

UNIVERSITI MALAYA

ORIGINAL LITERARY WORK DECLARATION

Name of Candidate: Tiong Khing Gueok

(I.C/Passport No: 900517138146)

Registration/Matric No: SGH130011

Name of Degree: MASTER OF TECHNOLOGY (ENVIRONMENTAL MANAGEMENT)

Title of Project Paper/Research Report/Dissertation/Thesis ("this Work"):

Adsorption Studies of Methylene Blue using Selected agro-wastes as Low Cost Adsorbents

Field of Study:

I do solemnly and sincerely declare that:

- (1) I am the sole author/writer of this Work;
- (2) This Work is original;
- (3) Any use of any work in which copyright exists was done by way of fair dealing and for permitted purposes and any excerpt or extract from, or reference to or reproduction of any copyright work has been disclosed expressly and sufficiently and the title of the Work and its authorship have been acknowledged in this Work;
- (4) I do not have any actual knowledge nor do I ought reasonably to know that the making of this work constitutes an infringement of any copyright work;
- (5) I hereby assign all and every rights in the copyright to this Work to the University of Malaya ("UM"), who henceforth shall be owner of the copyright in this Work and that any reproduction or use in any form or by any means whatsoever is prohibited without the written consent of UM having been first had and obtained;
- (6) I am fully aware that if in the course of making this Work I have infringed any copyright whether intentionally or otherwise, I may be subject to legal action or any other action as may be determined by UM.

Candidate's Signature

Date

Subscribed and solemnly declared before,

Witness's Signature Date

Name:

Date

Designation:

ABSTRACT

Today, there are a lot of dyes available commercially. Effluent discharge from textile industries to neighbouring water bodies is currently causing significant health problem. Synthetic dyes used in textile industries, if not treated prior to its disposal can enter our water systems and cause pollution. The study was performed using different agro-wastes namely kenaf (FH 990), banana stem, and sugarcane bagasse to produce low cost industrial adsorbents. Adsorption method was applied in removing methylene blue (MB) dye from aqueous solution. The aims of this study are to investigate the adsorption capacity under optimal parameters and compare the cost effectiveness together with the calorific value of adsorbents before and after the treatment. The characteristics of wastewater effluent was examined and the characteristics of adsorbents were determined by using FTIR, FESEM and BET analysis. The experiments were conducted in single adsorbate system by batch technique to determine the optimum condition for higher adsorbency. The determination of optimum conditions was carried out in different pH (2 - 10), agitation time (5- 300 minutes), initial concentration (10 – 70 mg/L) and temperature (20 - 100 °C). The adsorption isotherms of Langmuir and Freundlich were employed to examine the equilibrium adsorption data. Thermodynamic parameters such as ΔH° , ΔS° and ΔG° were also calculated. The optimal adsorption was achieved by banana stem with the adsorption capacity of 68.47 mg/L and maximum removal percentage of 97.82 % for initial methylene blue concentration of 70 mg/L. The adsorption of methylene blue can be well describes by Freundlich isotherm and the adsorption process was found to be exothermic and spontaneous for all the adsorbents. Thus, all results indicated that the selected agro-wastes could be employed as an effective new low cost adsorbent for the removal of textile dyes from aqueous solutions.

ABSTRAK

Kini, terdapat banyak pewarna yang boleh didapati secara komersial. Pembuangan efluen dari industri tekstil ke dalam sistem pengairan telah menyebabkan masalah kesihatan yang ketara. Pewarna sintetik yang digunakan dalam industri tekstil boleh menyebabkan pencemaran jika tidak dirawat sebelum dilepaskan ke dalam sistem air. Kajian ini dilakukan dengan menggunakan sisa pertanian terpilih iaitu kenaf (FH 990), batang pisang dan hampas tebu untuk menghasilkan penjerap perindustrian kos rendah. Kaedah penjerapan telah digunakan untuk menyingkirkan pewarna metilena biru (MB) daripada larutan cecair. Tujuan kajian ini adalah untuk mengkaji kapasiti penjerapan di bawah parameter optimum dan membandingkan keberkesanan kos bersama dengan nilai kalori adsorben sebelum dan selepas rawatan. Ciri-ciri air sisa efluen telah dikaji dan ciri-ciri penjerap ditentukan dengan menggunakan analisis FTIR, FESEM dan BET. Kajian ini telah dijalankan dengan menggunakan sistem penjerapan berkala untuk menentukan keadaan yang optimum untuk penyerapan yang lebih tinggi. Rawatan ini termasuk penentuan keadaan optimum pada pH yang berbeza (2 - 10), masa pergolakan (5-300 minit), kepekatan awal (10 - 70 mg / L) dan suhu (20 - 100 °C). Sesuhu penjerapan Langmuir dan Freundlich telah digunakan untuk mengkaji data penjerapan pada keseimbangan. Parameter termodinamik seperti ΔH° , $^\circ\Delta S$ dan ΔG° juga telah dikira. Penjerapan optimum telah diperolehi dengan menggunakan batang pokok pisang dengan kapasiti penjerapan 68.47 mg/L dan kadar penjerapan maksimum 97.82% bagi kepekatan metilena biru sebanyak 70 mg/L. Penjerapan metilena biru dapat diterangkan dengan isoterma Freundlich di mana penjerapan didapati adalah proses eksotermik dan spontan untuk semua bahan penjerap. Keputusan menunjukkan bahawa sisa pertanian boleh digunakan sebagai bahan penjerap baru yang berkesan untuk penyingkiran pewarna tekstil dari larutan cecair dengan kos yang rendah.

