# REMOVAL OF ACID BLUE 25 DYE BY USING DRIED WATER HYACINTH FROM AQUEOUS SOLUTION

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## REMOVAL OF ACID BLUE 25 DYE BY USING DRIED WATER HYACINTH FROM AQUEOUS SOLUTION

A thesis submitted in the the fulfillment of the requirements for the award of the degree of Bachelor of Chemical Engineering

Faculty of Chemical Engineering & Natural Resources Universiti Malaysia Pahang

# DECLARATION

I declare that this thesis entitled "Removal of Acid Blue 25 dye by using dried water hyacinth from aqueous solution" is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any degree.

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#### ABSTRACT

Water hyacinth (*Eichhornia crassipes*) is a free floating aquatic weeds that robustness in its growth used as an adsorbent to remove Acid Blue 25 dye from aqueous solution. The parameters studied include the adsorbent dosage, initial dye concentration, pH, and also contact time in a batch adsorption process at room temperature 21°C. The results shows the optimum conditions for each parameter studied, adsorbent dosage at 0.60 g, initial concentration 400 mg/L, pH 2 and 100 minutes contact time. The samples after the dye uptake were analyzed by using UV-Vis spectrophotometer. Furthermore, before and after the experiments, FTIR analyses were studied to know the functional groups of the water hyacinth. In addition, the equilibrium data fitted well pseudo-second order kinetics, Langmuir and Freundlich isotherm. The maximum sorption capacities for Langmuir equation were 83.33 mg/g whereas the amount of n for Freundlich is favourable. While for pseudo-second-order kinetics, it has a low error for equilibrium sorption capacity for experimental and calculated values. This study is favourable and economically feasible for the removal of Acid Blue 25.

### ABSTRAK

Keladi bunting merupakan gulma air yang mengambang yang digunakan sebagai adsorben untuk menyingkirkan pewarna Asid Biru 25 dari akuas larutan. Parameter yang dipelajari meliputi dos adsorben, kepekatan pewarna awal, pH, dan juga masa tindakbalas dalam proses jerapan batch pada suhu bilik 21° C. Keputusan menunjukkan keadaan optimum untuk setiap parameter yang diteliti, dos adsorben pada 0.60 g, kepekatan awal 400 mg / L, pH 2 dan masa tindakbalas 100 minit. Kesemua kepekatan akhir larutan dianalisa menggunakan UV-Vis Spectrophotometer. Selanjutnya, sebelum dan selepas percubaan, analisis FTIR dipelajari untuk mengetahui kumpulan-kumpulan berfungsi keladi bunting. Selain itu, data keseimbangan menepati kinetika orde pseudo-kedua Langmuir dan Freundlich isotherm. Kapasiti jerapan maksimum untuk persamaan Langmuir adalah 83.33 mg/g manakala untuk Freundlich isotherm nilai n sesuai. Sedangkan untuk kinetik pseudo-orde kedua, ia memiliki kesilapan rendah untuk kapasiti keseimbangan sorpsi untuk nilai eksperimental dan dikira. Penelitian ini menguntungkan dan layak secara ekonomi untuk menghilangkan Asid Biru 25.

# TABLE OF CONTENT

CHAPTER		ITEM	PAGE
	TIT	LE PAGE	i
	DEC	CLARATION	ii
	ACF	KNOWLEDGEMENT	iii
	ABS	STRACT	iv
	ABS	TRAK	V
	TAE	BLE OF CONTENTS	vi
	LIS	Г OF TABLES	ix
	LIS	Γ OF FIGURES	X
	LIST	Γ OF ABBREVIATIONS	xii
	LIST	Г OF APPENDICES	xiii
1	INT	RODUCTION	1
	1.1	Introduction	1
	1.2	Problem Statement	2
	1.3	Objectives	3
	1.4	Scope of Study	3
	1.5	Rationale and Significant	4
2	LIT	ERATURE REVIEW	5
	2.1	Adsorption	5
		2.1.1 Factors affecting adsorption	6
	2.2.	Adsorbent	7
		2.2.1 Low cost adsorbents	8

2.3	Water hyacinth	9
	2.3.1 Physical description	9
	2.3.2 Growth	10
	2.3.3 Chemical analysis	11
2.4	Dyes	12
2.5	Acid Blue 25 dye	13
	2.5.1 Characteristics	13
	2.5.2 Applications	13
	2.5.3 Effect to the human and environment	14
2.6	Summary of literature review	14
MAT	<b>FERIALS AND METHODOLOGY</b>	16
3.1	Overall methodology	16
3.2	Adsorbent preparation	19
3.3	Adsorbate preparation	20
3.4	Fourier transform infrared study	21
3.5	Adsorption experiments	21
	3.5.1 Effect of adsorbent dosage	21
	3.5.2 Effect of initial concentration	21
	3.5.3 Effect of pH	22
	3.5.4 Effect of contact time	22
RES	ULTS AND DISCUSSIONS	23
4.1	Effect of adsorbent dosage	23
4.2	Effect of initial concentration	25
4.3	Effect of pH	28
4.4	Effect of contact time	30
4.5	Kinetics of the adsorption process	32
4.6	Adsorption isotherm	33
	4.6.1 Langmuir isotherm	33
	4.6.2 Freundlich Isotherm	36
4.7	FTIR analysis	37

