CERTIFICATION OF APPROVAL

Removal of Organic Dye from Aqueous Solution by Adsorption on Sawdust

By
Ku Elianie Syarmy Ku Hilmy

A project Dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirements for the
BACHELOR ENGINEERING (Hons.)
(CHEMICAL ENGINEERING)

Approved by,

(Pn. Nurhayati Mellon)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK DARUL RIDZUAN
JUNE, 2004

1. Adsorption
2. Sawdust
3. CE -- Thesis

CERTIFICATION OF ORIGINALITY

This is certify that I am responsible for the work submitted in this project, that the original work I as my own except as specified in the references and acknowledgements, and that original work contained herein have not been undertaken or done by unspecified sources or persons.

(KU ELIANIE SYARMY KU HILMY)

STUDENT ID: 1731

ABSTRACT

Sawdust was evaluated for its ability to remove organic dye from aqueous solution and was found to be an effective adsorbent for clarification of some textile dyes. A thorough characteristics study of sawdust on organic dye adsorption was carried out. The effect of various experimental parameters such as contact time, initial dye concentration, initial pH, adsorbent dose and particle size of adsorbent was investigated by following a batch adsorption technique. Results show that it can remove 91% of color within two hours of operation without any pretreatment. The Methylene Blue was found to be effectively decolorized (89%-93%) by the optimum dose of 2.0g-5.0g and at particle size of 1000 µm. The percentage removal of dye increased with the decrease in initial dye concentration, particle size adsorbent and increase in contact time, pH of the dye solution and dose of adsorbent. An initial pH in the range of 5.0-7.0 was effective for the dye removal by the adsorbent. The adsorption system studied was proved to fit the Freundlich Isotherm model. By identifying the adsorption isotherm, it will be easier to predict the nature of sawdust acting as an adsorbent. The sawdust adsorbent was shown to be a promising material for removal of organic dye from aqueous solution.

ACKNOWLEDGEMENT

Upon completion of this project paper, I would like to express my heartfelt gratitude to my supervisor, Pn. Nurhayati Mellon for her supervision and guidance throughout this project. Her support and advices that enable this project to achieve its objectives and be completed successfully within the tine frame given is greatly appreciated.

Thanks are extended to the coordinators of the Final Year Project (FYP); Pn. Anis Suhaila Shuib and Miss Yuliana Yuhana for their support and commitment to schedule and organize all the activities in systematically.

I would also like to thank the Department of Chemical Engineering of Universiti Teknologi PETRONAS for allocating this project title for me. With this opportunity, I am able to deepen my knowledge, both in theory and practical.

With this given opportunity, I would also like to convey my appreciation and gratefulness to FYP's lab coordinator, Mr. Zaaba; whom without, the execution of this project is not possible. My thanks also go to all lab technicians who have been very helpful throughout the project.

Also to my beloved mother, Allah blesses her soul, who had been a great counselor to me. Your presence will always be missed.

Last but not least, I would like to acknowledge my family and friends and those who has directly or indirectly involved in this project, for their tremendous support and motivation during undertaking this project.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

1.0 INTRODUCTION

1.1 Background of Study

This research experiment is to explore the potential of sawdust/wood dust as an alternative adsorbent. This was in view with the large amount of wood dust being dumped as wood industrial waste around Malaysia and the relevancy to sort for cheaper adsorbents to replace the much expensive adsorbents like activated carbon.

Advanced wastewater treatment methods are usually needed to achieve effluent quality requirement. Physical, chemical and biological methods such as coagulation, flocculation, oxidation, filtration, electrochemical methods may be used for color removal from wastewater. However, these methods are quite expensive. Biological treatment processes are found to be efficient in the removal of chemical oxygen demand (COD) and biological oxygen demand (BOD) by largely ineffective in the removal of color from wastewater. Adsorption seems to be the most efficient color removal method.

To date, the most common commercially used adsorbent has been activated carbon for the removal of color by adsorption technique, but this is relatively expensive. Activated carbon has widely been used for the removal of inorganic and organic pollutants from aqueous solution. In a continuing search for the adsorbents, various lignocellulosic materials or agriculture wastes such as coconut shell, rice husks, saw dust, and wheat straw were used. Investigation of the suitability of sawdust and some other low cost adsorbents has recently received more attention owing to its economic advantages. Removal of color from aqueous solution by adsorption using sawdust as a low-cost adsorbent can overcome the economic constraints of activated carbon, and equally effective material for color removal. Thus, the objective of this project is to evaluate the adsorption characteristics of sawdust by removing the color from aqueous solution of organic dye.

The removal of organic color by adsorption onto agricultural residues has recently become the subject of considerable interest. There are reports on the removal of dyestuffs by sawdust (Poots et al., 1976), hardwood (Asfour et al., 1985), bagasse pith (McKay et al., 1987]), rice husk and bark (McKay et al., 1987), maize cob (El-Geundi, 1987), and banana pith (Namasivayan et al., 1993). Since these solid wastes are available abundantly at no or low cost, this approach has the potential to provide a low-cost solution to the problem. The adsorption of cations and anions by rubber charcoal was studied (Somboon et al., 1990) and was found to be very effective depend on ions.

1.2 Problem Statement

1.2.1 Problem Identification

The discharge of inorganic and organic contaminants in industrial wastewaters is being subjected to increasingly stringent and expanding array of regulatory controls, primarily driven by public opinion, health concerns and environmental forecasts. Dye wastewaters discharged from textile and dyestuff industries have to be treated due to their impact on water bodies, and growing public concern over their toxicity and carcinogenicity in particular. Dyes usually have synthetic origins and complex aromatic molecular structures (Banat et al., 1996). According to their dissociation in an aqueous solution, dyes can be classified as follows (Mishra and Tripathy, 1993):

- Anionic: acid, direct and reactive dyes
- Cationic: basic dyes
- Nonionic: disperse dyes.

Dyestuff wastewater from the textile and food industry has been the target of considerable attention in the field of wastewater treatment, not only because of its toxicity but also because of its visibility. Effluent water from textile industry which is used in preparation and dyeing processes is discharged with contaminants that require extensive wastewater treatment. Since the metal contaminants in textile dyeing effluent are present in the complexed form, conventional precipitation and/or reduction methods cannot effectively remove them from the effluent. This necessitates the removal of dye from wastewater effluents.

The de-colorization of textile industry wastewater is a worldwide problem to which several successful treatment technologies have been applied, including adsorption and oxidation. The oxidation methods are effective only in wastewater with a very low concentration of organic color. The adsorption process, by activated carbon and polymer resin, is expensive, and it is difficult to regenerate the adsorbent (Bousher et al).

1.2.2 Significant of Project

This research study is projected to be able to prove that sawdust can be used as a potential and effective adsorbent, which is useful for the wastewater treatment. A positive result will indicate that cost major saving can be achieved by replacing the much cheaper and widely available sawdust with the other adsorbent like activated carbon.

1.3 Objectives and Scope of Study

The principal aim and objective of this project is to demonstrate the efficacy of using low cost biodegradable adsorbent materials for the removal organic contaminants (organic dye) from industrial and wastewaters. This project is also to investigate the adsorption isotherm of sawdust in a chemical dye besides to explore its potential as an alternative adsorbent.

In this study, the possibility of using sawdust as a dye adsorbent, and determination of the influence of several important factors (pH, initial dye concentration, adsorbent dose, contact time and adsorbent's particle size) on the adsorption properties of sawdust is being investigated.

From the feasibility study, the research project is seen to be feasible in term of the availability of material, technology and time allocated. The sawdust is easily available and the university provides sufficient analytical equipment and chemical that is required to complete the research.

1.4 Gantt Chart

Refer below for student's time frame

Gantt Chart for Final Year Research Project

No.	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Project Topic	▨													
	Proposed Topic														
	Finalised Topic Selection														
2	Preliminary Research/Design Work		▨	▨											
	Introduction														
	Scope of Study/Objective														
	Project Planning														
3	Submission of Preliminary Report			■											
4	Project Work				▨	▨	▨	▨	▨	▨					
	Practical/Laboratory Work							▓	▓						
	Data Analysis								▓						
	Report									▓					
5	Submission of Progress Report									■					
6	Project Work Continue										▨	▨	▨	▨	▨
	~ List of References / Literature														
	~ Practical / Laboratory Work														

No	Detail/Week	15	16	17	18	19	20								
7	Submission of Dissertation First Draft	■													
8	Submission of Dissertation Final Draft				■										
9	Oral Presentation						■								
10	Submission of Project Dissertation						■								

CHAPTER 2

2.0 LITERATURE REVIEW AND/OR THEORY

2.1 Literature Review

2.1.1 Adsorption Characteristics of New Coccine Dye on to Sludge Ash

This topic was studied by Chih-Huang Weng. The adsorption characteristics of an anionic azo dye (New Coccine) on to sewage sludge ash were studied. Results showed that the ash could remove the dye effectively from aqueous solution. The adsorption rate was fast and could be expressed by the modified Freundlich equation. It was found that pH is the most important parameter affecting the adsorption characteristics. The experimental data were correlated well to the non-linear multilayer adsorption isotherm. The ash adsorption capacities for the dye were in the range 3.25-5.70 mol/g and were affected by the pH, ionic strength and temperature. Decreasing pH, ionic strength and temperature increased the adsorption density. The effect of electrical double-layer thickness on the adsorption was discussed. Thermodynamic parameters indicated that the adsorption was an exothermic process. Values of the first-layer adsorption energy, $G^0{}_1$, ranged from -6.86 to -7.45 kcal/mol, suggesting that the adsorption could be considered as a physical process simultaneously enhanced by the electrostatic effect. The multilayer adsorption energy, $G^0{}_2$, ranged from -4.33 to -4.51 kcal/mol, suggesting that the adsorption was of the typical physical type. On the basis of the monolayer dye adsorption capacity, the specific surface area of the ash was calculated as 3.84-6.73 m^2/g.

2.1.2 Fly ash based low cost method for COD removal from domestic waste water

The study was conducted by Vijender Sahu, R. P. Dahiya and K. Gadgil at Center for Energy Studies Indian Institute of Technology, New Delhi.

