbents and also give some essential information to develop the equation. This equation can be used for a certain purpose.

There are several equilibrium isotherms with different models were proposed in other to describe the adsorption process. Langmuir and Freundlich are suitable isotherm models in order to investigate the adsorption behaviour. The Langmuir isotherm is restricted for monolayer adsorption only whereas the Freundlich isotherm is based on empirical equation.

2.2.2.1 Langmuir Isotherm Equation

The Langmuir adsorption isotherm is familiar and mainly used in process of adsorption. However, the Langmuir adsorption isotherm is suitable for single-layer adsorption only (Grassi *et al.*, 2012). The theoretical Langmuir isotherm (Langmuir, 1918) takes the following simplified form:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{6}$$

Equation 6 can be rearranged to a linear form:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \tag{7}$$

Where q_e is the equilibrium adsorption capacity (mg/g), C_e is the equilibrium liquid phase concentration (mg/L), q_m is the maximum adsorption capacity, (mg/g), K_L is Langmuir equilibrium constant, (L/mg). 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.

The variation of the surface and porosity of the adsorbent can give influence to the adsorption capacity. A higher adsorption capacity is due by increasing surface area and pore volume. A dimensionless constant separation factor or called as the equilibrium parameter can showed the essential characteristics of the Langmuir isotherm (Langmuir, 1918). The equilibrium parameter, R_L can be developed as follow :

$$R_L = \frac{1}{1 + K_L C_o} \tag{8}$$

Where K_L is Langmuir equilibrium constant, (L/mg), C_o is initial concentration (mg/L) and R_L values indicating the type of isotherm. The R_L value indicates the adsorption to be unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 > R_L > 1$) or irreversible ($R_L = 1$).

2.2.2.2 Freundlich Isotherm Equation

The Freundlich isotherm equation is an empirical relationship to explain about the adsorbate adsorb to the adsorbent surface. In addition, this equation also used to describe the heterogeneous systems, reversible adsorption and characterized by heterogeneity factor, 1/n. Contrary to the Langmuir isotherm equation, the Freundlich isotherm equation not restricted to the formation of the monolayer only because this isotherm is suitable for a highly heterogeneous surface (Grassi *et al*., 2012).

The ordinary adsorption isotherm is expressed by the following equation:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{9}$$

The Freundlich equation also can be written in the following linear form:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{10}$$

C_e is the equilibrium liquid phase concentration (mg/L), q_e is the equilibrium adsorption capacity (mg/g), K_F is Freundlich equilibrium constant (L/mg) and n is the constant for intensity whereby values $n > 1$ represent favourable adsorption condition. The intercept value of K_F and the slope of $1/n$ can be obtained by plotting a linear graph of log q_e versus log C_e.

2.2.3 Thermodynamic Parameters

Spontaneity of a process can be determined by thermodynamic parameters. Thermodynamic parameters such as enthalpy change (ΔH^o), free energy change (ΔG^o), and entropy change (ΔS^o) can be estimated using equilibrium constants changing with temperature. During spontaneous process, increasing temperature will decrease the values of (ΔH^o) and (ΔG^o). The relationship between the thermodynamic equilibrium constant and the Gibbs free energy is given by the Van't Hoff equation below (Al-Omari, 2007):

$$\Delta G^o = -RT \text{ In} K_a \tag{11}$$

and

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{12}$$

Combination of both equations and taking the natural logarithms of both sides give:

$$\text{In } K_a = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad (13)$$

Where ΔG^o is the free energy change (kJ/mol), ΔH^o the change in enthalpy (kJ/mol), ΔS^o is the entropy change (kJ/mol K), T is the absolute temperature (K) and R is the universal gas constant (0.8314 x 10^{-3} kJ/mol K). $K_a = (q_e / C_e)$ is a single point or linear sorption distribution coefficient.

2.3 Adsorbent Material

2.3.1 Introduction of Adsorbent

Many types of adsorbent are used to remove dyes from wastewater and the most popular adsorbent is the activated carbon. Activated carbon has a capability to adsorb many types of dyes with a high adsorption capacity but it is expensive to be used in developing countries.

Consequently, many low-cost adsorbents that have been made or developed must have the characteristic either basis of their availability or depending on their nature (Grassi *et al.*, 2012). Oil palm leaves is the right choice to used as adsorbent because it readily available resources and cheap besides have excellent adsorption abilities for organic pollutants.

2.3.2 Oil Palm Leaves as Alternative Adsorbent

Malaysia is one of the largest producers and exporters of palm oil in the world. With the increase in the production of palm oil, the amount of wastes generated including oil palm leaves is increasing enormously. Oil palm leaves have no economic value and in fact often create a serious problem of disposal. Thus utilizing oil palm leaves as an alternative and low-cost adsorbent would increase the economic value, help to reduce the cost of disposal and consequently can reduce the environmental pollution (Grassi *et al.*, 2012).

The basic components that included in the oil palm leaves are lignin, cellulose and hemicelluloses with polyphenolic groups (Grassi *et al.*, 2012). These materials are most excellently to removal dyes from the wastewater through sorption mechanisms. Cellulose for example show a potential sorption capacity for various pollutants. This was observed by the absorption of methylene blue onto Sumac Leaves (Dülger *et al.*, 2013). Before methylene blue adsorption, the surface of Sumac Leaves is smooth and porous whereas after methylene blue adsorption, the surface has become rough and corroded. It is evident that cellulose has a potential sorption capacity for various pollutants. Thus, it is expected that the cellulose components in the oil palm leaves will become an active sites for the adsorption of dyes from aqueous solution.