5 CONCLUSIONS AND RECO		NCLUSIONS AND RECOMMENDATION	40
	5.1	Conclusions	40
	5.2	Recommendations	41
REFEREN	NCES		42
APPENDI	CES A		46
APPENDI	CES B		53
APPENDI	CES C		60
APPENDI	CES D		61

# LIST OF TABLES

TABLE	TITLE			
2.1	Summary of Literature Review	15		
4.1	Pseudo-second-order adsorption rate constants and	32		
	calculated and experimental qe values			
4.2	Langmuir isotherm constant for Acid Blue 25 sorption on	34		
	dried water hyacinth			
4.3	Freundlich isotherm constant for Acid Blue 25 sorption on	36		
	dried water hyacinth			
B1	Mass of dried water hyacinth during drying	53		
B2	Standard curves data 5			
В3	Percentage removal experimental data for the effect of	54		
	adsorbent dosage			
B4	Equilibrium adsorption data for the effect of adsorbent	54		
	dosage			
В5	Percentage removal experimental data for the effect of	55		
	initial concentration			
B6	Equilibrium adsorption data for the effect of initial	56		
	concentration			
B7	Percentage removal experimental data for effect of Ph	56		
<b>B</b> 8	Equilibrium adsorption data for effect of pH	57		
B9	Percentage removal experimental data for effect of time	58		
B10	Equilibrium adsorption data for effect of time	58		

# LIST OF FIGURES

FIGURE	<b>TITLE</b>		
2.1	Water hyacinths (Eichhornia crassipes)	9	
3.1	Flowchart of methodology	17	
3.2	Scope of study	18	
3.3	Dried water hyacinth after blended	20	
3.4	The structure of Acid Blue 25 dye	20	
4.1 (a)	Percentage removal for the effect of adsorbent dosage	24	
4.1 (b)	Amount of dye sorbed for the effect of adsorbent	25	
4.2 (a)	Percentage removal for the effect of initial concentration	27	
4.2(b)	Amount of dye sorbed for the effect of initial concentration	27	
4.3 (a)	Percentage removal for the effect of pH		
4.3 (b)	Amount of dye sorbed for the effect of pH	29	
4.4 (a)	Percentage removal for the effect of contact time	31	
4.4 (b)	Amount of dye sorbed for the effect of contact time.	31	
4.5	Pseudo-second- order adsorption kinetics of Acid Blue 25 at pH 2	33	
	and different initial Acid Blue 25 concentrations		
4.6	Langmuir isotherm plots for Acid Blue 25 sorption on dried water	35	
	hyacinth		
4.7	Separation factor for Acid Blue 25 sorption on dried water	35	
	hyacinth	36	
4.8	Freundlich isotherm plots for Acid Blue 25 sorption on dried	37	
	water hyacinth	37	
4.9	The FTIR analysis of dried water hyacinth before dye uptake	39	

4.10	The FTIR analysis of dried water hyacinth after dye uptake	39
A1	Collecting the water hyacinth at Gambang Lake, Pahang	
A2	Washing the aerial and leaf by using tap water	46
A3	After washing air dried before drying on the oven	47
A4	Water hyacinth before and after drying in the oven over 24-72	47
	hours	
A5	Blending process by using blender	48
A6	Dried water hyacinth	48
A7	Acid Blue 25 before adsorption process	49
A8	Orbital shaker	49
A9	Refrigerated centrifuge	50
A10	pH meter	50
A11	Desicator	51
A12	UV-Vis spectrophotometer	51
A13	Fourier transform infrared	52
C1	Standard curve for Acid Blue 25	60

# LIST OF ABBREVIATIONS

AB 25	=	Acid Blue 25
NH <sub>2</sub>	=	Amine
OH	=	Hydroxide
NH <sub>3</sub>	=	Ammonia
CAS	=	Ethylenediamine modified starch
COD	=	Chemical oxygen demand

# LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A B	Experimental Process And Equipment Used Experimental Data	46 54
С	Experimental Graph	60
D	Procedure For Sample Analysis	61

### **CHAPTER 1**

#### INTRODUCTION

#### 1.1 Introduction

Nowadays, in the world of globalization, there are a lot of potential industrial sector growths, especially in Malaysia. In Malaysia textile industry 'Batik' is well known material. The big consumers of dyes are textile, dyeing, paper and pulp, tannery and paint industries, and hence the effluents of these industries as well as those from plants manufacturing dyes tend to contain dyes in sufficient quantities (Gupta *et al.*, 2009). Approximately a half of all known dyes are azo dyes, making them the largest group of synthetic colourants (K.Selvam *et al.*, 2002). W.A.Sadik (2007) reported that azo dyes represent about 60-70% of the dye used. Moreover, azo dyes effluent that goes to the water stream will be a significant threat to environmental health and people. There are many types of azo dyes, such as Acid Blue 25, Acid Orange 52, Acid Red 14, Acid Brown dye, Acid Red 1 and many more. Acid blue 25 is a common dye shown in wastewater from the textiles industries.