In this study, combating potential of fly ash and a commercial grade activated carbon is determined to remove COD from the wastewater. For this purpose a system of standardized batch absorbers under steady state conditions is used to study the effect of these media. The influence of treatment time, adsorbent dose, pH of the media, initial COD concentration, agitation speed and adsorbent particle size on the rate of per cent COD reduction is evaluated. Fly ash has shown quite effective adsorbent capacity for COD reduction from the domestic wastewater. Though its capacity is lower than that of commercial grade activated carbon, the low material cost makes it an attractive option for the treatment of domestic wastewater.

Fly ash is a residue that results from the combustion of coal in power plants. One of the main advantages of COD removal by using fly ash over the other chemical treatment methods is that it is in abundance and easy availability makes it a strong choice in the investigation of an economic way of COD removal. Other advantage is that it could easily be solidified after the pollutants are adsorbed because it contains pozzolanic particles that react with lime in the presence of water, forming cementation calcium-silicate hydrates.

In the present study various parameters affecting adsorption like contact time between the waste water and the adsorbent, adsorbent dose, pH of the sample, initial COD concentration, agitation speed and size of the adsorbent particles have been investigated. All the experiments were carried out at ambient temperature in batch mode. Batch mode was selected because of its relative simplicity. The adsorption process for the studied adsorbent follows first order kinetics and Freundlich adsorption pattern. It is revealed from the studies that the treatment of domestic wastewater can be done by fly ash generated from thermal power plant to reduce the organic load. It is observed that the COD can be reduced up to the extent of 87.89 % by use of fly ash. Trend of % COD removal by fly ash are fairly comparable to that of commercial activated carbon. It is physically viable and economically viable approach.

2.1.3 Removal of Heavy Metal from Aqueous Solutions by Sawdust Adsorption – Removal of Copper

The result of this study was published in Journal of Hazardous Materials by Elsevier Science Publishers B.V. Amsterdam Netherlands. The article was jointly written by Yu, Bin; Zhang, Y.; Shukla, Alka; Shukla, Shyam S. and Dorris, Kenneth L who work with A&B Environmental Services in Houston, Texas, USA.

Locally available sawdust, a byproduct of the world industry, was found to be a low cost and promising adsorbent for the removal of copper (II) from wastewater. In this work, adsorption of copper on sawdust has been studied by using batch techniques. The equilibrium adsorption level was determined to be a function of the solution pH, contact time and sorbate concentration. The equilibrium adsorption capacity of sawdust for copper was obtained by using linear Freundlich and Langmuir isotherms. Ion exchange is probably one of the major adsorption mechanisms for binding divalent metal ions to the maple sawdust.

The results provide strong evidence to support the hypothesis of adsorption mechanism. It also supplies significant sawdust operation capacity for engineering design.

2.1.4 The Use of Eucalyptus Barks for the Adsorption of Heavy Metal Ions and Dyes

Eucalyptus barks harvested in Lebanon were used for the adsorption of pollutants such as heavy metal ions and dyes. Washing with water or pretreatment with formaldehyde was performed on the bark powder. The adsorption capacity of this material towards Cu^{II}, Cr^{III}, Cd^{II} and Ni^{II} was evaluated in a batch process for various parameters. The results obtained showed that the retention capacity increased with contact time, pH and initial metal ion concentration but decreased with temperature. The adsorption capacities were 2.61, 0.71, 2.24 and 0.75 mmol/g adsorbent for Cu^{II}, Cr^{III}, Cd^{II} and Ni^{II}, respectively. Eucalyptus barks are also very efficient for the adsorption of dyes (Acid Blue 25, Erichrome Blue Black B and Calmagite) because of interaction between the hydroxy and amino groups of the dyes and the phenolic moieties of bark. This adsorption was modified when metal ions had already been adsorbed on to the barks as a result of the formation of a 1:1 complex between the dye and the metal ion. Desorption was achieved by treating with the sodium salt of ethylenediamine- tetraacetic acid (EDTA) for metal ions and by heating at 75°C in aqueous medium for dyes. After desorption, the recycling of the support was tested for potential use as a means of concentrating pollutants.

2.1.5 Removal of Two Reactive Dyes by Quaternized Sawdust

This topic was studied by Hacgyu Lim, Sukjae Kim, Sang-Myuang Lee, Jangwoon Byun, Sunjong Ryoo, Yoon-Sik Lee and Jeyong Yoon from School of Chemical Enginnering, Seoul National University, Korea.

In this study, instead of using raw sawdust as the adsorption's adsorbent, the sawdust was first treated with a quaternization agent. The quaternized sawdust modified with N-(3-chloro-2-hydroxypropyl) trimethyl ammoniumm chloride (CHMAC) was evaluated for its ability to remove two reactive dyes (Reactive Blue 19 & Reactive Red 4) from aqueous solution. The adsorption capacities of Reactive Blue 19 & Reactive Red 4 on quaternized sawdust were approximately five and sixteen times higher than that of activated carbon (F-400), respectively. Moreover, adsorption on quaternized sawdust was hardly affected by salt concentration. It was also found that the degree of sawdust quaternization has a good linear relationship with the maximum adsorption capacity. This indicates that the electrostatic interaction between anionic sites in reactive dyes and quaternized cationic sites in sawdust is of primary importance in terms of the adsorption characteristics of the two reactive dyes. However, the desorption test of dyes adsorbed on quaternized sawdust showed poor performance in NaOH and NaCl solution, suggesting additional undefined binding forces.

The quaternized sawdust (SD-QA) used in this study was represented below:

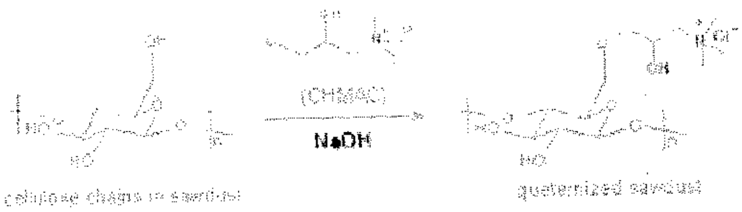

Figure 2.1: Preparation scheme: Quaternized Sawdust

The raw sawdust was pretreated with an aqueous solution of NaOH at room temperature in a reactor, and the quaternization reagent; N-(3-chloro-2-hydroxypropyl) trimethylammoniumm chloride (CHMAC) was added to synthesize the quaternized sawdust. The reaction product was washed with distilled water and vacuum-dried. The chemical compositions of sawdust are mainly lignin, cellulose and hemicelluloses. Lignin which originally constituted 25% of raw sawdust was removed by above NaOH pretreatment.

2.1.6 Novel Adsorbents

Several novel adsorbents have been studied due to the rapid industrialization which generated large volume of waste. The effort and attempt to find the cost effective and environmental friendly adsorbent has been done by few investigators (De and De, 1994; Namasivayam, 1995; Rai et al., 1998; Rao et al., 1999)

Material	Brief Procedure of Preparation	Investigator
Rock phosphate	Low grade rock Phosphate samples are sized and grounded. The grounded samples are used for studies	Prasad et al., 2000
Fly ash	Fly ash obtained from thermal plant is sieved and selected mesh size is chosen for studies	Singh and Rawat, 1993
Sawdust (Chemically modified)	Sawdust of rubber wood is washed with distilled water and dried. Grounded to -80/+230 sieve. Two parts of sawdust powder +20 parts of 0.2M H_2SO_4 + 5 parts of 50°C	Raji et al., 1997

	for six hours and stirred. Product is washed with distilled water dried at 60°C. Grounded in mortar to -81/+230 sieve	
Mango seed and seed shell	Samples procured and dried. Ground to 100-200 m, ash size, stored and used.	Mohammas Ali et al., 1997
Bagasse, Activated bagasse, activated coconut jute carbon, bagasses ash	Raw bagasse: Washed with water, dried at 200°C for 5 hours. Ground to 150-400 μm. Activated bagasse carbon: 4 parts (w/w) of raw bagasse + 3 parts conc. H_2SO_4 is heated in air oven at 150-160°C for 24 hours. It is then washed with water, dried at 105°C for 24 hours. Dried material is subjected to thermal activation at 780-850°C for 15 minutes. Ground to 150-400 μm. Same procedure for activated coconut jute carbon. Bagasse ash is used directly without any preparation.	Scrichand et al., 1994

A partial list of novel adsorbents is collected from literature (Rai et al., 1998), compiled with respect to the pollutant they are attempted to remove in the batch/column studies. The investigators have attempted novel methods to alter the structure of adsorbent. All of them have reportedly given satisfactory results of adsorption.

Since the material characteristics such as moisture content, ash content, bulk density and fixed carbon content are giving very little evidence to understand the pattern of adsorption over a variety of low-cost adsorbents, it is desired to study the effect of operating parameters on the pollutant removal efficiency. The operating parameters that identified based on their significance in batch studies of adsorption are adsorbent attempted, pH, equilibrium time, contact time, adsorbate concentration an adsorbent dosage.

A combination of operating and physico-chemical parameters has been studied for optimizing the sue of novel adsorbents in wastewater treatment and can be summarized as nature of adsorbent, adsorbate concentration, temperature and pH of aqueous media, kinetics of adsorption, adsorption isotherm, type of contacting system of adsorbent with adsorbate, contact time and speed of agitation.

2.2 Theory

2.2.1 Adsorption Process

Adsorption is a unit operation in which surface active materials in true solution are removed from the solvent by interphase transfer to the surfaces of an adsorbent particle. This process is used in environmental engineering practice for removal of various pollutants such as soluble organics, dyes, pesticides, lignins, etc., from wastewaters and for removal of colour and taste and odour-producing substances from natural waters that are to be used as potable water supplies.

The use of solids for removing substances from either gaseous or liquid solutions has been widely used since biblical times. This process, known as adsorption, involves nothing more than the preferential partitioning of substances from the gaseous or liquid phase onto the surface of a solid substrate. Adsorption phenomena are operative in most natural physical, biological, and chemical systems, and adsorption operations' employing solids such as activated carbon and synthetic resins are used widely in industrial applications and for purification of waters and wastewaters.The process of adsorption involve separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent, and the material concentrated or adsorbed at the surface of that phase is the adsorbate.