2.4 Previous Study

2.4.1 Previous study using oil palm as adsorbent

Fairus *et al.,* (2007) studied the application of palm oil fibre in removing methylene blue from aqueous solution. Color was effectively been removed at all selected pH, and the increase in activated carbon dose showed an increase in the removal's percentage. The adsorption capacity was rising with increasing of initial dye concentration. The adsorption equilibrium for colour was reached after 90 minutes of contact time. The adsorption followed both Langmuir and Freundlich isotherms.

In addition, Sidik *et al*., (2012) investigated the potential of lauric acid (LA) modified oil palm leaves (OPLsLA) for the removal of crude oil from the aqueous solution. They reported that equilibrium was achieved at about 60 minutes of contact time and the optimum pH for adsorption was around pH 4-5. The best dosage for adsorption was 1 to 2 g/L. The result maximum adsorption capacity of 1176.93 mg/g at 303K. The adsorption process was followed the pseudo second-order kinetic model and Langmuir isotherm. Results obtained indicate that palm oil fibre could be employed as a low cost alternative to commercial activated carbon in wastewater treatment for dye removal.

The comparison of adsorption capacities of oil palm leaves and corn husk for adsorption of Methylene Blue dye was studied by Suraya (2009). She reported that the best adsorption for both leaves was obtained at pH 6. The amount of dye adsorbed decreased with rising temperature from 310 K to 360 K, indicating the exothermic nature of the process.The adsorption kinetic and equilibrium fitted the pseudo second-order and Langmuir isotherm models respectively. The maximum capacity obtained was 315.6 mg/g for oil palm leaves and 304.6 mg/g for corn husk. Results obtained indicate that oil palm leaves could be employed as a low cost alternative to commercial activated carbon in wastewater treatment for dye removal.

2.4.2 Other studies using leaves as adsorbent

Leaves of different trees are very versatile natured chemical species as these contain a variety of organic and inorganic compounds. Cellulose, hemicellulose, pectins and lignin present in the cell wall are the most important sorption sites (Qaiser *et al.*, 2007). The important feature of these compounds is that they contain hydroxyl, carboxylic, carbonyl, amino and nitro groups which are important sites for metal sorption (Qaiser *et al.*, 2007).

Murugan *et al.*, (2010) investigated the potential of mango leaves powder for removal of Grey BL dye from aqueous solution. Scanning electron micrograph showed the presence of a rough surface morphology with pores of different sizes on mango leaves. It was found out that the percentage of dye adsorbed increased as the initial pH increased from pH 2 to 7, reaching a maximum value of 64.25 of dye removal at pH 7. The experimental data obtained fitted well to both Langmuir and Freundlich isotherm model. The maximum adsorption capacity (q_m) calculated based on Langmuir isotherm model was 33.7 mg/g. Kinetic study of the adsorption showed that equilibrium was reached within 1 hour of contact and the adsorption kinetic followed the pseudo second-order model.

Morever, Arivoli *et al.*, (2008), took Phoenix Sylvestric leaves as adsorbent, an indigenous agricultural waste was Sulphuric acid treatment was tested for its efficiency in removing. The adsorption followed first order reaction equation and the rate is mainly controlled by intra-particle diffusion. Freundlich and Langmuir isotherm models were applied to the equilibrium data. The adsorption capacity, q_m obtained from the Langmuir isotherm plots were 51.546, 47.236, 44.072 and 41.841 mg/g respectively at an initial pH of 7 at 30, 40, 50 and 60 ^oC. The temperature variation study showed that the adsorption is endothermic and spontaneous with increased randomness at the solid solution interface. Significant effect on adsorption was observed on varying the pH of the solutions. Almost 90% removal of was observed at 60 ^oC. The Langmuir and Freundlich isotherms obtained, positive ΔH^o value, pH dependent results and desorption of dye in mineral acid suggest that the adsorption of on PSC involves physic sorption mechanism.

Then, Chakravarty *et al.*, (2009) investigated the adsorption of Pb(II) ion from aqueous solution onto bael leaves. They found out that the percentage uptake increased with higher pH values, with pH 4 as the optimum pH for adsorption, having uptake of approximately 97%. Above pH 4, the percentage uptake of Pb(II) ion decreased. The optimum bael leaves dose was 0.2 g for concentration of 48.2 mg/L, 87.8 mg/L and 180.2 mg/L. The experimental data obtained fitted well with Langmuir isotherm (R^2 = 0.97) compared to Freundlich isotherm (R^2 = 0.80), indicating a monolayer adsorption. An analysis on the experimental data suggested that the kinetic for adsorption of Pb(II) ion onto bael leaves followed the pseudo second-order model.

Lastly, the potential use of dried Acacia nilotica leaves to remove Rhodamine B dye from aqueous solution was examined by Santhi *et al*., (2010). Maximum Rhodamine B dye sorption occurred around pH 6 to 7. The adsorption equilibrium and kinetic were best described using Langmuir isotherm and pseudo second-order kinetic models. The q_m of dried Acacia nilotica leaves at natural pH was found to be 89.37 mg/g based on the Langmuir isotherm model.

3 METHODOLOGY

3.1 Chemicals

Sodium hydroxide (NaOH), hydrochloric acid (HCl) and methylene blue (MB) were purchased from Merck (M) Sdn. Bhd, Malaysia with C.I.52015, purity of 99%, chemical formula of $C_{16}H_{18}ClN_3S$ and molecular weight of 319.852 g/mol. The maximum wavelength of this dye is 668 nm.

3.1.1 Preparation of Methylene Blue (MB)

The dyes solution of Methylene Blue was prepared by dissolving specific amounts of methylene blue in Milli-Q water to obtain a concentration of 1000 mg/L, and then the solution was dilute to various concentrations (50, 100, 200 and 400 mg/L).