Various physical, chemical, and biological methods, namely adsorption, biosorption, coagulation, precipitation, membrane filtration, solvent extraction, chemical oxidation and photochemical degradation have been used for the treatment of dye containing wastewater (Necip *et al.*, 2009). Bansal and Goyal (2005), adsorption is one of the processes, which besides being widely used for dye removal also has wide applicability in wastewater treatment. Various adsorbent wastes are used in colour

removal processes such as activated carbon, chitosan and natural wastes (e.g. cellulose derivatives, wood pulp, peat, feathers, hair, sawdust) (McKay G, 1996). Water hyacinth (*Eichhornia crassipes*) is useful as a medium or adsorbent to remove nutrients and heavy metals that contain toxic which could play a role against environmental pollution. While dried water hyacinth is commonly used instead of aquatic water hyacinth. One of the reason is because, dried water hyacinth did not affect the spreading of dengue fever to the residents near by.

In this study, the adsorption of Acid Blue 25 using the dried water hyacinth, *Eichhornia crassipes* was investigated. As they are readily available in great abundance water hyacinth roots could represent an economically source of adsorbent for acid dyes.

#### **1.2 Problem statement**

Acid dye has a big consumer in paper, paint, dyeing and others industries and one of it is Acid Blue 25. These dye have the capacity to release certain aryl amines which cause cancer risks. There are a lot of methods that can be used to remove dye from the wastewater. Some of the methods are relatively expensive, leaving the final environmental problem unsolved. The need to explore possibilities of utilizing unconventional materials as sources of wastewater treatment is extremely valuable (M.M. El Zawahry *et al.*, 2004). One of the valuable method is by using sorption.

Adsorption is widely used to remove pollutants from waste water (Mohammad I. El-Khaiary, 2007). The usage of activated carbon as an adsorbent for the removal of many pollutants has been widely applied, but activated carbon is expensive. Therefore, low-cost adsorbents are used as one of the alternatives adsorbent that have been tested extensively. Water hyacinth is chosen as an adsorbent because the removal of colour from wastewater of textile dyeing processes was studied by previous researcher. Besides, it is because the abundant supply of it and easy to get in low cost. Since the water

hyacinth is fast growth and the robustness of its seed, it becomes a major cause of water irrigation especially in rivers and drainage systems. During the raining seasons, it could blocked the drains and water sources due to its uncontrollable rapid growth.

There are some studies have been reported on the use of dried plant material as a potential adsorbent in industrial to remove Acid Blue 25 in the waste water systems. One of the studies is by using water hyacinth since it is cheap and easily to find because it is not a seasonal plant. In this study, dried water hyacinth is chosen as compared to the aquatic water hyacinth. The main reason is because dried water hyacinth is environmental friendly which cannot lead to growth of mosquitoes' pest which will lead to serious health problems. Furthermore, we can reduce the usage of transportation and the cost to transport itself.

#### 1.3 Objectives

The objective of this research is to study the removal of Acid Blue 25 dyes from aqueous solutions.

### 1.4 Scope of study

In order to achieve the objectives, the following scopes have been identified:

- 1) Effect of initial concentration.
- 2) Effect of dried water hyacinth dosage.
- 3) Effect of pH.
- 4) Effect of contact time.

### **1.5** Rationale and significance

This study is to remove Acid Blue 25 dye from the wastewater treatment and also as a reduction of environmental problems occur by the widespread of water hyacinth. Besides, it is used as a part of saving the cost to control spreading of water hyacinth. This study also uses adsorption process, a method of environmental control as an alternative to replace conventional method that may be ineffective or extremely expensive. Furthermore, the usage of dried of water hyacinth is another methods which is different from other research because it is easily to store and avoid dengue fever as compared to the aquatic water hyacinth. Next, there is no further treatment to use it as an adsorbent just dried it in the oven. Besides, it is due to aquatic water hyacinth is an environmental friendly in terms of the blockage of canals and rivers that can even cause dangerous flooding.