2.2.2 Adsorption Isotherms

Equations that are often used to describe the experimental isotherm data were developed by Freundlich, Langmuir and Brunauer, Emmet and Teller (BET isotherm) (Shaw, 1966). The quantity of adsorbate that can be taken up by an adsorbent is a function of both the characteristics and concentration of adsorbate and the temperature. The characteristics of the adsorbate that are of importance include: solubility, molecular structure, molecular weight, polarity and hydrocarbon saturation. Generally, the amount of material adsorbed is determined as a function of the concentration at a constant temperature, and the resulting function is called an *adsorption isotherm*.

Adsorption isotherm is developed by exposing a given amount of adsorbate in a fixed volume of liquid to varying of adsorbate. At the end of the test period, the amount of adsorbate remaining in solution is measured. The adsorbent phase concentration after equilibrium is computed using equation (Eq. 2.1) below. The adsorbent phase concentration data computed using Eq. 2.1 is then used to develop adsorption isotherms as described below.

$$q_e = \frac{(C_o - C_e)V}{m} \qquad (2.1)$$

Where:

q_e = adsorbent (i.e. solid) phase concentration after equilibrium

= mass adsorbate/mass adsorbent

C_o = initial concentration of adsorbate, mg/L

C_e = final equilibrium concentration of adsorbate, mg/L

V = volume of liquid in the reactor

m = mass of adsorbent, g

Experimental isotherms are useful for describing adsorption capacity to facilitate evaluation of the feasibility of this process for a given application, for selection of the most appropriate adsorbent and for preliminary determination of adsorbent dosage requirements. Moreover, the isotherm plays a crucial functional role in predictive modeling procedures for analysis and design of adsorption systems.

2.2.3 Linear Isotherm

Data that follow a linear law can be expressed by an equation similar to Henry's law.

$$\frac{x}{m} = K_f C_e \qquad (2.2)$$

Where:

x/m = mass of adsorbate adsorbed per unit mass of adsorbent

K = Linear isotherm constant

C_e = equilibrium concentration of adsorbate in solution after adsorption

This linear isotherm is not common, but in dilute region it can be used to approximate data of many systems. This model has the advantage of describing a given set of adsorption data in terms of a single parameter, K, and of simplicity for modelling purposes because it can be solved implicitly for any of the terms.

2.2.4 Langmuir Isotherm

In 1918 Langmuir used a simple model of the solid surface to derive an equation for an isotherm. Derived from rational considerations, the Langmuir adsorption isotherm is defined as:

$$\frac{x}{m} = \frac{q_o C_e}{K + C_e} \qquad (2.3)$$

Where:

x/m = mass of adsorbate adsorbed per unit mass of adsorbent

q_o = empirical constants

C_e = equilibrium concentration of adsorbate in solution after adsorption

This Langmuir model, originally developed for adsorption of gases onto solids, is predicted on the assumptions that there are only a fixed number of active sites available for adsorption, only a monolayer is formed, and the adsorption is reversible and reaches an equilibrium condition. Equilibrium is reached when the rate of adsorption molecules onto the surface is the same as the rate of desorption of molecules from the surface.

The rate at which adsorption proceeds is proportional to the driving force, which is the difference between the amount adsorbed at a particular concentration and the amount that can be adsorbed at that concentration. At the equilibrium concentration, this difference is zero.

Correspondence of experimental data to the Langmuir equation does not mean that the stated assumptions are valid for the particular system being studied, because departures from the assumptions can have cancelling effect.

2.2.5 Freundlich Isotherm

The Freundlich isotherm can be derived by modifying the Langmuir assumptions to allow for several kinds of adsorption sites on the solid, each kind having a different heat of adsorption. Freundlich isotherm is used most commonly to describe the adsorption characteristics of the activated carbon used I water and wastewater treatment. Derived empirically in 1912, the Freundlich isotherm is defined as follows:

$$\frac{x}{m} = K_f C_e^{n} \qquad (2.4)$$

Where:

x/m = mass of adsorbate adsorbed per unit mass of adsorbent

K_f = Freundlich capacity factor

= (mg adsorbate/g adsorbent) (L water/mg adsorbate)$^{1/n}$

C_e = equilibrium concentration of adsorbate in solution after adsorption

$1/n$ = Freundlich intensity parameter

The Freundlich isotherm equation, which is empirical, often approximates data for many physical adsorption systems and is particularly useful for liquids. The Freundlich equation is often applied to **adsorption of solutes from liquid solutions onto solids**.

CHAPTER 3

3.0 METHODOLOGY/PROJECT WORK

3.1 List of Material

1. Sawdust/Wood dust
2. Methylene Blue (MB) Dye
3. Deionized Water/Distilled Water
4. NaOH and HCl solution

3.2 List of Apparatus and Equipment

1. UV-VIS Spectrophotometer
2. Hot Plate and Stirrer
3. BET Surface Analyzer
4. Digital Weighing Balance
5. Stopwatch
6. Laboratory Drier/Oven
7. 200 ml Beaker
8. 1 liter Erlenmeyer Flask
9. Measuring Cylinder
10. Laboratory Siever
11. Conical Flasks
12. Pipette
13. Filtering Set
14. Stop Cocks
15. Aluminum Foil
16. Glass Funnel

3.3 Method/ Experimental Conditions

3.3.1 Analysis

Study for contact time. A sorption kinetic study was carried out by adding a known amount of sawdust into dye solution with an initial pH of 6. A portion of the solution was withdrawn at a desired time interval. The dye concentration of the clear solution was determined.

Study for adsorbent dose. The studies were conducted by varying the amount of adsorbent. A known volume of sample was treated with different doses of sawdust. The samples were agitated for specific time, filtered and then analyzed for the residual dye concentration.

Study for pH. pH effect was performed taking a specific concentration, adsorbent dose, & contact time and varying the pH values from 5.0-8.0 using dilute hydrochloric acid (NaOH) or sodium hydroxide (HCl) solutions. A known weight of sawdust was added to each solution. The samples were agitated for specific time, filtered and then analyzed for the residual dye concentration.

Study for initial dye concentration. These studies were performed by keeping all the conditions constant except changing the initial dye concentration by using simulated dye bearing solutions prepared by dissolving known amount of organic dye in distilled water.

Study for adsorbent particle size. Adsorbent particle size studies were performed by keeping all conditions constant and varying the particle size. The residual dye concentration was determined after each run. The removal of color was quoted (as %) relative to the values measured for the untreated effluent.

Study for adsorption isotherm. The adsorption isotherms were determined by shaking a fixed weight of sawdust into dye solutions, having a range of dye concentrations at room temperature, for certain amount of time.

3.4 Preparation of Chemical and Material

3.4.1 Methylene Blue Solution

1 gram of methylene blue powder was measured by using laboratory digital weighing balance. The powder was dissolved in 1 liter of distilled water to produce the concentrated methylene blue solution with initial concentration, C_o of 1000mg/L. Different amount of the C_o, concentrated dye solution was added into 5 different volumetric flasks and each was top-up with distilled water.

3.4.2 Sawdust

The sawdust was collected from a furniture workshop in Terengganu. The adsorbent was dried in a laboratory oven at 105°C for 24 hours to remove any moisture. The sawdust was then screened to remove the larger particles and sieved to discrete particles sizes. The sawdust was then ready to be used as adsorbents for the removal of methylene blue dye from aqueous solution.

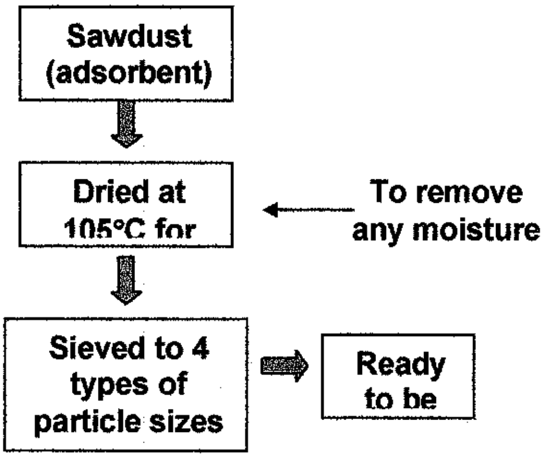

Figure 3.1: Preparation of Sawdust

3.5 Experimental Procedure

In a nutshell, the adsorption experiments were carried out at the ambient temperature. A stock solution of Methylene Blue, MB (1000mg/L) was prepared and diluted to the required initial concentrations (50-300 mg/L). The experiments were conducted in 250 mL of volumetric flask to which 200 mL of MB solution varying the concentration Of 50-300 mg/L and adsorbent dose of 1.0g-5.0g. The samples were stirred with a magnetic stirrer at 150 rpm.

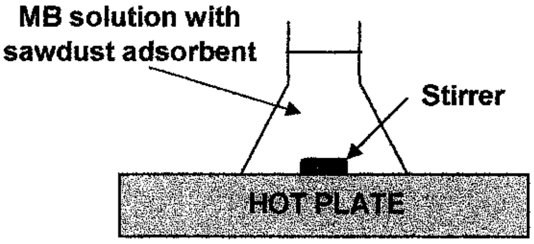

Figure 3.2: Experimental Setup

The flask was withdrawn at selected time interval to a certain hours of operation. After each adsorption experiment, the treated dye solution was filtered with whatmann #1 filter paper from adsorbent and analyzed the supernatant using UV-Vis Spectrophotometer at 667.8 nm. The experimental procedure is the same for all studies except in variation of difference parameters while keeping constant of the others.

3.5.1 Effect of Contact Time

Color uptake with contact time for a fixed initial dye concentration of 100 mg/L and pH of 6.0 with adsorbent dose of 3.0 g sawdust and particle size of 1 000 µm. The solution was analyzed using UV-Vis Spectrophotometer for every hour up to 16 hour.

3.5.2 Effect of Initial Dye Concentration

Effect of initial dye concentration on color removal from aqueous dye solution was studied. The initial dye concentration varies from 50 mg/L to 300 mg/L at fixed adsorbent dose of 3.0 g particle size of 1000 µm and contact time for 3 hours.

3.5.3 Effect of Adsorbent Dose

The effect of adsorbent dose on color uptake at initial Methylene Blue concentration of 100mg/L was studied to determine the optimum dose of adsorbent in adsorption process. The adsorbent dose is varies, 1 g, 2 g, 3 g and 5 g with particle size of 1 mm.