Figure 3.1 : Methylene blue (MB) dye

3.2 Oil Palm Leaves (OPL)

Oil palm leaves was collected from Pahang oil palm plantations, Malaysia. The oil palm leaves were cut into small pieces around 1-2 cm in length. To remove some impurities, the samples were soaked in distilled water for one night. Then, the samples were dried in oven over 80 ^{o}C for 24 hour before the samples were crushed and sieved around to 355-600 μm particle sizes. Again, the samples were oven-dried at 100 ^{o}C overnight until the weights were constant. Lastly, the samples were stored in a plastic bottle.

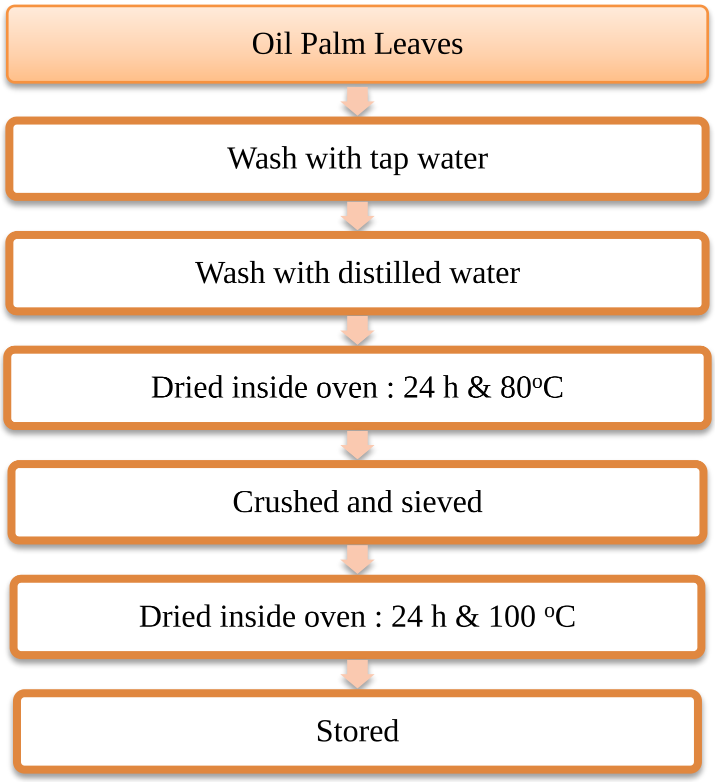


Figure 3.2 : Process flow of adsorbent preparation made from oil palm leaves.

3.2.1 Characterization of oil palm leaves

Scanning electron microscope (SEM) analysis was carried out in order to study the textural structure of the oil palm leaves before and after the adsorption process using Scanning Electron Microscopy (SEM, Zeiss Evo 50). Fourier-transform infrared (FTIR, Spectrum 100, Perkin Elmer) spectrometer was used to detect the infrared spectra and surface functional groups of oil palm leaves in over the range of 4000-400 cm^{-1}.

3.3 Instrumentation

The instruments used were oven, pH meter, weight machine, centrifuge, FTIR, SEM and UV-vis spectrophotometer.

3.4 Procedures

Adsorption experiments were carried out by adding a fixed dose of OPL (0.1 g) to a series of 250 mL conical flasks filled with 200 mL diluted solution of MB dye. The pH was adjusted to the desired value with NaOH or HCl solutions. The mixtures were prepared under constant stirrings at the room temperature (30 °C) to reach equilibrium. After that, the solutions were centrifuged for 15 minutes at 3500 rpm. Final concentration of dye in the solution was measured at maximum wavelength of the dye solution (668 nm) by a UV/VIS spectrophotometer using a1 cm quartz cell. Similar methodology was used for adsorption of MB onto Sumac Leaves (Dülger *et al*., 2013). The amount of adsorption at time t, q_t (mg/g), was calculated using the following formula:

$$q_t = \frac{(C_0 - C_t)}{W} \times V \qquad (13)$$

The dye removal percentage can be calculated as follows:

$$\text{Removal (\%)} = \frac{(C_0 - C_t)}{C_t} \times 100 \qquad (14)$$

Where q_t the amount of dye adsorbed at any time t (mg/g), C_o and C_t (mg/L) are the liquid phase concentrations of dye at initial and equilibrium, respectively. V is the volume of the solution (L), and W is the mass of dry adsorbent used (g).

The linear forms of the pseudo-first- and -second-order models are expressed as follows:

Pseudo-first-order equation: $In(q_e - q_t) = Inq_e - k_1 t$ (15)

Pseudo-second-order equation: $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$ (16)

Where q_e is the amount of dye adsorbed at equilibrium (mg/g), q_t the amount of dye adsorbed at any time (mg/g), k_1 is the rate constant of the pseudo-first-order adsorption (min^{-1}) , k_2 is the rate constant of the pseudo-second-order adsorption (g/mg min).

The non-linear regressions of the isotherm models can be represented by the following expressions:

Langmuir isotherm: $q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$ (17)

Freundlich isotherm: $q_e = K_F C_e^{1/n}$ (18)

Where C_e is the MB concentration at equilibrium (mg/L), q_e is the adsorption capacity at equilibrium (mg/g), q_m is the maximum adsorption capacity (mg/g), K_L is the Langmuir constant (L/mg), K_F is the Freundlich adsorbent capacity and n is the heterogeneity factor.