### **CHAPTER 2**

#### LITERATURE REVIEW

#### 2.1 Adsorption

Adsorption is the adhesion of molecules of gas, liquid, or dissolved solids to a surface. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent. It differs from absorption, in which a fluid permeates or is dissolved by a liquid or solid. The term sorption encompasses both processes, while desorption is the reverse of adsorption. Adsorption is present in many natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, capturing and using waste heat to provide cold water for air conditioning and other process requirements (adsorption chillers), synthetic resins, increase storage capacity of carbide-derived carbons for tunable nanoporous carbon, and water purification. Adsorption, ion exchange, and chromatography are sorption processes in which certain adsorbates are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column. In a simple word, adsorption is the collection of a substance onto the surface of adsorbent solids. It is a removal process where certain particles are bound to an adsorbent particle surface by either chemical or physical attraction. Adsorption of dyes from waste water has been studied before to find a suitable explanation of the mechanism and the kinetics. When designing the batch sorption systems, rate of reaction for the sorption is the most important consideration. More over it is important to know the time dependence of a system with vary process conditions. The adsorption process has been widely used for colour removal. Adsorption is one of the processes, which besides being widely used for dye removal also has wide applicability in wastewater treatment (Bansal and Goyal, 2005).

#### 2.1.1 Factors affecting adsorption

There are several factors that affecting the adsorption process. This effect is found by several researches that conducting adsorption. Researcher mostly investigates between these parameters to study its effect on adsorption process and how it can be improved to get the highest optimum uptake. All those parameters are effect of initial dye concentrations, adsorbent dosage, pH, contact time and temperature.

Firstly, for the effect of time and initial dye concentration, commonly for acid dyes, the uptake of dye from water was concentration dependent and increased with initial concentration. The removal of dye is rapid in the initial stages of contact time and gradually decreases with lapse of time until saturation. The removal curves are single, smooth and continuous, indicating monolayer coverage of dye on the outer surface of the adsorbent (R.Sivaraj *et al.*, 2000).

Furthermore, for the effect of pH, the increase of pH value, the adsorption capacity for each dye decreases. In the aqueous solution with the pH value above 1.5, the sulfonate groups of the dye dissociate and are converted to anionic ions Also, in the presence of H<sup>+</sup>, the amine groups of CAS become protonated. Then the ionic interaction (for example  $-NH_3^+$ ··· $-O3S^-$ ) between each dye and the adsorbent occurs. These suggest that the process of each dye adsorption is based on electrostatic attraction. Another fact should be noted that the capacities for individual dyes are different. The facts cannot be simply explained by electrostatic attraction, but hydrogen bonding. It can be seen that a great distinction of the dyes is the number of hydrophilic functional groups, which have a strong tendency to form hydrogen bonds. Therefore the adsorption

is co-directed by electrostatic attraction and hydrogen bonding ((Rumei Chenga *et al.*, 2009).

According to Mckay *et al.*, (1998) in the study of kinetic models for the sorption of dye from aqueous solution by wood, in the effect of temperature the equilibrium sorption capacity increases with temperature, indicating that a high temperature favours Basic Blue 69 removal by adsorption on wood. This effect is characteristic of a chemical reaction or bond being involved in the sorption process with the increase in temperature increasing the equilibrium conversion. This effect can be explained by assuming that at higher temperatures the total energy of the sorbate molecules is increased and consequently their escaping tendency is also increased, therefore the sorption of the sorbate species is lowered.

Moreover, according to the M.M. Karim *et al.*, (2006) the increase of adsorbent dosage will increase the amount of percentage removal. The increasing value of percentage removal of dye uptake might be due to increase of surface area which means increasing of availability of sorption sites for removal of dye with the increase in adsorbent dosage. Whereas, the decreasing in dye sorbed per unit mass with increasing of adsorbent dosage can be because of reduction in effective surface area, or in other word, the adsorbate is saturated. This also can explained the constant value of percentage removal, where the dye had caused particles to aggregate and thereby resulting in unavailability of active sites for adsorption.

#### 2.2 Adsorbent

An adsorbent is a substance, usually porous in nature and with a high surface area that can adsorb substances onto its surface by intermolecular forces. Adsorbents are also used for extraction purposes removing traces of organic materials from large volumes of water very efficiently (solid phase extraction devices). There are a lot of adsorbent currently used in treating the wastewater, either on removal of dye, heavy metals, phenols, toxic and others. Adsorbent such as clay, activated carbon, zeolites, and silica gel (Gupta *et al.*, 2009) is widely used but remaining the environmental problems unsolved since it is expensive. However, by using low-cost adsorbent (LCA), we could reduce the cost on treating the waste water itself.

#### 2.2.1 Low-Cost Adsorbents (LCAs)

Natural materials or the wastes/by-products of industries or synthetically prepared materials, which cost less and can be used as such or after some minor treatment as adsorbents are generally called low-cost adsorbents (LCAs). These low-cost alternative adsorbents (Gupta *et al.*, in press) may be classified in two ways which are:

(i) On basis of their availability:

- (a) Natural materials such as wood, peat, coal and lignite.
- (b) Industrial/Agricultural/ Domestic wastes or by-products such as slag, sludge, fly ash, bagasse fly ash, red mud and others.
- (c) Synthesized products;

(ii) Depending on their nature:

- (a) Inorganic
- (b) Organic

A lot of LCAs commonly used such as chitin, chitosan, saw dust, rice hust, orange peel, banana peel, baggase pith, water hyacinth and others that come from waste into a very usefull adsorbent. It has their own ability to uptake either basic or acidic dyes that polluted the water stream around the world. In this study, the usage of dried water hyacinth as a low cost adsorbent is a wise decision. It is because of instead of cheap

materials, we could also reduce the environmental problems that came from water hyacinth growth.

