

**REMOVAL OF METHYLENE BLUE BY BENTONITE BASED  
ADSORBENT FILM: CHARACTERIZATIONS AND PERFORMANCES  
STUDY**

**by**

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**Thesis submitted in fulfillment of the  
requirements for the degree of  
Master of Science**

**September 2016**

## ACKNOWLEDGEMENTS

In the name of ALLAH S.W.T, the most gracious and merciful, Alhamdulillah, I am able to finish my research and thesis on time without any problems. Thanks for His blessing, the health and easiness along my research journey. All come from ALLAH S.W.T.

First and foremost I would like to thank you to my beloved parents, Tuan Zarawi bin Tuan Jusoh and Tengku Fariza binti Che Ku Zanggi, and all my family members for their endless support, prays and encouragement throughout my study. They are my inspirations.

I would like to express my deepest gratitude to my supervisor, Dr. Suzylawati Ismail, who helped me a lot in this research. I am grateful to her for her academic guidance and positive criticism which helped me improve my skills and knowledge of this research study. I would like to thank you for her encouragement and motivation throughout this research study that helped me finish my study without any hurdles.

I would also like to acknowledge all the academic and non-academic staff of School of Chemical Engineering, Universiti Sains Malaysia for their assistance and support especially to non-academic staff of Process Control Laboratory and Analytical Laboratory. They taught and helped me a lot during my research.

Special thanks goes to my friends and all the members of Process Control Laboratory and Membranes Technology Development Centre (MTDC) with whom I worked during my research study for their advice and moral support. Finally, not forget to Ministry of Higher Education for their financial support paying my study fees. To those that I might have forgotten to mention, I owe you my deepest thanks and gratitude.

*Tuan Syahiira binti Tuan Zarawi*

*April 2016*

## TABLE OF CONTENTS

	<b>Page</b>
<b>ACKNOWLEDGMENTS</b>	<b>ii</b>
<b>TABLE OF CONTENTS</b>	<b>iv</b>
<b>LIST OF TABLES</b>	<b>ix</b>
<b>LIST OF FIGURES</b>	<b>xi</b>
<b>LIST OF PLATES</b>	<b>xiii</b>
<b>LIST OF ABBREVIATIONS</b>	<b>xiv</b>
<b>LIST OF SYMBOLS</b>	<b>xv</b>
<b>ABSTRAK</b>	<b>xvii</b>
<b>ABSTRACT</b>	<b>xix</b>
<b>CHAPTER ONE : INTRODUCTION</b>	
1.1 Textile Industry	1
1.2 Water Pollution	2
1.3 Environment and Health Impact of Dye	3
1.4 Current Practice of Textile Wastewater Treatment	4
1.5 Problem Statement	6
1.6 Research Objectives	7
1.7 Scope of Study	8
1.8 Organizations of The Thesis	9
<b>CHAPTER TWO : LITERATURE REVIEW</b>	
2.1 Dyes	11

2.2	Technology for Colored Wastewater Treatment	14
2.2.1	Biological Treatment	16
2.2.2	Chemical Treatment	18
2.2.3	Physical Treatment	20
2.3	Adsorption	21
2.4	Adsorbent	23
2.5	Bentonite	25
2.6	Acid Activation Bentonite	26
2.7	Adsorbent Coating	28
2.8	Adsorptive Membrane	30
2.9	Polysulfone and 1-Methyl-2-Pyrrolidon	31
2.10	Adsorption Isotherm	32
2.10.1	Langmuir Isotherm	32
2.10.2	Freundlich Isotherm	34
2.10.3	Temkin Isotherm	34
2.11	Adsorption Kinetic	35
2.11.1	Pseudo-first Order	36
2.11.2	Pseudo-second Order	36
2.12	Adsorption Thermodynamic	37

### **CHAPTER THREE : METHODOLOGY**

3.1	Materials	41
3.2	Calibration Curve	42
3.3	Formulation and Fabrication of Adsorbent Film	42
3.3.1	Preparation of Acid Activated Bentonite	42