The adsorption enthalpy (ΔH^o), entropy (ΔS^o) and Gibbs free energy (ΔG^o) were calculated using the following thermodynamic functions:

$$\ln K_D = \frac{-\Delta G^o}{RT} = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{R}\frac{1}{T} \tag{19}$$

$$K_D = \frac{C_e(adsorbent)}{C_e(solution)} \tag{20}$$

$$\Delta G^o = -RT \ln K_D \tag{21}$$

where K_D is the equilibrium constant of the adsorption.

3.5 Process Flow Diagram

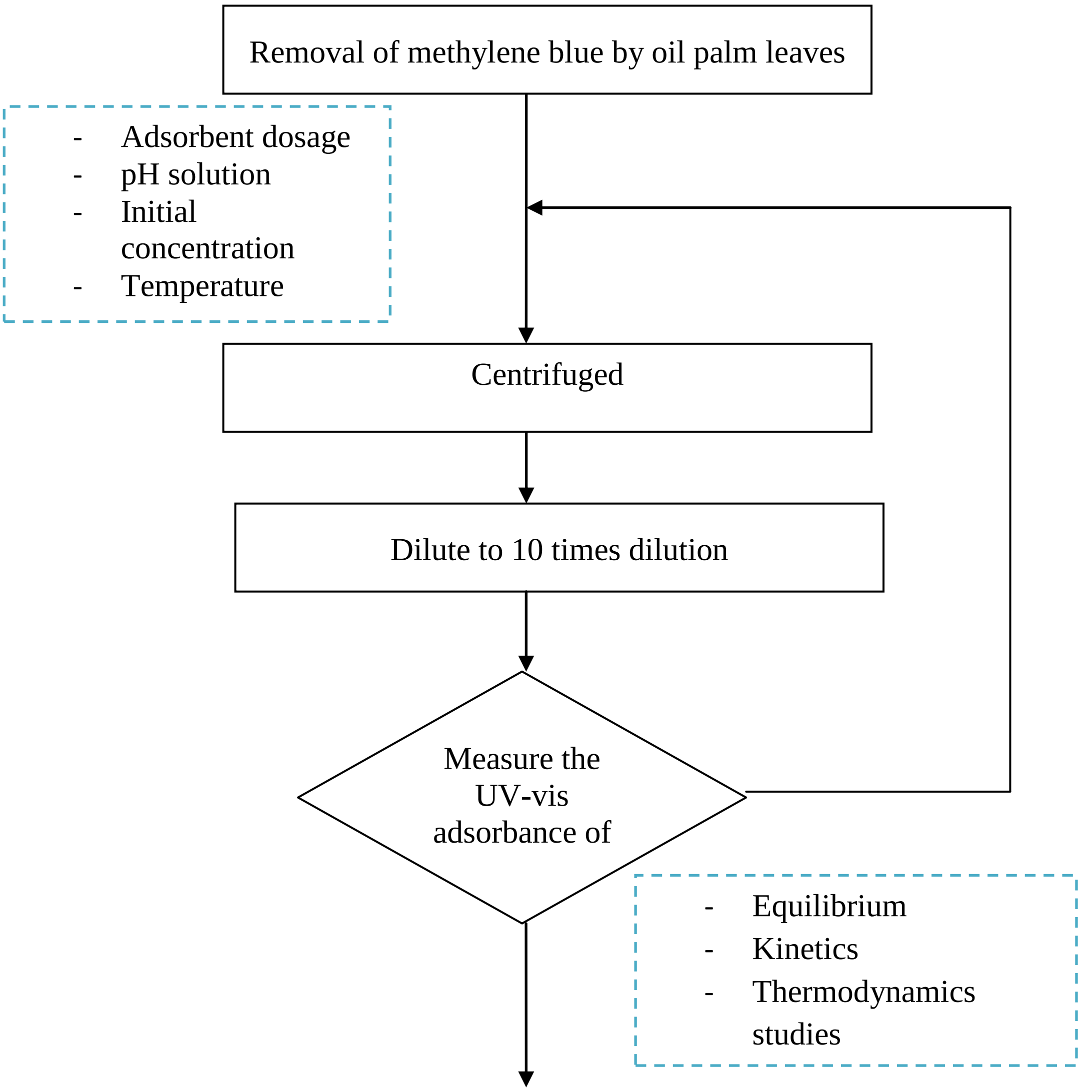


Figure 3.3: Flow diagram of procedure the experiment

4 RESULTS AND DISCUSSION

4.1 Effect of adsorbent dosage

The effect of the dose of OPL on MB adsorption is presented as % removal versus the OPL dose in Figure 4.1. With increase in OPL dose, from 0.25-2.0 g/L for MB concentration of 100 mg/L, the amount of adsorbed MB increases from 70.04% to 77.53%. Maximum dye removal was achieved with 0.5 g/L OPL dose.

After that, the amount of adsorbed per unit mass of adsorbent and percent removal of MB on OPL remained almost constant. It is apparent that by increasing the dose of OPL, the number of sorption sites available for adsorbent-solute interaction is increased, thereby resulting in the increased percentage of MB removal from the solution.

Similar phenomenon was observed for adsorption of MB onto Sumac Leaves (Dülger *et al.*, 2013), removal of methylene blue from aqueous solutions by adsorption using teak tree (Tectonagrandis) bark powder (Satish *et al.*, 2011) and the removal of methylene blue using grass waste (Hameed, 2008). On the basis of the results obtained, 0.5 g/L of the OPL was used for the further experiment.