ACKNOWLEDGEMENT

I am grateful and would like to express my gratitudes to my supervisors Dr. Fauziah Shahul Hamid and Dr. Sharifah Mohamad for their invaluable guidance, continuous encouragement and constant support for making this research possible. I appreciate their guidance which enabled me to develop an understanding of this research thoroughly. Without their advice and assistance it would be difficult to complete.

I would like to offer my special thanks to National Kenaf and Tobacco Board (IKTN), Malacca for their support in providing kenaf (FH-990) samples and ideas for this research. My extended thanks to all lab assistants and seniors of Central Analytical Lab, Environmental Microbiology Lab and Postgraduate Environmental Lab, Faculty of Science, University Malaya for their help to accomplished this research by offering technical support and knowledge sharing.

I wish to acknowledge the help provided by my friends to finish this research. Finally, my heartfelt thanks to my lovely parents who spends their time years after years to grow me up and encourage me with moral and spiritual supports throughout my studies.

TABLE OF CONTENT

Content	PAGE
ABSTRACT	II
ABSTRAK	III
ACKNOWLEDGEMENT	IV
CONTENT	V
LIST OF FIGURES	IX
LIST OF PLATES	XI
LIST OF TABLES	XII
LIST OF SYMBOLS AND ABBREVIATIONS	XIV
CHAPTER 1 INTRODUCTION	1
1.1 Background of Study	1
1.1.1 Water Crisis	1
1.1.2 Usage of Dyes in Industry	2
1.1.3 Environmental Impacts of Dyes	3
1.1.4 Methods of Dye Removal	4
1.1.4.1 Chemical Methods	4
1.1.4.2 Biological Methods	4
1.1.4.3 Physical Methods	5
1.2 Problem Statement	6
1.3 Significance of Study	7
1.4 Objectives of Study	7
CHAPTER 2 LITERATURE REVIEW	8
2.1 Textile Industry in Malaysia	8
2.2 Environmental Aspects	11
2.3 Wastewater Treatment in Textile Industry	13
2.4 Colorant	14

2.5	Dye	14
2.6	Classification of Dyes	16
2.6.1	Acid Dyes	16
2.6.2	Premetalized Acid Dyes	16
2.6.3	Mordant Dyes (Chrome Dyes)	17
2.6.4	Cationic Dyes (Basic Dyes)	17
2.6.4.1	Methylene Blue	17
2.6.5	Direct Dyes (Substantive Dyes)	18
2.6.6	Disperse Dyes	18
2.6.7	Naphthol Dyes	19
2.6.8	Reactive Dyes	19
2.6.9	Sulfur Dyes	19
2.6.10	Vat Dyes	19
2.7	Existing Approaches of Dye Removal	21
2.7.1	Biodegradation	22
2.7.2	Coagulation-Flocculation	22
2.7.3	Adsorption by Activated Carbon	23
2.7.4	Ozone Treatment	25
2.7.5	Electrochemical Processes	27
2.7.6	Reverse Osmosis	27
2.7.7	Nanofiltration	28
2.7.8	Ultrafiltration-Microfiltration	29
2.7.9	Ion Exchange	30
2.7.10	Fenton's Reagent ($\text{H}_2\text{O}_2\text{Fe}^{2+}$ salts) Treatment	30
2.7.11	Photochemical (H_2O_2 -UV radiation)	31
2.7.12	Photocatalytical (TiO_2 -UV radiation)	31
2.8	Adsorption	33
2.8.1	Physisorption	34
2.8.2	Chemisorption	35
2.8.3	Adsorbent	36
2.8.4	Adsorption Mechanism	37
2.8.5	Factors Affecting Adsorption	39
2.9	Previous Studies of Adsorption using Agricultural Waste Products	42
2.9.1	Characteristics of Agricultural Wastes as Adsorbents	42