### 2.3 Water hyacinth

Water hyacinth or it scientific name *Eichhornia crassipes* is a free floating aquatic weed. Figure 2.1 is a picture of water hyacinth taken at Gambang Lake. From that picture, it can be seen that water hyacinth is abundantly growth.



Figure 2.1: Water hyacinths (*Eichhornia crassipes*)

## 2.3.1 Physical description

The water hyacinth is a free floating aquatic weed originated in the Amazon in South America (Bolenz *et al.*, 1990) where it was kept under control by natural predators (Lee, 1979). The plant has, through introduction by man, spread throughout the whole tropical zone (Aweke, 1993). Due to it fast growth and the robustness on its seeds, it caused a major problems in the whole area such as obstruction of shipping routes and

losses of water in irrigation systems due to higher evaporation and interference with hydroelectric schemes and increase sedimentation by trapping silt particles (C.C.Gunarson *et al.*, 2007).

#### 2.3.2 Growth

Water hyacinths regenerate prolifically from fragments of stems and the seed can remain viable for more than six years. These ways of regeneration make it very difficult to control the weed (Lee, 1979). The number of plants can more than double in seven days in conditions of high temperature and humidity and up to 140 ton of DM/ha and yr are produced. The plant normally forms cohesive floating mats and can cover large areas of the water surface. The spreading of the water hyacinth is also thought to be enhanced by winds. The plant flourishes in nutrient-rich waters and on shallow shores with mud rich in nutrients (C.C.Gunarson *et al.*, 2007).

Furthermore, water hyacinth grows over a wide variety of wetland types and prefers nutrient-enriched waters. However, it can tolerate considerable variation in nutrients, temperature and pH levels. The optimum pH for growth of water hyacinth is 6–8. It can grow in a wide range of temperature from 1 to 40°C (optimum growth at 25–27.5°C) but it is thought to be cold-sensitive (Wilson *et al.*, 2005). Growth rates increase with the increase in water nitrogen amounts. These mats competitively exclude native submerged and floating-leaved plants and its associated fauna, thereby causing an imbalance in the aquatic micro-ecosystem. Diversity of fish stocks is also affected. Low oxygen conditions beneath the mats create good breeding conditions for mosquito vectors of malaria, encephalitis and filariasis. Lately the hyacinth has invaded many tropical lakes including Lake Victoria, East Africa where it caused several of the above described problems such as reduction in fish catch, interference with transportation and water supply and breeding of snails, mosquitoes and snakes (A.Malik, 2007).

Moreover, the major problem when working in the water hyacinth infested areas is the risk of catching waterborne diseases e.g.; malaria and diarrhea. Attempts to control the weed have caused high costs and labour requirements, leading to nothing but temporary removal of the water hyacinths. Since the most favourable conditions for the growth of the water hyacinth often are found in developing countries, very limited resources have been put into curbing them. Fighting the water hyacinth generates neither food nor income, and the weeds are therefore left to cover the lakes. Fast growth is a feature valued in crops grown by man. The water hyacinth would, therefore, have a great potential if seen as raw material for industries or if incorporated into agricultural practice (C.C. Gunnarsson *et al.*, 2007).

#### 2.3.3 Chemical analysis

The water hyacinth has an excellent ability to take up nutrients and other chemicals from its environment, and the chemical composition of the water hyacinths depends strongly on its environment (Poddar *et al.*, 1991). Besides, Poddar *et al.* (1991) reported a nitrogen content of 1.78% (db) in water hyacinths growing in marshy land where the nitrogen level in the water was only 2.40 mg/L. Abdelhamid and Gabr (1991) state the nutrient content is lower in the stem and root compared with the nutrient content in the leaves.

Besides, there are also several studies by using water hyacinth as the main material for the biosorption process. The potential use of water hyacinth to absorb heavy metals and as a general medium for environmental clean-up has been presented. Water hyacinth has also been used for the removal of phenols (Wolverton and Mckown, 1976). Removal of some heavy metals from polluted water had been demonstrated (Muramoto and Oki, 1983). It has also been used to remove arsenic, cadmium, lead and mercury from wastewater (Chigbo *et al.*, 1982). Some studies using the water hyacinth were done on effluents from the rubber industry (John, 1984) for the metals and organic sulphur compounds; and the palm oil industry (Yusof *et al.*, 1984) for the removal of metals and

lipids. Heavy metal phytoremediation by water hyacinth at the Erh-Chung constructed wetlands in Taiwan showed the ability of water hyacinth to absorb and translocate cadmium, lead, copper, zinc, and nickel (Liao and Chang, 2004).