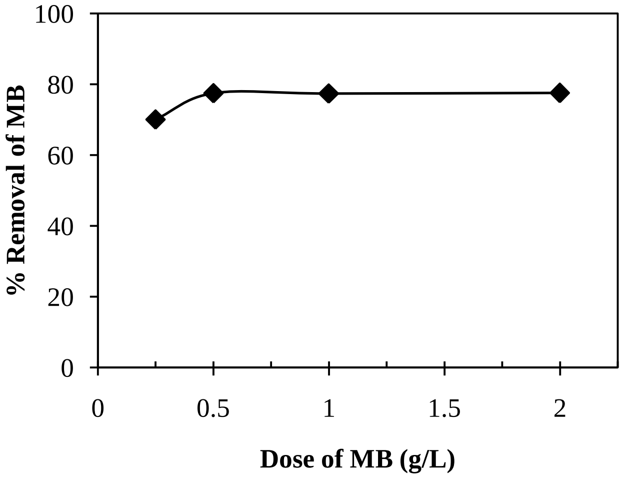


Figure 4.1: Effect of adsorbent dosage on the adsorption of MB dye onto OPL leaves (T = 30 °C, pH = 6, intial concentration = 100 mg/L)

4.2 Effect of pH

The pH of dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity, influencing not only the surface charge of the adsorbent and the degree of ionization of adsorbent in the solution but also the dissociation of functional groups on the active sites of the adsorbent (Dülger *et al.*, 2013). The effect of pH value on the adsorption of MB onto oil palm leaves was investigated in the range of 2–8, and the result are presented in Figure 4.2. The pH of the solution was controlled by the addition of HCl or NaOH. Since the amount of HCl or NaOH added to the solution is very small, HCl or NaOH did not involve in the reaction and it was confirmed by FTIR spectroscopy in Figure 4.6 where there is no signal assigned to the interaction between OPL with HCl or NaOH.

The adsorption rate was lower under conditions that were highly acidic and became higher as the pH increased. The maximum adsorption capacity was found at pH 6. Above and under this point, adsorption of methylene blue on OPL tends slightly to decrease. Similar observations have been reported for the adsorption of MB by giant duckweed (Waranusantigul *et al.*, 2003) and pineapple stem (Hameed *et al.*, 2009).

At lower pH as 2, the surface charge may be positively charged, thus making (H^+) ions compete effectively with dye cations causing a decrease in the amount of dye adsorbed. At higher pH the surface of OPL may be negatively charged which enhances the positively charged dye cations through electrostatic force at attraction (Ahmad *et al.*, 2010). Since the adsorption process was higher at pH 6, further experiments were carried out at this pH.

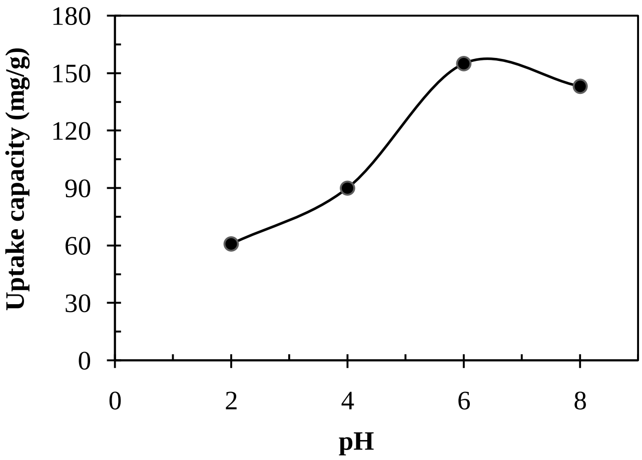


Figure 4.2: Effect of pH value on the adsorption of MB dye onto OPL leaves (T = 30 °C, intial concentration = 100 mg/L, adsorbent dosage = 0.1 g/L)

4.3 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 (Dülger *et al.*, 2013; Ashtoukhy, 2009).

The adsorption data for the uptake MB versus contact time at different concentration (Figure 4.3) indicates that the adsorption capacity increased with increase in MB concentration. This is due to increase in the driving force of the concentration gradient, as an increase in the initial dye concentration.

The adsorption capacity for MB increased from 78.52 mg/g to 571.22 mg/g as the MB concentration increased from 50 to 400 ppm. It is also evident from Figure 4.3 that the contact time needed for MB solutions with initial concentration of 50 to 400 ppm to reach equilibrium was less than 1 hour. The time required to attain this state of equilibrium is termed equilibrium time, and the amount of dye adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operation conditions.

The surface of OPL may contain a large number of active sites and the solute (MB) uptake can related to the active sites on equilibrium time. Also up to 90-95 % of the total amount of dye uptake was found to occur in the first rapid phase (40 min) and hereafter the sorption rate was found to decrease. A similar trend was also observed for the adsorption of basic blue onto palm ash (Abdulbari *et al.*, 2006) and for the adsorption of Basic Yellow 24 using dried activated sludge biomass (Chu *et al.*, 2002).

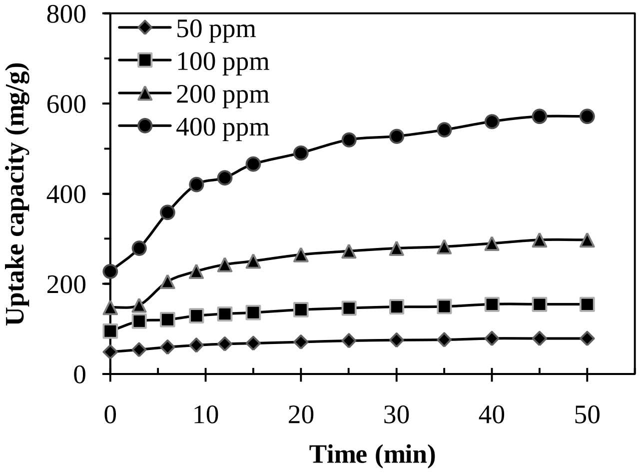


Figure 4.3 : Effect of initial concentration on the adsorption capacity of oil palm leaves (T = 30 °C, pH = 6, adsorbent dosage = 0.1 g/L)