3.3.2	Preparation of Adsorbent Film	43
3.3.3	Screening of Adsorbent Film Formulation	45
3.3.3.1	Different Types of Adsorbent	45
3.3.3.2	Different Adsorbent Loading	46
3.4	Characterization Studies	46
3.4.1	Surface Morphology	47
3.4.2	Surface Area	47
3.4.3	Particle Size of Adsorbent	47
3.4.4	Zeta Potential	48
3.4.5	Contact Angle	48
3.4.6	Pore Size Evaluation	49
3.5	Performance Evaluation	49
3.5.1	Effect of Initial Dye Concentration	49
3.5.2	Effect of Temperature	50
3.5.3	Effect of pH	50
3.5.4	Effect of Different Types of Dye	51
3.5.5	Reusability	51
3.6	Adsorption Isotherm	53
3.7	Adsorption Kinetic	55
3.8	Adsorption Thermodynamic	56

## **CHAPTER FOUR : RESULT AND DISCUSSION**

4.1	Formulation and Fabrication of Adsorbent Film	58
4.1.1	Effect of Different Types of Adsorbent	58
4.1.2	Effect of Adsorbent Loading	61

4.2	Characterization Studies	63
4.2.1	Surface Morphology	63
4.2.2	Surface Area of Adsorbent	67
4.2.3	Particle Size of Adsorbent	68
4.2.4	Zeta Potential	68
4.2.5	Contact Angle	69
4.2.6	Pore Size Evaluation	70
4.3	Performance Evaluation	71
4.3.1	Effect of Initial Dye Concentration	72
4.3.2	Effect of Temperature	73
4.3.3	Effect of pH	74
4.3.4	Effect of Different Types of Dye	76
4.3.5	Reusability	78
4.4	Adsorption Isotherm	79
4.5	Adsorption Kinetic	82
4.6	Adsorption Thermodynamic	89
<b>CHAPTER FIVE : CONCLUSION AND RECOMMENDATIONS</b>		
5.1	Conclusion	92
5.2	Recommendations	94
<b>REFERENCES</b>		95

## **APPENDICES**

APPENDIX A : Fifth schedule of Environmental Quality (Industrial Effluent)

Regulation 2009. Acceptable conditions for discharge of industrial effluent or mixed effluent of standards A and B

APPENDIX B : Calibration curve of (a) Methylene Blue, (b) Congo Red (c)

Direct Yellow 8 and (d) Reactive Brilliant Blue

## LIST OF TABLES

	Page	
Table 2.1	Classification of dyes based on chemical structure	12
Table 2.2	Classification of dyes based on application	13
Table 2.3	Advantages and disadvantages of current wastewater treatment	15
Table 2.4	Differences between physisorption and chemisorption.	23
Table 3.1	List of chemicals and materials used in experiment	41
Table 4.1	Surface area of raw bentonite and AAB	67
Table 4.2	Particle size analysis of raw bentonite and AAB	68
Table 4.3	Zeta potential of raw bentonite and AAB	69
Table 4.4	Contact angle of AAB film	69
Table 4.5	Pore size of adsorbent film before and after dye adsorption	71
Table 4.6	Adsorption isotherm parameters for Methylene Blue adsorption by AAB film	81
Table 4.7	Pseudo-first order and Pseudo-second order kinetic parameters for the Methylene Blue adsorption by AAB film at 30 °C	86
Table 4.8	Pseudo-first order and Pseudo-second order kinetic parameters for the Methylene Blue adsorption by AAB film at 50 °C	87
Table 4.9	Pseudo-first order and Pseudo-second order kinetic parameters for the Methylene Blue adsorption by AAB film at 70 °C	88