3.5.4 Effect of Particle Size

The removal of organic dye in aqueous solution with the variation of particle size at the dye concentration of 100 mg/L is studied. Adsorbent dose, particle size and contact time are fixed at 3.0 g, 1000 µm and 3 hours respectively.

CHAPTER 4

4.0 RESULTS

4.1 Calibration Curve

The peak or absorbance of the 7 different concentrations of methylene blue was analyzed by using UV-VIS Spectrophotometer. UV-VIS is a Windows compatible computer program that simulates an ultraviolet (UV)-visible spectrophotometer with a wavelength range of 200 to 800 nm. The raw data of the calibration curve, as shown in Table 4.1 below, was then used to plot the calibration curve, as illustrated in Figure 4.1 below. The graph is actually a linear graph. It shows that the higher the concentration of methylene blue, the higher the peak value will become.

Table 4.1: Calibration Table

Sample Standard	Dye concentration (mg/L)	Peak
Std_1	20.0	3.587
Std_2	10.0	1.831
Std_3	50.0	0.829
Std_4	3.0	0.719
Std_5	1.0	0.288
Std_6	0.5	0.154
Std_7	0.2	0.094

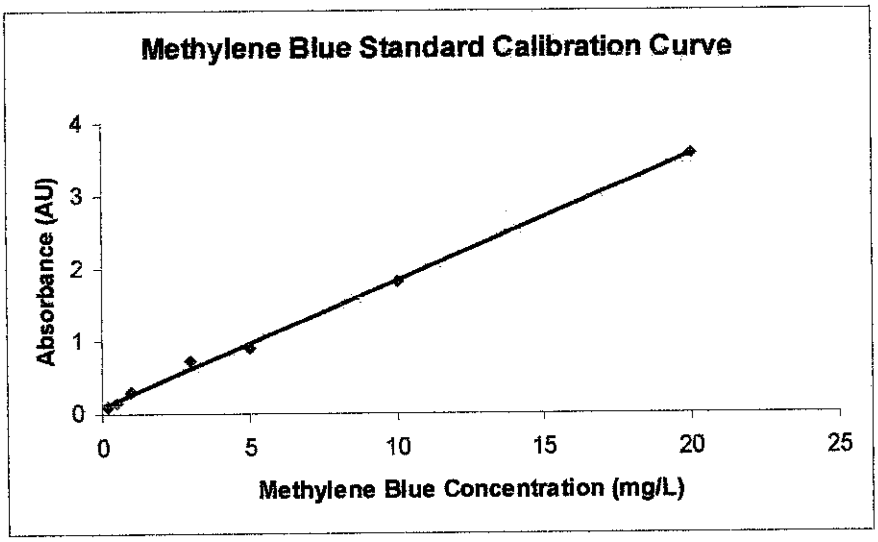

Figure 4.1: Calibration Curve

4.2 Effect of Contact Time

Data observed are tabulated as below (*Please refer Table 4.2: Data for Study on Contact Time*). Figure 4.2 represents the removal of dye from aqueous solution as a function of time. The removal of MB dye from aqueous solution varying the contact time was studied to determine the equilibrium stage. The removal rate was increased to a constant value with the increase in contact time. The equilibrium of color removed by the adsorbent was reached within 2-4 hours of operation.

Table 4.2: Data for Study on Contact Time

Initial Dye Concentration : 100 mg/L	
Adsorbent dose : 3.0 g	
Particle Size : 1000 µm	
pH : 6.0	
Contact Time (Hour)	**Percentage of Color Removal (%)**
1	87.075
2	90.423
3	91.625
4	91.663
8	91.674
16	91.678

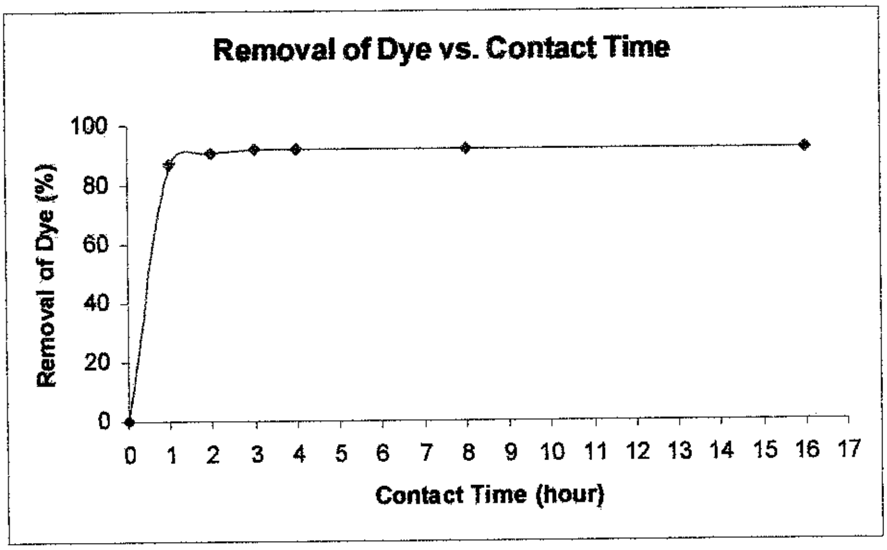

Figure 4.2: Effect of Contact Time on Adsorption of Dye

4.3 Effect of Initial Dye Concentration

Data observed are tabulated as below (*Please refer Table 4.3: Data for Study on Initial Dye Concentration*). Figure 4.3 depicts that the percentage of dye removal decreased with the increasing in the initial dye concentration of MB. The utmost removal of about 92% was recorded with the concentration of 50-300 mg/L for 3 hours operation. The higher dye concentration shows lower dye removal as the adsorbent was lack of surface areas for adsorption of excess dye concentration.

Table 4.3: Data for Study on Initial Dye Concentration

Contact Time : 3 hour	
Adsorbent dose : 3.0 g	
Particle Size : 1000 µm	
pH : 6.0	
Initial Dye Concentration (mg/L)	**Percentage of Color Removal (%)**
50	92.124
100	91.625
150	90.87
200	88.403
300	74.71

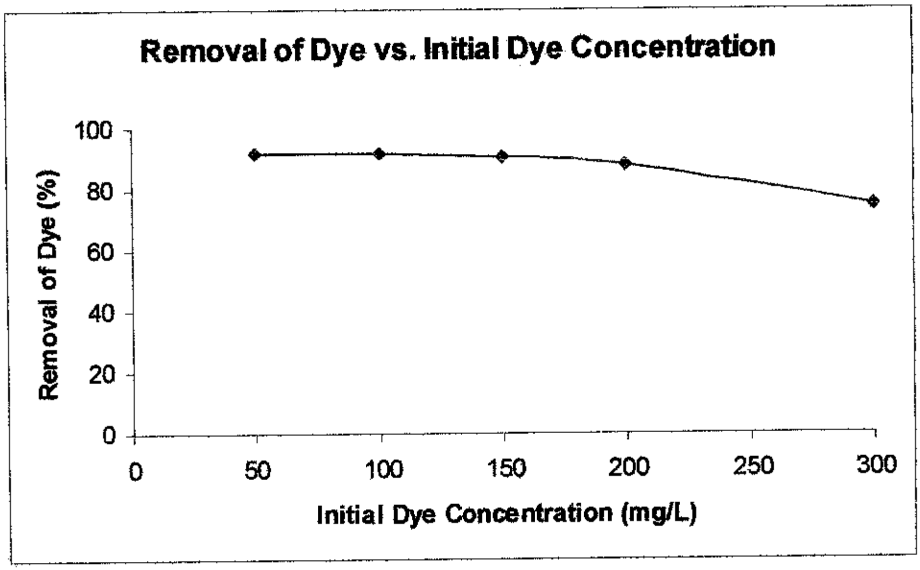

Figure 4.3: Effect of Initial Dye Concentration on Adsorption of Dye

4.4 Effect of Adsorbent Dose

Data observed are tabulated as below (*Please refer Table 4.4: Data for Study on Adsorbent Dose*). Figure 4.4 shows that the removal rate was found to be effective with the adsorbent dose of 2.0-5.0 g and the higher the adsorbent dose, the higher the percentage removal of color.

Table 4.4: Data for Study on Adsorbent Dose

Initial Dye Concentration : 100 mg/L	
Contact Time : 3 hour	
Particle Size : 1000 µm	
pH : 6.0	
Adsorbent Dose (g)	**Percentage of Color Removal (%)**
1.0	64.347
2.0	91.068
3.0	91.625
5.0	92.106

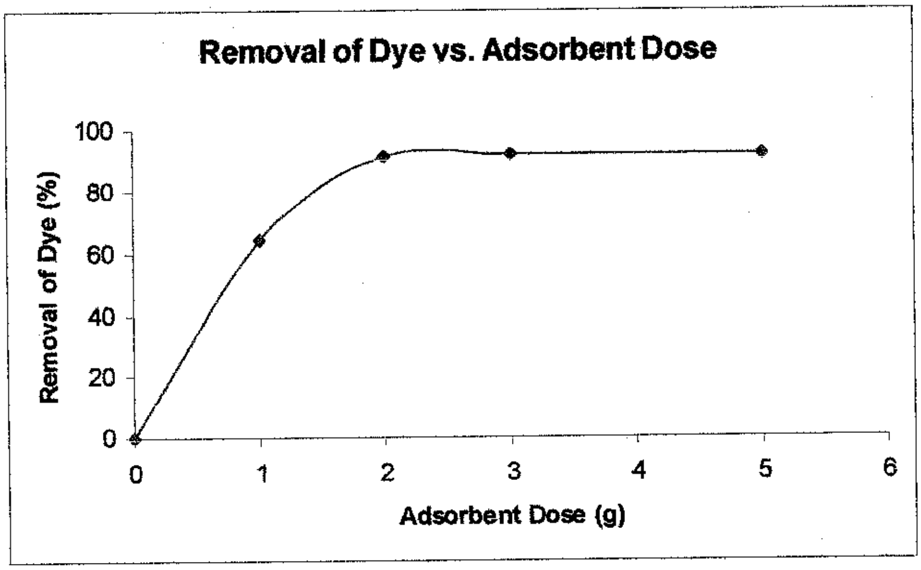

Figure 4.4: Effect of Adsorbent's Dose on Adsorption of Dye

4.5 Effect of Adsorbent's Particle Size

Data observed are tabulated as below (*Please refer Table 4.5: Data for Study on Adsorbent's Particle Size*). Fig. 4.5 represents the effect of particle size on the removal of dye. It was observed that the extent of adsorption decreased with increasing particle size.