Instead of heavy metals, water hyacinth also use for the removal of dyes. It is not specifically for basic dyes, but also for all types of dyes. A study reported by Low *et al.*, (1995) for the removal of methylene blue and Victoria blue by using water hyacinth root as an adsorbent. Besides, on the removal of azo and anthraquinone dyes from aqueous had been demonstrated (M.M.Elzawahry *et al.*, 2004).

## 2.4 Dyes

A dye can generally be described as a colored substance that has an affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber. Both dyes and pigments appear to be colored because they absorb some wavelengths of light preferentially. In contrast with a dye, a pigment generally is insoluble, and has no affinity for the substrate. Some dyes can be precipitated with an inert salt to produce a lake pigment, and based on the salt used they could be aluminum lake, calcium lake or barium lake pigments.

Dye molecules comprise of two key components: the chromophores, responsible for producing the colour, and the auxochromes, which can not only supplement the chromophore but also render the molecule soluble in water and give enhanced affinity (to attach) toward the fibers. Dyes exhibit considerable structural diversity and are classified in several ways. These can be classified (Hunger, 2003) both by their chemical structure and their application to the fiber type. Dyes may also be classified on the basis of their solubility: soluble dyes which include acid, mordant, metal complex, direct, basic and reactive dyes; and insoluble dyes including azoic, sulfur, vat and disperse dyes. Besides this, either a major azo linkage or an anthraquinone unit also characterizes dyes chemically. It is worthwhile noting that the azo dyes are the one most widely used and accounts 65–70% of the total dyes produced.

### 2.5 Acid blue 25 dye

Acid Blue 25 dyes or it is synonyms as 1-amino-9, 10-dihydro-9, 10-dioxo-4-(phenylamino)-2-Anthracenesulfonic acid is categorize as anthraquinone dyes. The anthraquinone dyes is weak and expensive. Acid Blue 25 is acidic dyes which act as anionic molecules when it is diluted in the distilled water.

## 2.5.1 Characteristics

Acid Blue 25 has a molecular formula  $C_{20}H_{14}N_2O_5S$ . Particularly at room temperature it appears as solid, odorless, dark blue powders which become a blue solution when dissolved in water. The molar mass is 416.39 g/mol and its solubility in water is 40 (g/l) at 80 C. It has pH at the range 7-9 depends on the dilution itself.

#### 2.5.2 Applications

Similar with other commonly used dyes, Acid Blue 25 had widely applied in the wool, nylon, silk, paper, ink, aluminum, detergent, wood, fur, cosmetics, biological stain. The anthraquinonic dye Acid Blue 25, represent the second most important class of commercial dyes after azo-compounds and are mainly used for dyeing wool, polyamide and leather (H. Ghodbane *et al.*, 2009).

#### 2.5.3 Effect to human and environment

Most of the dyes are stable to biological degradation. Colour affects the nature of the water and inhibits sunlight penetration into the stream and reduces photosynthetic action. Some of the dyes are carcinogenic and mutagenic. The presence of chemicals like hydrogen sulphide, sulphide and sulphur dyes causes rapid depletion of dissolved oxygen, affecting aquatic life adversely. Various chemicals are present in the effuent, such as phenols, benzene, toluene and other hydrocarbons, many of which are potential carcinogens. Toxicity of various azo dyes especially benzidine based dyes are well known because of their mutagenicity and carcinogenicity. It is rather diffcult to treat dye effuents because hot and strongly coloured textile dyeing wastewater is notoriously known to contain a large amount of suspended solids, high COD concentration and with a highly fluctuating pH. Hence there is a need to remove dyes from dyeing wastewater before it mixes with water bodies (R.Sivaray *et al.*, 2000).

### 2.6 Summary of literature review

Table 2.1 showed that there are a lot of adsorbent use in order to removes variety dyes from the waste water. It is successfully explained from the various journals from 1995 until 2009. These previous studies are important to be made as indication of how effective is the dried water hyacinth as a adsorbent and to compare which adsorbent is the most effective to remove Acid Blue 25 from aqueous solution.