2.9.2	Studies of natural form of agricultural waste adsorbents	43
CHAPTER 3	MATERIALS AND METHODS	47
3.1	Characteristics of Textile Effluent	47
3.1.1	Biological Oxygen Demand (BOD)	47
3.1.1.1	Reagents and Standards	47
3.1.1.2	Preparation of Solution	48
3.1.1.2	Sample Preparation	48
3.1.2	Chemical Oxygen Demand (COD)	48
3.1.3	Total Dissolved Solids (TDS)	48
3.1.4	Total Suspended Solids (TSS)	48
3.1.5	pH	49
3.1.6	Total Solid	49
3.1.7	Turbidity	49
3.2	Preparation of Adsorbent	49
3.3	Characteristics of Adsorbents	49
3.4	Adsorption Studies	50
3.4.1	Effect of pH	50
3.4.2	Determination of Optimum Agitation Time	50
3.4.3	Effect of Initial Concentration	51
3.4.4	Effect of Temperature	51
3.5	Isotherms	51
3.5.1	Removal Efficiency of Adsorbents	51
3.5.1	Adsorption Capacity	52
3.5.2	Langmuir Isotherm	52
3.5.3	Freundlich Isotherm	53
3.6	Adsorption Thermodynamic	54
3.7	Determination of Calorific Value Bomb Calorimeter	54
3.7.1	Calculation of Temperature Rise	55
3.7.2	Calculation of Gross Heat of Combustion	56
CHAPTER 4	RESULTS AND DISCUSSIONS	57
4.1	Characteristics of Textile Effluent	57
4.1.1	Characteristics of Textile Effluent before the Treatment	57
4.1.2	Characteristics of Effluent after the Treatment	58

4.2	Characteristics of Adsorbent	62
4.2.1	FTIR (Fourier transform infrared spectroscopy) Analysis	63
4.2.2	Morphology Observation via FESEM (Field Emission Scanning Electron Microscope)	64
4.2.3	BET Surface Area Analysis of Agro-wastes	67
4.3	Adsorption Studies	68
4.3.1	Calibration Curve of Methylene Blue	68
4.3.2	Effect of pH	69
4.3.3	Determination of Optimum Agitation Time	70
4.3.4	Effect of Initial Concentration	72
4.3.5	Effect of Temperature	73
4.3.6	Maximum Adsorption Capacity under Optimum Condition	75
4.4	Isotherm Studies	76
4.4.1	Langmuir Isotherm	76
4.4.2	Freundlich Isotherm	79
4.5	Adsorption Thermodynamic	82
4.6	Calorific Value	84
4.7	Economic Feasibility	86
CHAPTER 5 CONCLUSION		88
REFERENCES		90
LIST OF PUBLICATIONS AND PAPERS PRESENTED		99

LIST OF FIGURES

NO.		PAGE
Figure 2.1	Examples of chromophore groups (Lam, 2005)	15
Figure 2.2	Structure of methylene blue (Cragon, 1999)	18
Figure 2.3	Coagulation-flocculation process	23
Figure 2.4	Activated carbon in different forms	25
Figure 2.5	Ozone treatment process	26
Figure 2.6	Components of reverse osmosis membrane	28
Figure 2.7	Types of materials that can be filtered by nanofiltration	29
Figure 2.8	Basic process of adsorption (Worch, 2012)	34
Figure 2.9	Mechanism of adsorption (Sharifah Nhatasha Syed Jaafar, 2006)	38
Figure 4.1	FTIR spectra of kenaf, banana stem and sugarcane bagasse	63
Figure 4.2	Calibration of methylene blue dye using various dye concentrations	68
Figure 4.3	Determination of optimum pH of adsorbents for methylene blue dye in 70 mg/L concentration	69
Figure 4.4	Determination of optimum agitation time for removing methylene blue dye	71
Figure 4.5	Determination of optimum initial concentration for methylene blue dye	72
Figure 4.6	Determination of optimum temperature of kenaf, banana stem and sugarcane bagasse for removing methylene blue dye	75
Figure 4.7	Maximum adsorption capacity of kenaf, banana stem and sugarcane Bagasse	76
Figure 4.8	Langmuir plot for MB dye by using kenaf	77