Table 4.10 Thermodynamic parameters for Methylene Blue adsorption by AAB film 90

## LIST OF FIGURES

	Page
Figure 1.1 Colored wastewater treatment plant by a) Siang Poh Knitting Sdn. Bhd (b) M & V III Co., LTD Wastewater Treatment Plant and (c) Tack-Fat Garment Wastewater Treatment Plant	5
Figure 2.1 Illustration of (a) Adsorption process and (b) Desorption process	21
Figure 3.1 Flow chart of research plan	40
Figure 4.1 Percentage removal of Methylene Blue at different type of adsorbent film at 30°C with 100 mg/L initial concentration of MB	59
Figure 4.2 Performance of adsorbent film with different weight of adsorbent at 30°C with 100 mg/L initial concentration of MB	62
Figure 4.3 Surface morphology of adsorbent film with (a) raw bentonite (b) acid activated bentonite and (b) acid activated bentonite after adsorption of methylene blue with 5000x magnification	65
Figure 4.4 Surface morphology of adsorbent film with (a) raw bentonite (b) acid activated bentonite and (b) acid activated bentonite after adsorption of methylene blue with 3000x magnification	66
Figure 4.5 Image of the contact angle of distilled water on the (a) front surface of AAB film and (b) back surface of the AAB film	70

Figure 4.6	Percentage removal of Methylene Blue on different initial concentration at 30°C	72
Figure 4.7	Percentage removal of Methylene Blue on different temperature with 100 mg/L initial concentration of MB	73
Figure 4.8	Percentage removal of Methylene Blue on different pH at 30°C with 100 mg/L initial concentration of MB	75
Figure 4.9	Percentage removal of Methylene Blue on different types of dye at 30°C with 100 mg/L initial concentration of each dye	77
Figure 4.10	Cycle of AAB film at 30°C with 100 mg/L initial concentration of MB	78
Figure 4.11	Adsorption isotherms of MB on AAB film (a) Langmuir (b) Freundlich and (c) Temkin isotherm at temperature 30, 50 and 70 °C	80
Figure 4.12	$R_L$ against $C_0$	82
Figure 4.13	Pseudo-first order at (a) 30 °C, (b) 50 °C and (c) 70 °C	83
Figure 4.14	Pseudo-second order at (a) 30 °C, (b) 50 °C and (c) 70 °C	84
Figure 4.15	Plots of ' $\ln k_L$ ' versus $1/T$ for Methylene Blue removal by AAB film	89
Figure 4.16	Plots of ' $\ln k_2$ ' versus $1/T$ for Methylene Blue removal by AAB film	90

## LIST OF PLATES

	Page
Plate 3.1 Powder of (a) raw bentonite (b) activated bentonite	43
Plate 3.2 Ingredients used for the production of adsorbent film solution.	44
Plate 3.3 Method of adsorbent film fabrication (a) Adsorbent film solution being casted by using film applicator (b) Adsorbent film soaked in distilled water and (c) Adsorbent film after being dried	45
Plate 4.1 Adsorbent film after and before adsorption of Methylene Blue dye. Adsorbent film with (a) raw bentonite and (b) activated bentonite	60
Plate 4.2 Methylene Blue solution before and after adsorption by (a) adsorbent film with raw bentonite and (b) adsorbent film with activated bentonite.	61

## LIST OF ABBREVIATIONS

AAB	Acid activated bentonite
AB294	Nylosan Blue EBL
ADMI	American Dye Manufacturing Institute
AR57	Nylosan Red EBL
BB3	Basic Blue
BOD	Biological Oxygen Demand
BR2	Basic Red
BV3	Basic Violet 3
BV10	Basic violet 10
COD	Chemical Oxygen Demand
CR	Congo Red
CV <sup>+</sup>	Crystal Violet
DR8	Direct Yellow 8
MIDA	Manufacturing Industry Development Authority
MB	Methylene Blue
NMP	1-Methyl-2-Pyrrolidane
PSf	Polysulfone
RAS	Recycle Alum Sludge
RBB	Reactive Brilliant Blue
SEM	Scanning Electron Microscopic
SS	Suspended Solid
TOC	Total Organic Carbon
WHO	World Health Organization