ADSORBENT	SPECIES	REFERENCE
Hazelnut shells	Methylene Blue, Acid Blue 25	(F.Ferrero, 2007)
Wood sawdust	Methylene Blue, Acid Blue 25 Acid Yellow 36	(F.Ferrero, 2007) (Malik, 2003)
Water Hyacinth (Eichhornia Crassipes)	Acid Blue 25 Methylene Blue, Victoria Blue Acid Red 1, Acid Red 40, Acid Green 27, Reactive Blue 19, Acid Blue 80, Acid Blue 25	(Lee <i>et al.</i> , 1999) (Mohammad I. El-Khaiary, 2006),(Low <i>et al.</i> , 1995) (M.M. El Zawahry <i>et al.</i> , 2004)
Banana pith	Direct Red, Acid Brilliant Blue	(C. Namasivayam et al., 1998)
Sunflower seed shells	Reactive Black 5	(Johann <i>et al.</i> , 2007)
Rice husk	Acid Yellow 36	(Malik, 2003)
Soy meal hull	Acid Red 14	(Arami et al., 2006)
Cane (bagasse) pith	Acid Blue 25	(Juang <i>et al.</i> , 2001)
Ethylenediamine modified starch (CAS)	Acid Orange 10, Acid Green 25 And Amido Black 10B	(R.Cheng <i>et al.</i> , 2009)
Tetrachloride	Acid Blue 25	(H.Ghodbane et al., 2009)
Orange peel	Acid Violet 17	(R.Sivaraj <i>et al.</i> , 2000)

**Table 2.1:** Summary of Literature Review

## **CHAPTER 3**

### MATERIALS AND METHODOLOGY

### 3.1 Overall methodology

Water hyacinth was collected from near by lake at Gambang, Pahang. Then, in the very beginning of the experiments, dried water hyacinth was prepared. Before proceed to the first parameter, dried water hyacinth was analyzed using Fourier Transform Infra Red Spectrometer (Thermo Nicolet). Adsorption experiments were carried out in batch process by using the solutions of Acid Blue 25 purchased from Sigma Aldrich with 45% of dye content. There are four parameters to be considered in these experiments which are the effect of initial dye concentrations, adsorbent dosage, pH and also contact time. Before proceeding on each parameter, a stock solution of Acid Blue 25 was prepared and standard solution were diluted which is 1M of Acid Blue 25 from the stock solution. A standard curve was performed to have the equation relating the adsorbent (OD) and concentration.



Figure 3.1: Flowchart of methodology

The experiments were then proceed by performing all the parameters in the Orbital Shaker at 200 rpm and at room temperature, 21°C using 250 mL conical flasks containing 50 mL dye solution at different initial concentrations and pH values of Acid Blue 25 solution. The initial pH values of the solutions were adjusted with 0.1 M Sodium Hydroxide, NaOH or 0.1 M Hydrochloric Acid, HCL before each experiment. The pH was measured by using a (Metrohm Model) pH meter. A number of doses of dried water hyacinth were added to each flask, and then the flasks were sealed up with parafilm or aluminium foil to prevent any spillage. After shaking the flasks for a period of time, the aqueous samples were taken and then centrifuge by using (Eppendorf

Centrifuge 5810R) at 5000 rpm, 21°C for about 30 minutes. After centrifuge, the supernatant were collected by using disposable pipet and transfer into the sample bottles before analyzing the OD at the (Hitachi, Model U - 1800) UV-Vis Spectrophotometer at its maximum wavelength, 600 nm.



Figure 3.2: Scope of study

Next step is calculating the percentage removal of Acid Blue 25. The percentage of Acid Blue 25 dye removal was calculated by:

$$R \% = \frac{c_{o-} c_t}{c_o} X \, \mathbf{100} \tag{3.10}$$

where  $C_o$  is the initial concentration of Acid Blue 25 (mg/L) and  $C_t$  is the concentration of Acid Blue 25 at any time (mg/L). The equilibrium amount of adsorption,  $q_t$  (mg/g), was calculated by:

$$q_t = \frac{(C_o - C_t) V}{W}$$
(3.20)

where V is the volume of solution in L and W is the mass of adsorbent used in g.

#### 3.2 Adsorbent preparation

Water hyacinth is collected from the local Gambang Lake, near by the Caltex petrol pump stations. They were washed thoroughly by using tap water for several times in order to removes dirt on the aerial and leafs. It is chopped into small pieces to ease of drying. The water hyacinth then dried in the oven at 60°C, 24 -72 hour until the moisture content is remained the same. Moisture content is calculated by:

$$u = \frac{m_{wet} - m_{dry}}{m_{dry}} \times 100 \tag{3.30}$$

where u is the percentage of moisture content,  $m_{wet}$  is the mass of adsorbent initial (g),  $m_{dry}$  is the mass of the adsorbent after several times intervals in the oven (g).

After the moisture content percentage is remained constant, the adsorbent is then blended by using dry blender. Next, the adsorbent were sieved by using sieve shaker for about 5 minutes. Only the adsorbent with size 45  $\mu$ m (C.Namasivayam *et al.*, 1996) is used for overall experiments. Moreover, the adsorbent stored in the plastics container in order to remained the moisture content.



Figure 3.3: Dried water hyacinth after blended.