Figure 4.9	Langmuir plot for MB dye by using banana stem	78
Figure 4.10	Langmuir plot for MB dye by using sugarcane bagasse	78
Figure 4.11	Freundlich plot for MB dye using kenaf	80
Figure 4.12	Freundlich plot for MB dye using banana stem	80
Figure 4.13	Freundlich plot for MB dye using sugarcane bagasse	81
Figure 4.14	Van't Hoff plot for the estimation of thermodynamics parameters	83

LIST OF PLATES

NO.		PAGE
Plate 4.2	Field emission scanning electron microscopy for kenaf	65
Plate 4.3	Field emission scanning electron microscopy for banana stem	66
Plate 4.4	Field emission scanning electron microscopy for sugarcane bagasse	66

LIST OF TABLES

NO.		PAGE
Table 1.1	Dye loss as effluent for different dye-fiber systems (Shertate And Thorat, 2013; Chun, 2010)	2
Table 2.1	Malaysian made textile and apparel	9
Table 2.2	Malaysian exports of textiles and apparel by years (Malaysian Knitting Manufacturers Association, 2014)	10
Table 2.3	Specific pollutants from textile wet processing operations (Eglia, 2007)	12
Table 2.4	Application classes of dyes and their chemical types (Chun, 2010)	20
Table 2.5	Advantages and disadvantages of different wastewater treatment used in textile industry	32
Table 2.6	Comparison between physical and chemical adsorption (Sharifah Nhatasha Syed Jaafar, 2006)	35
Table 4.1	Characteristics of textile effluent	57
Table 4.2	Characteristics of textile effluent before and after treatment	59
Table 4.3	Percentage reduction of pollutant in textile effluent	62
Table 4.4	BET surface area characterization	67
Table 4.5	Langmuir isotherm constants and regression data for adsorption of methylene blue	77
Table 4.6	Freundlich isotherm constants and regression data for adsorption of methylene blue	82

Table 4.7	Thermodynamics parameters for kenaf, banana stem and sugarcane bagasse	82
Table 4.8	Calorific value before and after the treatment for kenaf, banana stem and sugarcane bagasse	84
Table 4.9	Calorific value of agro wastes (AZUEZ, 2012)	85
Table 4.9	Cost of using kenaf, banana stem and sugarcane bagasse as adsorbent	86

LIST OF SYMBOLS AND ABBREVIATIONS

mL	Millilitre
cm ⁻¹	unit used for wavenumber
%	Percentage
mg/L	Milligram per litre
L/mg	Litre per milligram
J K ⁻¹ mol ⁻¹	Gas constant
ΔG°	Gibbs free energy change
ΔS°	Entropy change
ΔH°	Enthalpy change
nm	Nanometre
μm	Micrometre
Kj/mol	Kilojoule per mole
K	Kelvin
°C	Degree Celsius
g	Gram
L	Litre
mm	millilitre
min	minute
g/L	Gram per litre
mg/g	Milligram per gram
R ²	Linear correlation
mV	Megavolt

m^3/mol	Metre square per mole
cm	Centimetre
atm	Atmospheric pressure
FAU	Formazin Attenuation Unit
cm^3	Centimetre square
Å	Angstrom
m^2/g	Metre square per gram
cm^2/g	Centimetre square per gram
K_F	Freundlich constant
n	Freundlich exponent related to adsorption intensity
Q_m	Maximum amount of adsorption
b	Adsorption equilibrium constant
MIDA	Malaysia Industrial Development Authority
Matrade	Malaysia External Trade Development Corporation
NaOH	Sodium hydroxide
H_2O_2	Hydrogen peroxide
AOX	Adsorbable organic halides
IUPAC	International Union of Pure and Applied Chemistry
MB	Methylene Blue
LMB	Leukomethylene blue
COD	Chemical oxygen demand

BOD	Biological oxygen demand
RO	Reverse osmosis
DO	Dissolved oxygen
rpm	Rate per minute
FTIR	Fourier transform infrared spectroscopy
UV-VIS	Visible and Ultraviolet Spectroscopy
TDS	Total dissolved solids
TSS	Total suspended solids
FESEM	Field Emission Scanning Electron Microscopy