4.4 Effect of temperature

The adsorption studies were carried out at five different temperatures 30, 40, 50, 60 and 70 ^{o}C, and the results of these experiments are presented in Figure 4.4. The results indicate that when the temperature increased from 30 ^{o}C to 50 ^{o}C, the adsorption capacity of methylene blue onto oil palm leaves increased from 560.36 mg/g to 694.60 mg/g. However, when the temperature increases from 50 ^{o}C to 70 ^{o}C, the adsorption capacity decreased from 694.60 mg/g to 632.10 mg/g.

For higher temperature the surface coverage increased, may be because of increase of dye penetration inside micro pores at higher temperatures or the creation of new active site as increase surface area. It was also observed that the maximum adsorption occurred at 50^{o}C. Since the adsorption is increasing at higher temperatures it is endothermic in nature. Similar dependence was observed for unburned carbon as a low cost adsorbent for treatment of methylene blue containing wastewater (Wang *et al.*, 2005).

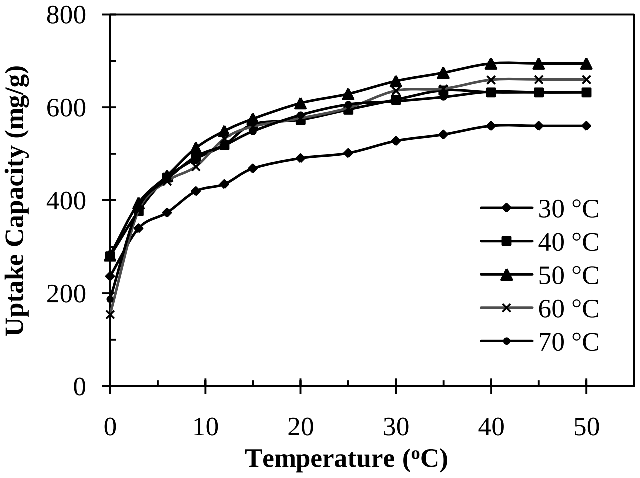


Figure 4.4: Effect of temperature on the adsorption capacity of oil palm leaves (initial concentration = 400 mg/L, pH = 6, adsorbent dosage = 0.1 g/L)

4.5 Adsorption Kinetics

The study of adsorption kinetics describes the solute uptake rate, which controls residence time of the adsorbate at the solid/solution interface. In order to investigate the mechanism of adsorption various kinetic models have been suggested. The kinetics of MB adsorption on OPL was analyzed using Lagergren pseudo-first-order (Lagergren, 1898) and Ho pseudo-second-order (Ho and McKay, 1999) kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2, values close or equal to 1). A relatively high R^2 values indicate that the model successfully describes the kinetics of dye adsorption.

A plot of In$(q_e - q_t)$ versus t was linear, and rate constant (k_1) and adsorption capacity at equilibrium (q_e) were determined from the slope and intercept of the plot, respectively. The value of R^2 (0.9801-0.9971) indicates that the first-order Lagergren model did not fit the complete range of the adsorption process well. The parameters of pseudo-first order kinetic model are given in Table 4.1.

In many cases the first-order equation of Lagergren does not fit well to whole range of contact time and is generally applicable over the initial stage of the adsorption process (Ho and McKay, 1999). Therefore, the pseudo-second-order kinetic model was used to study the adsorption kinetic of the present system.

For pseudo-second order model, a straight line of t/q_t against t was plotted. The k_2 and qe values determined from the slopes and intercepts of the plot are presented in Table 4.1 along with the corresponding R^2 values. This procedure is more likely to predict the behavior over the whole range of adsorption. The linear plot shows a good agreement between the experimental and calculated q_e values (Table 4.1).

The corresponding R^2 values (R^2 = 0.9988-0.9993) for the pseudo-second-order kinetic model were greater than pseudo-first-order kinetic model for all MB concentration, indicating the applicability of the pseudo-second-order kinetic model to describe the adsorption (Santhi *et al.*, 2010). It suggests that the adsorption process is controlled by chemisorptions. Similar kinetics results have been reported for methylene blue adsorption onto Sumac Leaves (Dülger*et al.*, 2013) and for the adsorption of basic blue onto palm ash (Abdulbari *et al.*, 2006).

Table 4.1: First- and second-order kinetic parameters for the adsorption of MB onto oil palm leaves at different initial concentrations

Concentration (ppm)	Experimental	Pseudo first order			Pseudo second order		
	q_e (mg/g)	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (g/mg min)	R^2
50	78.5185	28.4970	0.0672	0.9971	81.9672	0.0047	0.9989
100	154.9407	50.7808	0.0674	0.9867	161.2903	0.0027	0.999
200	297.3782	141.5793	0.0683	0.9801	312.5000	0.0008	0.9993
400	571.2217	314.9198	0.0688	0.9902	625.0000	0.0003	0.9988

4.6 Adsorption Isotherm

The adsorption isotherm indicates how the adsorbed molecules were distributed between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose. Several models have been published in the literature to describe the experimental data of adsorption isotherms. The Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1906) models are the most frequently employed models. In this work, both models were used to describe the relationship between the amount of dye adsorbed and its equilibrium concentrations.