Table 4.5: Data for Study on Adsorbent's Particle Size

Initial Dye Concentration : 100 mg/L	
Contact Time : 3 hour	
Adsorbent Dose : 3.0 g	
pH : 6.0	
Particle Size (μm)	**Percentage of Color Removal (%)**
<250	94.155
250	94.108
500	93.265
1000	91.625

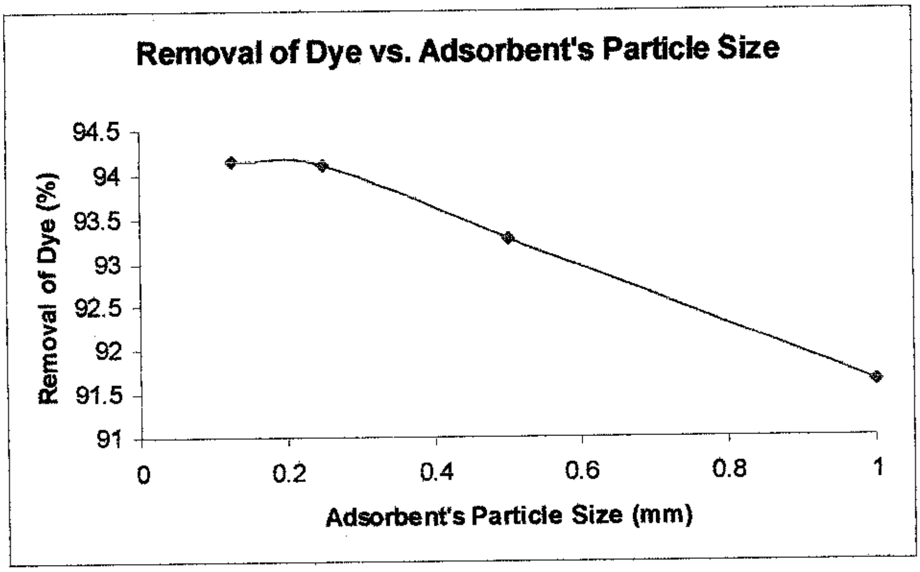

Figure 4.5: Effect of Adsorbent's Particle Size on Adsorption of Dye

4.6 Effect of pH

The variation of color removal with initial pH is shown in Figure 4.6. The pH primarily affects the degree of ionization of the adsorbate and the surface properties of adsorbent i.e. surface charge of the adsorbent. The results indicated that at lower pH, the removal rate was lower. Data showed the optimum pH values of 5.0-8.0.

Table 4.6: Data for Study on pH

<table>
<tr><th colspan="2">Initial Dye Concentration : 100 mg/L</th></tr>
<tr><th colspan="2">Contact Time : 3 hour</th></tr>
<tr><th colspan="2">Adsorbent Dose : 3.0 g</th></tr>
<tr><th colspan="2">Particle Size : 500 µm</th></tr>
<tr><th>pH</th><th>Percentage of Color Removal (%)</th></tr>
<tr><td>3.0</td><td>89.495</td></tr>
<tr><td>5.0</td><td>91.542</td></tr>
<tr><td>6.0</td><td>91.625</td></tr>
<tr><td>8.0</td><td>91.619</td></tr>
</table>

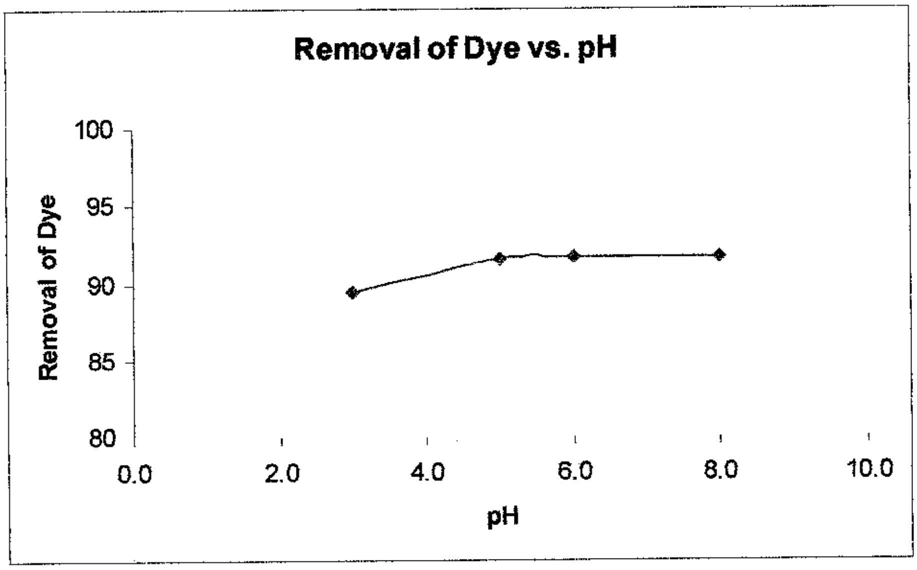

Figure 4.6: Effect of pH on Adsorption of Dye

4.7 Development of Adsorption Isotherm

The data obtained from the analysis of UV-VIS Spectrophotometer on study of contact time was used to determine which isotherm fits the adsorption. This was achieved by first constructing Table 4.7.1 and Table 4.7.2 as shown below.

Table 4.7.1: Calculated Data for Plotting Adsorption Isotherm

Contact time (hr)	Adsorbate concentration (mg/L)			m (g)	x/m
	C_o	C_e	$(C_o-C_e)=x$		
3	50	7.876	42.124	3.0	14.041
3	100	8.375	91.625	3.0	30.542
3	150	9.130	140.870	3.0	46.957
3	200	11.597	188.403	3.0	62.801
3	300	25.290	274.710	3.0	91.570

Table 4.7.2: Data for Plotting Freundlich and Langmuir Isotherm

Linear Isotherm		Freundlich Isotherm		Langmuir Isotherm	
C_e	x/m	Log C_e	Log (x/m)	$1/C_e$	1/(x/m)
7.876	14.041	0.896	1.147	0.127	0.071
8.375	30.542	0.923	1.485	0.119	0.033
9.130	46.957	0.960	1.668	0.110	0.021
11.597	62.801	1.064	1.798	0.086	0.016
25.290	91.570	1.403	1.962	0.040	0.011

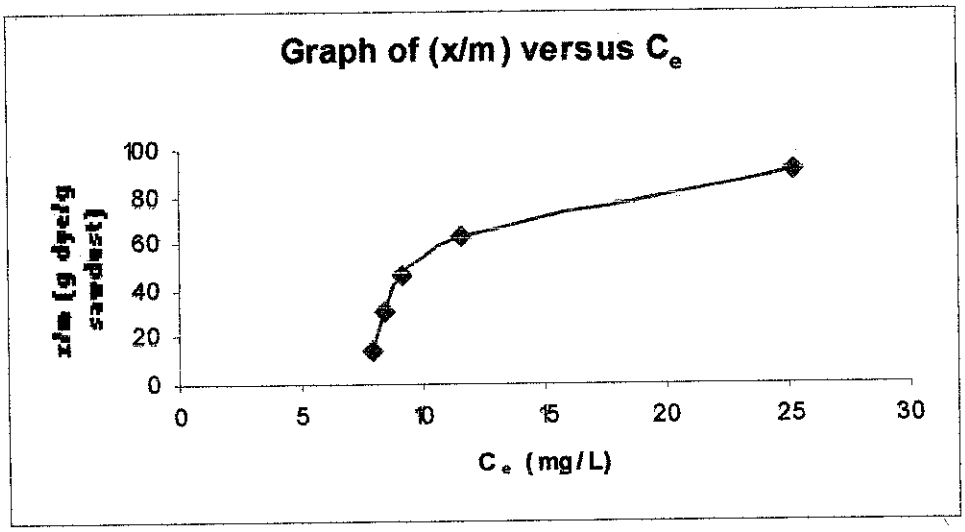

Figure 4.7: Type I Isotherm

4.7.1 Langmuir Isotherm

By utilizing data in Table 4.7.1, the graph of 1/(x/m) versus $1/C_e$ was then plotted as depicted in Figure 4.7.1 below.

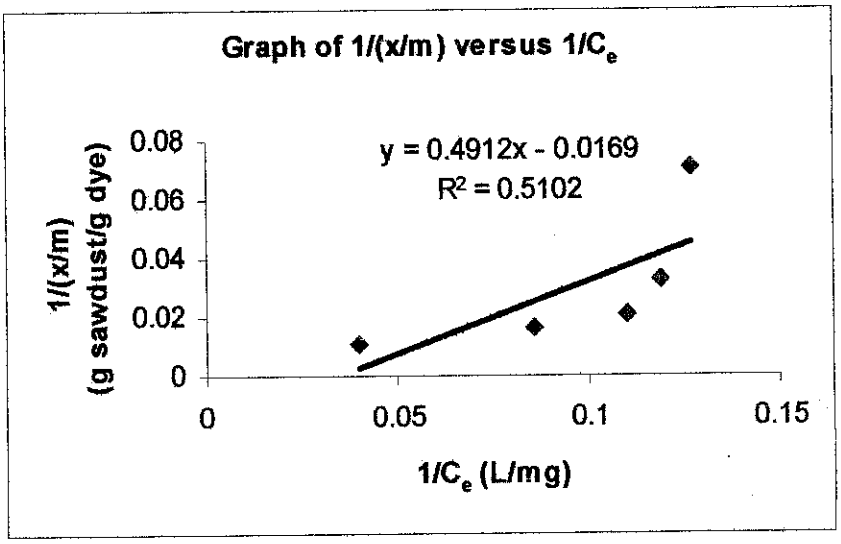

Figure 4.8: Langmuir Adsorption I Isotherm

4.7.2 Freundlich Isotherm

By utilizing data in Table 4.7.2, the graph of log (x/m) versus log C_e was then plotted as depicted in Figure 4.7.1 below.