## LIST OF SYMBOLS

$\lambda$	Wavelength
$R^2$	Correlation coefficient
$q_e$	The amount of dye per unit mass of adsorbent at equilibrium
$q_m$	The maximum amount of dye adsorbed per unit mass of adsorbent
$C_e$	The equilibrium concentration of the adsorbate
$k_L$	Langmuir constant related to energy of adsorption
$C_o$	The initial concentration of the adsorbate
$k_F$	Freundlich constant
$n$	The degree of non-linearity
$k_T$	The equilibrium binding constant corresponding to the maximum binding energy
$b_T$	Temkin isotherm constant
$q_t$	The amount of dye per unit mass of adsorbent at any contact time
$k_1$	Pseudo first order constant
$k_2$	Pseudo second order constant
$R$	The universal gas constant
$T$	The absolute solution temperature
$E_a$	Arrhenius activation energy of adsorption
$A$	Arrhenius factor
$C_t$	The concentration of MB by time

v	The volume of the MB solution
W	The weight of the adsorbent.
$\Delta G^\circ$	Standard Gibbs free energy
$\Delta H^\circ$	Standard enthalpy
$\Delta S^\circ$	Standard entropy
T	Temperature

**PENYINGKIRAN METILINA BIRU OLEH FILEM PENJERAP  
BERASASKAN BENTONIT: KAJIAN PENCIRIAN DAN PRESTASI**

**ABSTRAK**

Sisa air berwarna terutamanya dari industri pakaian mesti diambil serius kerana sifat mereka yang berbahaya boleh menyebabkan kemudaratan kepada alam sekitar dan juga sumber air harian kita. Pelbagai rawatan sisa air berwarna telah diperkenalkan oleh penyelidik-penyelidik. Walau bagaimanapun, kebanyakan rawatan mempunyai beberapa kelemahan. Penjerapan adalah rawatan yang terbaik untuk sisa air berwarna. Ini disebabkan oleh prestasi pemisahannya yang tinggi. Tujuan penyelidikan ini adalah untuk memperkenalkan aplikasi baru iaitu filem penjerap untuk penyingkiran pewarna. Filem penjerap ini dibentuk dengan cara menggunakan acuan. 1-Metil-2-Pirrolidan (NMP) digunakan sebagai pelarut, polysulfona (PSf) digunakan sebagai pengikat dan bentonit asli atau bentonit yang diaktifkan oleh acid digunakan sebagai penjerap. Prestasi penjerapan filem bentonit asli dan filem bentonit yang diaktifkan oleh asid (AAB) dibandingkan dan filem bentonit yang diaktifkan oleh asid telah dipilih sebagai filem penjerap yang paling cekap untuk menjerap Metilina Biru (MB) di dalam larutan akueus. Beban AAB juga dikaji bagi menghasilkan formula baru filem penjerap dan 4 g AAB telah dipilih. Ciri-ciri fizikal filem AAB telah dianalisa dan didapati bahawa permukaan filem dipenuhi dengan penjerap secara seragam dan sekata beserta keratan rentas filem yang strukturnya seperti span. Luas permukaan AAB adalah  $61.42 \text{ m}^2/\text{g}$ , lebih besar daripada bentonit asli,  $23.00 \text{ m}^2/\text{g}$  beserta potensi zeta  $-19.9 \text{ mV}$  dan  $-46.3 \text{ mV}$  masing-masing. Kesan kepekatan awal larutan MB ( $100 - 700 \text{ mg/L}$ ), suhu ( $30, 40,$