According to Choy *et al.*, (1999), Namasivayam *et al.*, (2001a, 2001b, 2002), Tsai *et al.*, (2001), Rozada *et al.*, (2003) and Wong *et al.*, (2004), Langmuir isotherms based on the assumption that maximum adsorption corresponds to saturated monolayer of dye molecules on the adsorbent surface. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface.

When C_e/q_e is plotted against C_e, a straight line with slope a_L/K_L and intercept $1/K_L$ is obtained, which shows that the adsorption of MB follows Langmuir isotherm model. The linearized form of Langmuir isotherm is found to be linear over the whole concentration range studied. The value of correlation coefficient R^2 (0.9512-0.9664) which is greater than 0.89 suggests in accord with Jaynes and Boyd (Jaynes and Boyd, 1991) that the isotherm could be described by Langmuir model.

Conformation of the experimental data with the Langmuir isotherm model indicates the homogenous nature of OPL surface; that is, MB/OPL adsorption has equal adsorption activation energy; the results also demonstrate the formation of monolayer coverage of dye molecule at the outer surface of OPL. The maximum adsorption capacity of OPL (q_m) and the Langmuir equilibrium constant (K_L), calculated from the slope and the intercept of the linear plot C_e/q_e against, were 500 mg/g and 0.0029558 L/g at 50 ^{o}C, respectively.

Table 4.2 shows that the OPL studied in this work has very high absorption capacity. The OPL used in these experiments proved that had a very high equilibrium adsorption capacity, which determines an adsorption rates very fast and also, a quickly period of time to reach equilibrium. All of these indicate a high degree of affinity between MB and OPL. The values of R_L for the studied system were found to be 0.3574-0.45799 and which confirmed that the OPL is favourable for adsorption of MB dye under conditions used in this study.

The Freundlich isotherm is an empirical adsorption model based on adsorption on heterogeneous surface. 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 were 16.095 mg/g and 1.0509 L/mg at 50 ^oC, respectively. The R^2 value (0.898-0.961) is lower than Langmuir's isotherm model. The value of $1/n$ (1.0509-1.19976) points out the unfavorable adsorption conditions. This means that the data does not follow the Frenudlich models.

Hence, Langmuir isotherm model was fits the experimental data better since the values of the regression coefficient and $1/n$ indicate that the data satisfactorily follow Langmuir models. The best fit isotherm expressions confirm the monolayer coverage process of MB on OPL.

Table 4.2: Langmuir and Freundlich parameters for methylene blue adsorbed onto oil palm leaves

Temperature (^oC)	Langmuir isotherms				Freundlich isotherm		
	q_m (mg/g)	K_L (L/mg)	R^2	R_L	n	K_F (mg/g)	R^2
30	166.6667	0.0045	0.9664	0.3574	1.1997	11.1403	0.961
40	233.6133	0.0041	0.9650	0.3883	1.1643	13.2317	0.957
50	500.0000	0.0029	0.9512	0.4579	1.0509	16.0953	0.898
60	459.3443	0.0034	0.9599	0.4398	1.1087	15.6842	0.917
70	396.8902	0.0039	0.9616	0.4000	1.1209	14.8432	0.932

4.7 Thermodynamics of adsorption

Spontaneity of a process can be determined by thermodynamic parameters. Thermodynamic parameters such as the free energy change (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o), were calculated from the variation of the thermodynamic equilibrium constant, K_o, with temperature. The values of ΔH^o, ΔG^o, and ΔS^o for different temperature are shown in the Table 4.3.

The negative values of ΔG^o indicate the feasibility and spontaneous nature of methylene blue sorption onto oil palm leaves. The magnitude of ΔG^o, increased with increasing temperature, revealing that the degree of spontaneity increased at higher temperatures.

The positive values of entropy change (ΔS^o=151.63 J/mol) reflect an increased degree of disorderliness at the solid/liquid interface during the adsorption of methylene blue onto oil palm leaves for 30-50 ^{o}C.

The exothermic nature of dye sorption by oil palm leaves was confirmed by the negative values of ΔH^o for temperature of 30 ^{o}C to 50 ^{o}C. For the temperature 50 ^{o}C to 70 ^{o}C, the positive value of ΔH^o indicates that the adsorption process was endothermic and that the magnitude (42.10 kJ/mol) was out the heat range of physisorption (<40 kJ/mol).

The enthalpy value for a sorption process may be used to distinguish between chemical and physical sorption. For chemical sorption, values of enthalpy change range from 83 to 830 kJ/mol, while for physical sorption they range from 8 to 25 kJ/mol. The low values of ΔH^o give clear evidence that the interaction between methylene blue and oil palm leaves was weak. On this basis we concluded that dye sorption by oil palm leaves is a chemical adsorption process.

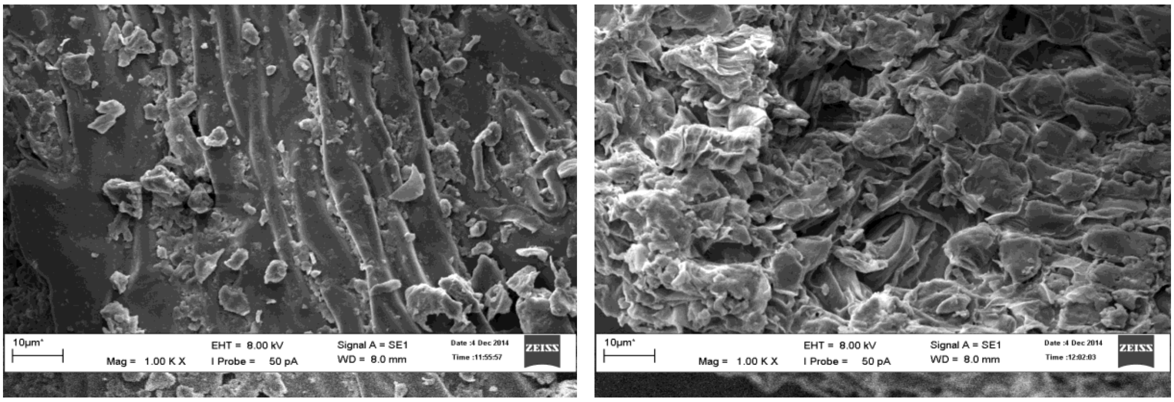
Table 4.3: Thermodynamic parameters for the adsorption of MB onto oil palm leaves