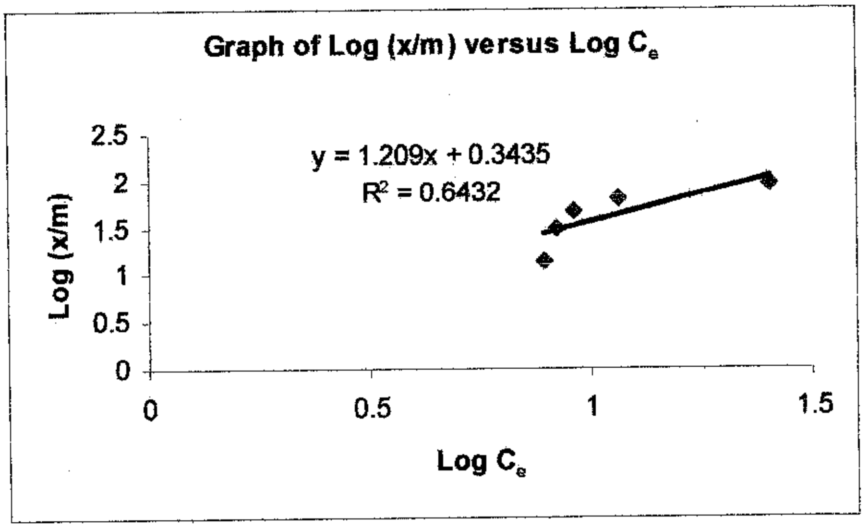

Figure 4.9: Freundlich Adsorption I Isotherm

Since the linearity for the Freundlich isotherm is higher compared to the Langmuir model, it is to be concluded that the adsorption of organic dye fits the Freundlich isotherm. Linearization of Freundlich isotherm:

$$\log(x/m) = \log K_f + n\log C_e$$

Figure 4.7.2 shows a linear graph. From the figure, log K_f is the intercept at y-axis and the slope is the dimensionless exponent n. The dimensions of K_f depend on the value of n. this gives the value of $K_f = 2.2055$ and $n = 1.209$. Thus Eq (2.4) becomes;

$$\frac{x}{m} = 2.2055C_e^{1.209}$$

CHAPTER 5

5.0 DISCUSSION

5.1 Effect of Contact Time

Adsorption is a slow process and adequate contact time is necessary to allow the system to approach equilibrium (S. Hassan et al., 2000). According to Md Zahangir Alam (2003), one to two hours contact with vigorous agitation is sufficient for approaching equilibrium but this can vary with the sample.

Figure 4.2 represents the percentage removal of color for different contact time by the sawdust. It seems that dye removal has been achieved to the extent of more than 60% by sawdust at a maximum time period of 30 minute. From the removal curve (Figure 4.2), it has been seen that equilibrium attained in 180 minutes. The uptake of color is very rapid in the first 30 minutes then followed by a slower process after 60 minutes. This behavior was agreed by K. K. Wong et al (2003), where he suggests the occurrence of rapid external mass transfer followed by a slower internal diffusion process which may be the rate determining step.

There are essentially three consecutive mass transport steps associated with the adsorption of solutes from solution by porous adsorbent (after Weber, 1981). The first step, bulk transport of solute in the solution phases, is usually rapid because of mixing and advective (convective) flow. The second step, film transport, involves diffusion of the solute through a hypothetical "film" or hydrodynamic boundary layer. Except for a small amount of adsorption that occurs on the exterior of the adsorbent, the solute then must diffuse within the pore volume of the adsorbent and/or along pore-wall surfaces to an active adsorption sites (intra-particle transport).

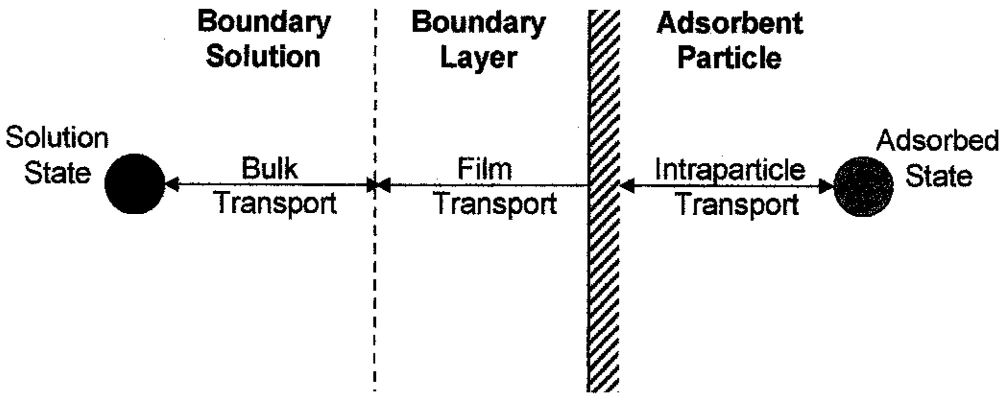

Figure 5.1: Mass Transport Steps in Adsorption by Porous Adsorbents

The actual adsorption of solute on interior surface sites is generally considered to be very rapid, equivalent to an equilibrium reaction, and thus insignificant in the context of overall adsorption rate (Weber and Morris, 1963; Neretnieks, 1976; Crittenden and Weber, 1978). Film and intraparticle transport are thus the major factors controlling rates of adsorption from solution by porous adsorbents.

The experimental result shown in Figure 4.2 indicates that the uptake of dye increases as the contact time between the dye solution and sawdust is longer. It might due to the longer agitation rate that exposed to the adsorbent-adsorbate system and reduced the film boundary layer surrounding the sorbent particles thus increasing the external film mass transfer coefficient and hence the rate uptake (K.K. Wong et al., 2003). External diffusion or film transport controls the transfer of solute from bulk solution through the boundary layer of fluid immediately adjacent to the external surface of the adsorbent particle. The smooth and independent nature of curve indicates formation of monolayer cover of the adsorbate on the outer surface of the adsorbent. The adsorption process for the studied adsorbent follows first order kinetics and Freundlich adsorption pattern.

The steep curve in the first hour of dye uptake is the characteristics of highly favorable adsorption, and it is suggested that sawdust is an effective adsorbent for organic dye from aqueous solution. The high initial rates of dye uptake indicates that the adsorption occurred mainly at the ash exterior surface (M. A. Hashim and K. H. Chu, 2002) and this facts was agreed by Sing et al. (1984) that the possibility of a monolayer adsorption of organic dye on sawdust.

5.2 Effect of Initial Dye Concentration

Figure 4.3 indicates the effect of initial dye concentration on percentage color reduction by sawdust at the optimum pH, adsorbent dose and the contact time as predicted from Table 4.3. The sawdust seems to be fairly active adsorbent even at higher initial concentrations.

Weber (1972) stated that the extent of adsorption also relates to certain properties of the adsorbate relative to the solution phase, notably those of surface tension and solubility; which is relates to the solution's concentration. It greatly influenced by the solvophobicity or lyophobicity of a compound that is, its "dislike" for, or insolubility in the solvent phase. The greater its solvophobicity with respect to a given solvent, the greater is the tendency of an adsorbate to be adsorbed from that solvent at interfaces with other phases. Bonding between a substance and the solvent in which it dissolved must be broken first before adsorption from the solvent can occur. The greater the solubility (lower initial dye concentration) of the compound, the stronger the bond, and thus the extent of adsorption is smaller.

At lower initial concentrations, the ratio of the initial number of moles available to the adsorbent surface area is low and subsequently the fractional adsorption becomes independent of initial concentration. At higher concentrations, the available sites of adsorption become fewer and hence the percentage removal of dye depends upon the initial concentration.

High concentration gradient will also increase the rate of adsorption, though a high concentration of solute can eventually have a negative effect on the adsorption capacity. This explained the reason why the adsorption capacity of dye solution on sawdust decreases once the initial dye concentration is 300 mg/L.

5.3 Effect of Adsorbent's Dose and Particle Size

Figure 4.4 depicted the effect of amount of adsorbent's dose on percentage color reduction by sawdust at the optimum pH, adsorbent dose and the contact time as predicted from Table 4.4. The removal rate was found to be effective with the adsorbent dose of 2.0-5.0 g and the higher the adsorbent dose, the higher the percentage removal of color.

In Figure 4.5, it shows that the amount of color adsorbed increased with the decrease of particle size of sawdust. This is due to the increase in available surface area with the decrease in particle size. In general, the intra-particle mass transfer effect will increase with the increasing particle size.

Higher color removal percentage at higher dose of adsorbent and smaller particle size was due to increased of surface area where there are more adsorption sites available. Both results are in agreement with Zahangir (2003) in his studies on the same topic.

The surface area of an adsorbent is a fundamental property and usually related to adsorption capacity. Adsorption capacity may be simply defined as the quantity of adsorbate absorbed per unit weight of adsorbent. Of all characteristics, adsorptive capacity is paramount because it describes the key economic factor in the adsorption process. The surface area of all commercially significant adsorbents is contained within an internal pore structure of the adsorbent particles. This is true for any adsorbents which may have a smaller particle size.

The size and distribution of pores within the sawdust particle are related to available surface area simply due to the fact that a potion of the surface area may be inaccessible to adsorbate molecules of larger size. Reduction in particle size does improve adsorption rate, as depicted in Figure 4.5. Powdered sawdust adsorb more rapidly than granular sawdust and fine granules more rapidly than coarse one.

5.4 Effect of pH

The effect of the pH of organic dye solution was studied by varying the pH values from 3.0 to 8.0. The pH was adjusted by adding 0.1 M HCl and 0.1 M NaOH at room temperature.

Figure 4.6 depicts the effect of pH on percent color reduction by sawdust. The runs were taken at the constant initial dye concentration, adsorbent dose and the contact time. The results indicate that at all pH levels below 5.0; the sawdust has consistently higher adsorption capacity for dye. From the graph, the percentage of color removal at room temperature 30°C was increasing from pH 3.0 to 6.0 and slightly decreases after pH 7.0. It found that the critical pH is from 4.0-6.0.