50, 60 and 70 °C), pH (3-11) telah dikaji. Keputusan kajian menunjukkan kapasiti maksimum filem AAB adalah 166.67 mg/g pada suhu 30 °C. Filem AAB telah memberi peratusan penyingkiran yang tinggi pada suhu yang tinggi iaitu 70 °C dan masa yang diambil untuk mencapai 99.99% penyingkiran MB juga menurun sebanyak dua kali pada 70 °C. Nilai pH dari 3 hingga 9 tidak memberi sebarang pengaruh yang ketara pada kecekapan penjerapan filem AAB. Selain menyingkirkan MB, filem AAB juga boleh menyingkir Congo Red (CR) dan Direct Yellow 8 (DY8). Keputusan kadar penggunaan balik filem AAB menunjukkan bahawa filem AAB boleh digunabali sehingga 10 kali sebelum mencapai tahap tepu. Kajian terhadap kinetik dan isoterma menunjukkan bahawa penjerapan Metilina Biru sesuai dengan model pseudo-kedua dan isoterma Langmuir. Manakala, data termodinamik menunjukkan bahawa proses penjerapan melalui proses endotermik, spontan dan rawakan meningkat semasa proses penjerapan tersebut. Hasil daripada kajian menunjukkan bahawa filem AAB berpotensi digunakan sebagai penyingkir warna di dalam air sisa.

**REMOVAL OF METHYLENE BLUE BY BENTONITE BASED  
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STUDY**

**ABSTRACT**

Color wastewater especially from the textile industry must be taken seriously due to their hazardous properties which can caused harm to environment and also our daily water sources. Various color wastewater treatments already be introduced by researchers. However, some of them have some drawbacks. Adsorption is the best treatment for color wastewater due to their high separation performance. The aim of this research is to introduce new applications of adsorbent film for dye removal. The adsorbent film was fabricated in a casting method by using 1-Methyl-2-pyrrolidone (NMP) as the solvent, polysulfone (PSf) as the binder and raw or acid activated bentonite as the adsorbent. The performance of raw and acid activated bentonite film was compared and the acid activated bentonite (AAB) film was later employed as an efficient adsorbent to remove Methylene Blue (MB) in an aqueous solution. The AAB loading was also investigated for new formulation of AAB film and 4 g of AAB was chosen. The physical characteristics of AAB film were analyzed and it was found that the adsorbent well distributed on the surface of the film with sponge-like structure film's cross section. The surface area of the AAB was 61.42 m<sup>2</sup>/g, larger than raw bentonite, 23.00 m<sup>2</sup>/g with the zeta potential of -19.9 mV and -46.3 mV respectively. The effect of initial solution concentration (100 – 700 mg/L), temperature (30, 40, 50, 60 and 70 °C) and pH (3-11) were investigated. Results showed that the maximum adsorption capacity of AAB film was 166.67 mg/g at 30

°C. The AAB film gave high percentage removal at high temperature of 70 °C and the time consuming to reach 99.99% MB removal also decreased two times at 70 °C. The values of pH from 3 to 11 gave no significant effect on the AAB film adsorption efficiency. Instead of removal of MB, the AAB film also able to remove Congo Red (CR) and Direct Yellow 8 (DY8). Reusability of AAB film result showed that it can be recycled till 10<sup>th</sup> times before reached saturation. Kinetic and isotherm studies revealed that Methylene Blue adsorption described well with pseudo-second order and Langmuir isotherm models. While, the thermodynamic data showed that the adsorption process undergoes endothermic, spontaneous and the randomness increased during the adsorption process. The outcomes from this study indicate that AAB film has high potential for dye removal in wastewater.

## CHAPTER ONE

### INTRODUCTION

#### 1.1 Textile Industry

In 2014, textile industry was in the top 10<sup>th</sup> largest export earner of textile and textile products in the world. As stated by the Manufacturing Industry Development Authority (MIDA), it is about 662 licensed textile and apparel factories and 1000 small scale factories existed in Malaysia (MIDA, 2016).

It is expected the trend of textile development will continuously growth as the demand for the textile product keep increasing year by year (Wulfhorst *et al.*, 2006). One of the process involve during production of textile product is the coloration. It consists of two methods, dyeing and printing. Different types of dye are used for different fiber materials. Thus, it involved many types of dye since there are many types of fiber materials existed (Wulfhorst *et al.*, 2006).