Temperature (^{o}C)	ΔH^o (J/mol)	ΔS^o (J/mol K)	ΔG^o (J/mol)
30-50	42104.59	151.6307	-3839.52
50-70	-25829.1	-58.6503	-6885.06

4.8 Characterization of OPL

The surface structure of OPL before and after MB adsorption was analyzed using scanning electron microscopy (SEM). The SEM images of OPL before and after MB adsorption were recorded and are shown in Figure 4.5. In the SEM micrograph shown in Figure 4.5 (a), the bright spots show the smooth and porous surface of the adsorbent. This indicates that there is a good possibility for MB dye to be trapped and adsorbed into the surface.

In Figure 4.5 (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. It is evident that upon adsorbing the MB the adsorbent structure has changed.



(a) before (b) after

Figure 4.5: SEM micrograph of (a) oil palm leaves before MB adsorption and (b) oil palm leaves after MB adsorption

The FTIR spectra obtained revealed that there were various functional groups detected on the surface of OPL. The broad peaks detected at 3434 and 3435 cm^{-1} (Figure 4.7) respectively found in the spectrum of the OPL before and after MB adsorption, could be assigned to O-H stretching vibration of hydroxyl functional groups (Sekhar *et al.*, 2009).

Other functional group found on both the OPL before and after MB adsorption were C-H stretching vibration and NH_2 deformation, respectively recorded at 2852-2923 cm^{-1} and 1602-1640 cm^{-1}. However, the intensities of the peaks became weaker after MB adsorption. Other peaks detected on the OPL before MB adsorption were located at 1164 cm^{-1} assigned to C-N stretching vibration. Nevertheless, this functional group disappeared after MB adsorption.

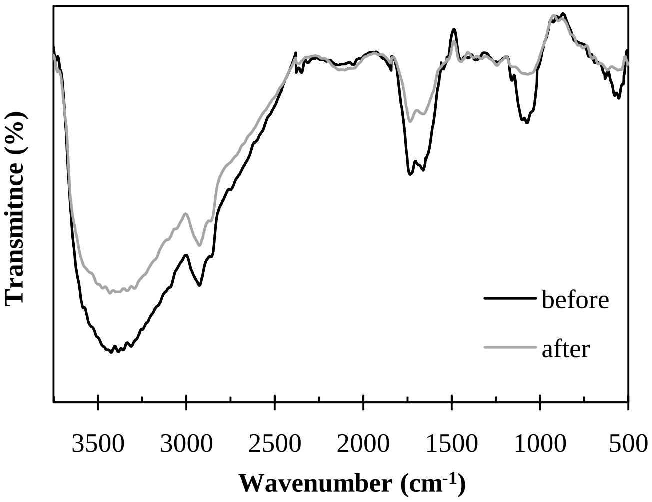


Figure 4.6: FTIR spectrum of the OPL before and after MB adsorption

5 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In this study, adsorption of MB from aqueous solution on OPL has been studied. Adsorption of MB was found to be dependent on, adsorbent dose, initial pH of solution, initial MB dye concentration, and temperature. The 0.5 g/L of adsorbent dose proved to be effective for discoloration of a solution of MB having 400 mg/L. The adsorption equilibrium is achieved in 40 min. The percentage of removal increased with the increasing adsorbent dose, initial solution pH, increasing concentration and temperature. Value of R_L in the range of 0-1 confirmed that the OPL is favorable for adsorption of MB dye. According to the R^2 and $1/n$ values, the Langmuir model shows best fit to the equilibrium MB adsorption data than the Freundlich model. The suitability of the Langmuir isotherm model suggests monolayer coverage of dye molecule on the adsorbent surface with q_{max}=500 mg/g. The suitability of pseudo-first-order and pseudo-second order kinetic models for the adsorption of MB on OPL were also discussed. The kinetic modelling studies have shown that the experimental data were found to follow pseudo-second-order model. The negative value of free energy change indicated the spontaneous nature of adsorption and confirmed affinity of OPL for the MB basic dye. It was concluded that eco friendly adsorbent OPL can be effectively used as adsorbent for the removal of MB from aqueous solutions.

5.2 Recommendation

Oil palm leaves had been shown to have the potential in removing methylene blue from aqueous solution. Thus in order to further investigate its effectiveness, the following study could be carried out:

- To used the real wastewater sample from the industries to see the efficiency of the natural sorbent in removing dye.
- Application of oil palm leave to remove heavy metal ions such as Cu(II), Cd(II), Cr(II), Ni(II), Pb(II) and Zn(II) ions from aqueous solution.
- Chemical modification of oil palm leaves to enhance its adsorption capacity.
- As to commercialize the uses of proposed adsorbent in the industries, the adsorbent shall be used in a granule form or to be made into a filter cloth in order to be used in one level of treatment at the wastewater treatment plant.

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APPENDICES

Figures of laboratory testing

(a) Before (b) After

Result before and after the adsorption process

The samples of the solution at 3 and 5 minutes time interval