Generally, the effect of pH on the adsorption of dye on sawdust can be explained on the basis of an aqua-complex formation owing to the charge develops on the surface of the oxides of the ash in an acidic medium as follow:

$$SDO + HOH \rightarrow SDOH_2^+ + OH^-$$

Where SD is sawdust adsorbent

According to surface sorption by ions solids theory, the properties and effects of solids contact with water have to of with the sorption of solutes by solid surface. Surfaces in finely divided solids tend to have excess surface energy because of an imbalance of chemical forces among surface atoms, ions and molecules. Surface energy level may be lowered by a reduction in surface are. Normally this reduction is accomplished by aggregation of particles or by sorption of solutes species.

The relationship between pH and adsorption capacity can be elucidated in term of metal chemistry of solution and surface chemistry of sawdust (S. Hasan et al., 2000). The pH where maximum adsorption of dye takes place was related to first hydrolysis product of the organic dye. The exact nature and distribution of hydroxo complexes depends on the concentration of ligands which is the solution pH and on the soluble dye concentration (S. Hasan et al., 2000).

The highest adsorption capacity that lies between these pH values was due to the influence of pH on the surface adsorption characteristics of the sawdust. Furthermore, it is believed that the surface charge of the ash becomes negative as a result of deprotonation of surface functional groups with the increase in pH.

The relationship between pH and adsorption capacity that explained earlier was valid for this case. At maximum adsorption capacity (acidic medium), the coulombic attraction between positively charged dye ions and negatively charged sawdust would increase (S. Hasan et al., 2000). Nevertheless, at lower pH the surface of the adsorbent was surrounded by hydronium ions (H+), which prevented the dye ions from approaching the binding sites on the sorbent (K.K. Wong et al., 2003).

At high pH the capacity of the adsorbent gets recessed. The reason for the better adsorption capacity observed at low pH levels may be attributed to the larger number of H+ ions present, which in turn neutralize the negatively charged adsorbent surface, thereby reducing hindrance to the diffusion of organics at higher pH. The reduction in adsorption may be possible due to the abundance of OH-ions, causing increased hindrance to diffusion of organics ions. The hydroxide precipitation occurred at high pH and thus reduces the amount of free dye ions which can be binded to the sawdust (S. Hasan et al., 2000). The hydroxide precipitation occurred at high pH and thus reduces the amount of free dye ions which can be binded to the ash (S. Hasan et al., 2000).

5.5 Development of Adsorption's Isotherm

The adsorption isotherm is a relationship between adsorption capacity and residual concentration on an equilibrium basis. Adsorption isotherms are important for the description of how adsorbate (dye) will interact with sawdust and are critical in optimizing the use of sawdust as an adsorbent.

When the adsorption data was tested using equations (2.3) and (2.4), they best fitted to the Freundlich model as indicated by its relatively higher linear correlation coefficients. From Figure 4.7 itself, it can be seen that the adsorption fits Type I of isotherm.

In monolayer adsorption (Type I Isotherm) all the adsorbed molecules are in contact with the surface layer of the adsorbent. In multilayer adsorption the adsorption space accommodates more than one layer of molecules so that not all adsorbed molecules are in direct contact with the surface layer of the adsorbent. In a monolayer adsorption all the adsorbed dye molecules are in contact with the surface layer of the sawdust adsorbent. Whereas, in multilayer adsorption the adsorption space accommodates more than one layer of molecules so that not all adsorbed molecules are in direct contact with the surface layer of the adsorbent (Slejko, 1985).

5.5.1 Interpretation of Adsorption Isotherm

i. Data generation and treatment

The data generated from the adsorption isotherm depends on the measurement of residual adsorbate remaining in the organic dye solution. The concentration is measured as a gross value through UV absorbance. Data obtained from the adsorption test for removal of organic ye from aqueous solution is presented in Table 4.7.1.

After data points are plotted the graphical relationship between the adsorption capacity (x/m) and residual concentration (c) is developed. Inspection of the adsorption isotherm plot resulting

ii. Single or similar adsorbates

For a single component system, the plot of concentration versus adsorption capacity should produce a straight line plot following the Freundlich equation independent of whether gross or specific analytical methods are used.

iii. Isotherm slope

Useful information can be obtained by inspecting the slope of an isotherm plot. What can be predicted from shallow slope shown if Figure 4.9 is that the adsorbate removal per weight of sawdust is nearly equal at all equilibrium concentrations along the isotherm plot. The organic dye shows a high affinity for the sawdust adsorbent independent of equilibrium concentration.

5.5.2 Usefulness of Adsorption Isotherm

i. The adsorbability of a component or, in other words, its relative affinity for the adsorbent

ii. The weight pickup or the concentration of the adsorbate on the adsorbent. This is expresses as weight of contaminant adsorbed per weight of adsorbent or in percentages.

iii. The degree of removal achievable as indicated by the equilibrium adsorbate concentration which remains unchanged with increasing adsorbent dosage. A constant concentration indicates a nonadsorbable component.

iv. Sensitivity to adsorbate concentration change as indicated by relative steepness of the isotherm line. Based on a log-log plot data, a steep line would mean that, for a small change in concentration, the adsorption capacity changes drastically.

CHAPTER 6

6.0 CONCLUSION

The research on adsorption of organic dye from aqueous solution by sawdust adsorbent had been successfully conducted. There are five parameters that have been studies which are effect of contact time, initial dye concentration, adsorbent's dose, adsorbent's particle size and pH of organic dye solution. The experiments were done under batch mode. Continuous adsorption could not been studied due to time and facilities constraints. After the investigation of sawdust characteristic as an adsorbent has completed, the adsorption isotherm is then to be studied.

This experiment and research will exposed student to the new development of removal of organic dye from aqueous solution/wastewater using adsorption by low-cost-adsorbent (Sawdust) and at the same time gain some knowledge on wastewater treatment. This research has been completely done as the time frame is followed.

The study showed that the adsorbent sawdust had higher adsorption capacity of 91% of dye removal within two hours of operation without any pretreatment. The shorter operating time proves that it can be very economical to use sawdust as an adsorbent, particularly for the industries that are looking for ways to cut down the operational cost. The Methylene Blue was effectively decolorized (89%-93%) by the optimum dose of 2.0g-5.0g. The adsorption system studied was proved to fit the Freundlich Isotherm model. By identifying the adsorption isotherm, it will be easier to predict the nature of sawdust acting as an adsorbent.

Removal of organic dye using sawdust was found to be favorable and hence, sawdust could be considered as alternatives to commercial adsorbents i.e. activated carbon for the treatment of dye/textile effluents, especially for the removal of colors.

CHAPTER 7

7.0 RECOMMENDATIONS FOR FUTURE PROJECT WORK

7.1 Continuous Adsorption

Continuous adsorption or column experiment should be carried out since it is relatively close to the scenario in the existing industrial waste water treatment plant. In industrial granular activated carbon column generally has greater size in term of deep and column diameter. In the laboratories, smaller scale equipment can be used in order to stimulate actual operating conditions accurately and by reducing the flow rates proportionally. The suggested experimental setup is illustrated as in Figure 7.1 below.

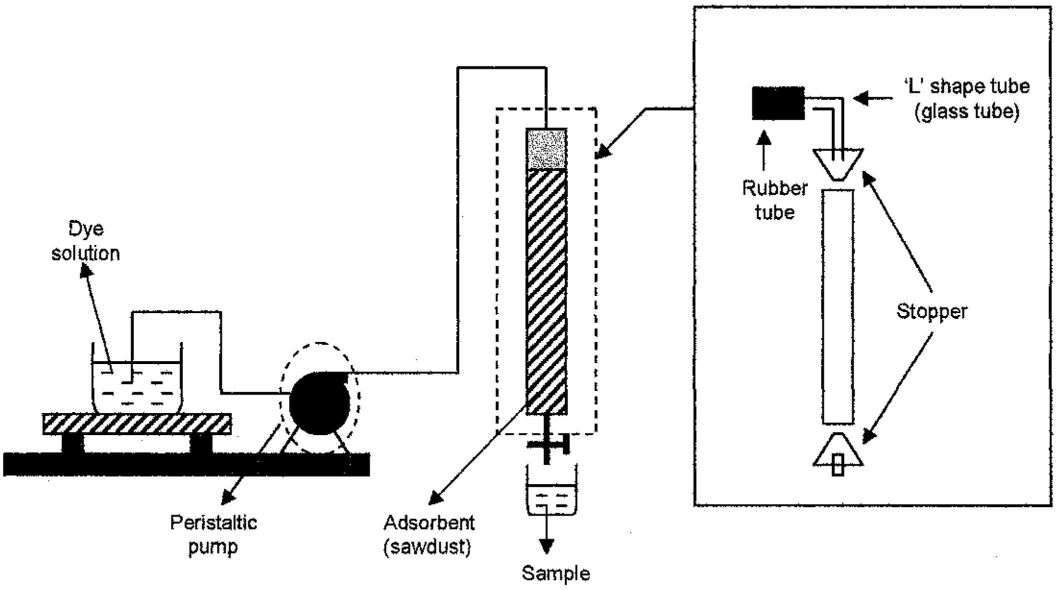

Figure 7.1: The Laboratory Column Experiment

7.2 Exploration of other Parameters

Generally, regardless whether it is a chemical or physical process, many parameters are considered in achieving its optimum operating condition. Through this research, the adsorption isotherm and the effect of contact time, initial dye concentration, adsorbent's dose, adsorbent's particle size and pH have been explored and determined. However, it will also be useful for the students in future to further explore other parameters or characteristics such ad the pore volume, pore distribution, specific area (BET analyzer), packing density DP, compressive strength, abrasion resistance, temperature or even pressure. A few of the more important physical characteristics of adsorbent will be highlighted here.

7.2.1 Pore Volume and Diameter Distribution

Both of these characteristics can be determined by helium and mercury porosimeters and by nitrogen adsorption (or desorption). Because of its small size, helium can access all the voids and is used to determine the structural density DST of the solid by considering that its adsorption is negligible.

A mercury porosimeter is used to measure the volume of mercury penetrating in the solid versus the hydrostatic pressure, and thereby to calculate the grain density DG and the skeleton density DSK.