Textile industry generates huge amount of colored wastewater from the coloration process. If those colored wastewater was discharged into the environment without any treatment, it will definitely give a serious impact to the environment in as well as living organisms. High values of chemical oxygen demand (COD), biochemical oxygen demand (BOD<sub>5</sub>) and presence of particulate matters in the colored wastewater causes depletion of dissolved oxygen, which gives effect on the aquatic ecological system (Wang *et al.*, 2001). This situation leads to critical water pollution.

## **1.2 Water Pollution**

Pollution is refers to introduction of contaminants chemical or substances in concentration greater than the concentration that would occur under natural conditions into the environment. Major water pollutants include dyes, microbes, heavy metals, organic chemicals, oil and sediments. Usually, the untreated waste water from the industry is high in color, COD, BOD, total organic carbon (TOC), suspended solids (SS), pH, temperature, turbidity and pH (Pang and Abdullah, 2013).

Colored wastewater discharged is one of the biggest problems faced by the industry. Human being depends on clean water to survive, but right now they are facing towards a water crisis due to the discharged of the wastewater into the water sources. Currently, nature environment lack of clean water sources due to those pollutants. The main sources that use for drinking water and for daily life are already being overdrawn or contaminated with pollution (NRDC, 2014).

Colored wastewater is already regulated in the Environmental Quality (Industrial Effluent) Regulation 2009. The fifth schedules tabulated the acceptable conditions for discharge of industrial effluent or mixed effluent for standard A and B (shown in Appendix A). For color, the wastewater from Standard A cannot exceed 100 ADMI and for standard B, they cannot exceed 200 ADMI (DOE, 2015). Therefore, it is an obligation for every textile industries to treat their colored wastewater in order to meet this legislative requirement.

### **1.3 Environmental and Health Impact of Dye**

There are various types of dye and each dye has its complex structure. These make them very difficult to be treated. There were no record on detail statistical data for the quantity of colored wastewater discharged into the environment but there were information of about 15% of the dye lost and discharged to the environment during dyeing process in the textile industry (Gupta and Suhas, 2009; Hai *et al.*, 2007).

Colored wastewater discharged from industry is one of the biggest problems faced by the industry and the environment. This situations lead to water crisis and problem for the environment and health aspects. Dyes contain in color effluent is resistant to aerobic digestion and have high color intensity which it can destruct the aquatic life present in the ecosystem (Pang and Abdullah, 2013; Gupta and Suhas, 2009; Crini, 2006).

For health aspects, the harmful and toxicity of the colored effluent can cause respiratory or skin sensitization. In German Hospital, it was estimated about 1-2% of the total allergies diseases treated were caused by contact with textile and most of them were due to dyes (Wulfhorst *et al.*, 2006). Besides, the color effluent is mutagenic and carcinogenic. They will affect the human health by causing the growth of tumor and cancer in human body (Wulfhorst *et al.*, 2006).

#### **1.4 Current Practice of Textile Wastewater Treatment**

Practically, the industries used the combination of many types of methods for their wastewater treatment. Some of them used the combination of biological method and chemical method, some of them used chemical method and physical method and some of them used the combination of all the types of the methods. For example, in Malaysia, Siang Poh Knitting Sdn. Bhd used the combination of physical and chemical treatment followed by the biological treatment to treat their colored wastewater (WEPA, 2013). Their daily amount of treated wastewater was about 96 m<sup>3</sup>/day.

While in Cambodia, M & V III Co., LTD Wastewater Treatment Plant and Tack-Fat Garment Wastewater Treatment Plant used the combination of chemical and biological process to treat their colored wastewater (WEPA, 2013). They produced about 300 m<sup>3</sup>/day and 4500 m<sup>3</sup>/day of treated wastewater daily for M & V III Co., LTD Wastewater Treatment Plant and Tack-Fat Garment Wastewater Treatment Plant respectively. Figure 1.1 below shows the flow diagram of the colored wastewater treatment for each company.