7.2.2 Operating Pressure

At atmospheric pressure, mercury (adsorbate) fills only the interparticle volume (measurement of grain density). When pressure is increased, it penetrates into smaller pores according to the equation below:

$$r = -\frac{2\sigma\cos\theta}{P} \qquad (7.1)$$

Where:

r = Radius of the pore

P = Pressure

σ = Interfacial tension (0.48 N/m)

θ = Angle of Contact (180°C)

This equation can be reduces to $r = 9600/P$ with r in nm and P in bar. For example, for an intrusion pressure of 4200 bar, the highest normally used, the equivalent pore radius is 2.4 nm. In this way, the macro- and meso-pore volume and the skeleton density of the solid are measured. Such relation can also be applied to other types of adsorbate (Sawdust) besides mercury.

7.2.3 Size Distribution of Pores

Adsorption (or desorption) of nitrogen at 77 K can be used to characterize the size distribution of the pores between 10 and 150 Å via the capillary condensation phenomenon, on the basis of the Kelvin equation. The adsorption isotherm is also used to determine the Dubinin volume and the specific are (BET method) (Gregg, 1982).

Sometimes a more detailed characterization of the micro pore size and volume is necessary. Here adsorption measurement by probe molecules of different sizes is used. Pores of adsorbent are often classified according to their diameter as macropores (>500 Å), mesopores (20 to 500 Å) and micropores (<20 Å).

7.2.4 Operating Temperature

Research on the effect of operating temperature to adsorption effectiveness is also an important aspect to explore. This can simply be done by conducting the experiment at different temperature. The amount of adsorbate adsorbed will be the indication of the effectiveness.

7.3 Activation of Sawdust

Although sawdust is a readily available base adsorbent material, the potential of quaternized sawdust as a dye adsorbent has not been fully demonstrated. Thus, instead of using sawdust without any pre-treatment (student's research), it would be interesting to see the difference in removal of color if the sawdust is to be activate/quaternized first before using it as an adsorbent. The characteristics of quaternized sawdust adsorption on color are to be studied and compared with plain sawdust (without any pre-treatment, save the removal of moisture).

Suggested quaternized sawdust preparation (Hacgyu Lim, 2003):
The raw sawdust was pretreated with an aqueous solution of NaOH at room temperature in a reactor, and the quaternization reagent; N-(3-chloro-2-hydroxypropyl) trimethylammoniumm chloride (CHMAC) was added to synthesize the quaternized sawdust. The reaction product was washed with distilled water and vacuum-dried at 40C for total of 24 hours. The chemical compositions of sawdust are mainly lignin, cellulose and hemicelluloses. Lignin which originally constituted 25% of raw sawdust was removed by above NaOH pretreatment. The quaternized sawdust is then ready to be used.

7.4 Cost Analysis

Cost analysis comparing between activated carbon and sawdust as an adsorbent can be done to further justify the possibility of using sawdust as a low-cost biodegradable color adsorbent.

REFERENCES

[1] Frank L. Slejko, 1985, *"Adsorption Technology: A Step-by-Step Approach to Process Evaluation"*, New York, Marcel Dekker, Inc.

[2] Hasan S., Hashim, M.A. and Gupta, B.S., 1999, *"Adsorption of Ni $(SO)_4$ on Malaysian Rubber-Wood Ash"*, Bioresource Technology **72: 153-158**

[3] Wong K.K., Lee C.K., Low K.S., Haron M.J., 2003, *"Removal of Cu and Pb by Tartaric Acid Modified Rice Husk from Aqueous Solution"* , Chemosphere **50: 23-28**

[4] McKay G. 1995, *"Switching Use of Adsorbents for the Removal of Pollutants from Wastewaters"*, USA, CRC Press.

[5] J.D. Seader and Ernest J. Henley, 1998, *"Separation Process Principles"*, John Wiley

[6] Ira N. Levine, 2002, *"Physical Chemistry"*, Fifth Edition, McGraw-Hill International Edition

[7] Christie J. Geankoplis, 1993, *"Transport Processes and Unit Operations"*, Third Edition, Prentice Hall PTR

[8] S. Lowell and Joan E. Shields, 1991, *"Powder Surface Area and Porosity"*, Third Edition, CHAPMAN & HALL

[9] József Tóth, 2002, *"Adsorption: Theory, Modeling and Analysis "*, Marcel Dekker, Inc, **Vol. 107**

[10] Md. Zahangir Alam and Suleyman Aremu Muyibi, 2003, "*Removal of Organic Dye from Aqueous Solution by Adsorption on Sawdust*", Proceedings of International Conference On Chemical and Bioprocess Engineering, Universiti Malaysia Sabah, Kota Kinabalu

[11] Hacgyu Lim, Sukjae Kim, Sang-Myung Lee, Jangwoong Byun, Sunjong Ryoo, Yoon-Sik Lee and Jeyong Yoon, 2003, "*Removal of Two Reactive Dyes by Quaternized Sawdust*", J. Ind. Eng. Chem, **Vol.9, No. 4**

[12] I. A. Rahman and B. Saad, 2003, "*Utilization of Guava Seeds as a source of Activated Carbon for Removal of Methylene Blue from Aqueous Solution*", Malaysian Journal of Chemistry, **Vol. 5, No. 1, (8-14)**

APPENDIX

i. Compilation of Experimental Condition and Results

Date	Contact Time (Hour)	Initial Dye Concentration (mg/L)	Adsorbents' Dose (g)	Particle Size (µm)	pH
Exp_1	**1**	100	3.0	1000	6.0
Exp_1	**2**	100	3.0	1000	6.0
Exp_1	**3**	100	3.0	1000	6.0
Exp_1	**4**	100	3.0	1000	6.0
Exp_1	**8**	100	3.0	1000	6.0
Exp_1	**16**	100	3.0	1000	6.0
Exp_2	3	**50**	3.0	1000	6.0
Exp_2	3	**100**	3.0	1000	6.0
Exp_2	3	**150**	3.0	1000	6.0
Exp_2	3	**200**	3.0	1000	6.0
Exp_2	3	**300**	3.0	1000	6.0
Exp_3	3	100	**1.0**	1000	6.0
Exp_3	3	100	**2.0**	1000	6.0
Exp_3	3	100	**3.0**	1000	6.0
Exp_3	3	100	**5.0**	1000	6.0
Exp_4	3	100	3.0	**<250**	6.0
Exp_4	3	100	3.0	**250**	6.0
Exp_4	3	100	3.0	**500**	6.0
Exp_4	3	100	3.0	**1000**	6.0
Exp_5	3	100	3.0	500	**3.0**
Exp_5	3	100	3.0	500	**5.0**
Exp_5	3	100	3.0	500	**6.0**
Exp_5	3	100	3.0	500	**8.0**

Experiment 1

Constant Parameter:

Initial Dye Concentration: 100 mg/L

Adsorbents' Dose: 3.0 g

Particle Size: 1000 μm

pH: 6.0

Varied Parameter;

Contact Time: 1, 2, 3, 4, 8, 16 hours(s)

Initial Dye Concentration : 100 mg/L			
Adsorbent dose : 3.0 g			
Particle Size : 1000 μm			
pH : 6.0			
Contact Time (hour)	**Concentration after Adsorption**		
	1st Reading	**2nd Reading**	**Average Reading**
1	12.939	12.911	12.925
2	12.672	12.653	12.663
3	8.378	8.371	8.375
4	8.337	8.336	8.337
8	8.325	8.327	8.326
16	8.319	8.325	8.322

Experiment 2

Constant Parameter:

Contact Time: 3 hours

Adsorbents' Dose: 3.0 g

Particle Size: 1000 μm

pH: 6.0

Varied Parameter;

Initial Dye Concentration: 50, 100, 150, 200 and 300 mg/L

Contact Time : 3 hour			
Adsorbent dose : 3.0 g			
Particle Size : 1000 μm			
pH : 6.0			
Initial Dye Concentration (mg/L)	**Concentration after Adsorption**		
	1st Reading	**2nd Reading**	**Average Reading**
50	7.877	7.874	7.876
100	8.378	8.371	8.375
150	9.131	9.128	9.130
200	11.608	11.586	11.597
300	25.201	25.378	25.290

Experiment 3

Constant Parameter:

Contact Time: 3 hours

Initial Dye Concentration: 100 mg/L

Particle Size: 1000 µm

pH: 6.0

Varied Parameter;

Adsorbents' Dose: 1.0, 2.0, 3.0 and 5.0 g

Initial Dye Concentration : 100 mg/L			
Contact Time : 3 hour			
Particle Size : 1000 µm			
pH : 6.0			
Adsorbent Dose (gram)	**Concentration after Adsorption**		
	1st Reading	**2nd Reading**	**Average Reading**
1.0	35.653	35.653	35.653
2.0	8.933	8.931	8.932
3.0	8.378	8.371	8.375
5.0	7.983	7.984	7.984

Experiment 4

Constant Parameter:

Contact Time: 3 hours

Initial dye Concentration: 100 mg/L

Adsorbents' Dose: 3.0 g

pH: 6.0

Varied Parameter;

Particle Size: <250, 250, 500 and 1000 µm

Initial Dye Concentration : 100 mg/L			
Contact Time : 3 hour			
Adsorbent Dose : 3.0 g			
pH : 6.0			
Particle Size (µm)	**Concentration after Adsorption**		
	1st Reading	**2nd Reading**	**Average Reading**
<250	5.844	5.845	5.845
250	5.889	5.895	5.892
500	6.732	6.738	6.735
1000	8.378	8.371	8.375

Experiment 5

Constant Parameter:

Contact Time: 3 hours

Initial dye Concentration: 100 mg/L

Adsorbents' Dose: 3.0 g

Particle Size: 500 µm

Varied Parameter;

pH value: 3.0, 5.0, 6.0 and 8.0

Initial Dye Concentration : 100 mg/L			
Contact Time : 3 hour			
Adsorbent Dose : 3.0 g			
Particle Size : 500 µm			
pH	**Concentration after Adsorption**		
	1st Reading	**2nd Reading**	**Average Reading**
3.0	10.505	10.505	10.505
5.0	8.4618	8.455	8.458
6.0	8.378	8.371	8.375
8.0	8.379	8.383	8.381

ii. Percentage of Color Removal

$$\%ofColor\,Removal = \frac{InitialDyeConcentration - ConcentrationAfterAdsorption}{InitialDyeConcentration} \times 100$$