## 3.3 Adsorbate preparation

Acid Blue 25 dye is anionic dye with the molecular formula  $C_{20}H_{13}N_2NaO_5S$  which commonly used in textiles, paper and also detergent industries. The maximum adsorption wavelength of Acid Blue 25 by using UV-VIS is 600 nm. The structures of Acid Blue 25 were shown in the figure 3.4. The Acid Blue 25 was used directly without any purification or pre-treatment process or procedures and diluted by using distilled water. The stock solution of 1000 mg/L was prepared by dissolving Acid Blue 25 in 1000 mL distilled water.



Figure 3.4: The structure of Acid Blue 25 dye
#### 3.4 Fourier Transform Infra Red study

Fourier Transform Infra-Red (FTIR) analysis was carried out on the dried water hyacinth to determine its functional groups, by using FTIR Spectrometer, Thermo Nicolet, with spectra were set from 4000 to 400 cm<sup>-1</sup>.

## **3.5** Adsorption experiments

#### 3.5.1 Effect of adsorbent dosage

The initial dye concentration of 300 to 5000 mg/L were used in 50 mL of solution in conjunction with dried water hyacinth sample of 0.01 to 1.0 g. Contact time, speeds and pH were 60 minutes, 200 rpm and 3, respectively. The dye concentrations are varied to observe the pattern of results for optimum dosage. The value of optimum dose is used for other parameters.

#### 3.5.2 Effect of initial concentration

The adsorbent dosage of 0.30 - 0.80 g were used in 50 mL of 80 - 500 mg/L of initial dye concentrations were the other parameters such as contact time, speeds and pH were at 60 minutes, 200 rpm and 3. The value for the optimum initial dye concentrations is used for the next parameters.

The pH was manipulated from the range 1.0 - 11 at different values of initial dye concentrations in order to see the trend of the experiments. The first and second parameters achieved optimum before is used in this experiment. Only pH value is manipulated.

## 3.5.4 Effect of contact time

The effect of contact time is investigated for 10 to 120 minutes at pH 2 and at different values of initial concentrations near their optimum values. The similar pattern of results for the optimum value is obtained.

## **CHAPTER 4**

## **RESULTS & DISCUSSIONS**

## 4.1 Effect of adsorbent dosage

The study of adsorbent dosage effect on Acid Blue 25 dye, has been conducted by using dried water hyacinth dosage from range (0.1 - 1.0g) while other parameters remain constant ( $C_0 = 300 \text{ mg/L}$ , pH = 3.0, contact time = 60 minutes, speed = 200 rpm). Results are as shown in figure 4.1 (a). It shows that the uptake of the Acid Blue 25 increased with the increase amount of adsorbent dosage. The adsorption percentage remains constant after 93% at dosage of 0.60 g even after increasing the dosage of the adsorbent. Whereas for the the amounts of dye adsorbed per unit mass remain decreased from 81.75 to 18.68 mg/g as shown in figure 4.1 (b). The experiment is repeated by using different initial concentration which is 400mg/L and 500mg/L while the other parameter is remains constant. This experiment is performed to see the trend of percentage removal of dye and similar results and trends as in the earlier experiment were obtain as shown in figure 4.1 (a) were dosage is 0.60g. It shows that, the optimum adsorbent dosage for removal of Acid Blue 25 is at 0.60 g of dried water hyacinth. It is similar trend shown by M.M.El. Zawahry et al., (2004) with relating low error between this experiments and his journal on removal of azo and anthraquinone dyes from aqueous solutions by Eichhornia crassipes.

The percentage removal of Acid Blue 25 increased with the increase in adsorbent dosage. It is might be due to increased adsorbent surface area and availability of more adsorption sites resulting from the increase of adsorbent dosage. This result is similar with the results from the Low *et al.*, (1995) and M. Arami *et al.*, (2008) for removal of the methylene blue by using dried water hyacinth. However, the decreasing of adsorption dye per unit mass with increasing of adsorbent dosage is because of there is reduction on effective surface area or in simple words it is already saturated. Similar results by H. Aydin *et al.*, (2006) on adsorption of acid dyes by shells of bittim M. M. El Zawahry *et al.*, (2004) on removal of azo and anthraquinone dyes by water hyacinth.



Figure 4.1 (a): Percentage removal for the effect of adsorbent dosage for removal of Acid Blue 25. Time = 60 min, speed = 200 rpm, pH = 3.0, C<sub>o</sub> = 300 - 500 mg/L, dosage = 0.1 - 1.0 g, at room temperature.



Figure 4.1 (b): Amount of dye sorbed for the effect of adsorbent dosage for removal of Acid Blue 25. Time = 60min, speed = 200 rpm, pH = 3.0, C<sub>o</sub> = 300 - 500 mg/L, dosage = 0.1 - 1.0 g, at room temperature.

## 4.2 Effect of Initial concentration

The study of initial concentration effect on Acid Blue 25 dye uptake can be observed in Figure 4.2. Experiment is performed by varying the value of initial concentration from the range of 80 mg/L to 500 mg/L and fixed the value for other parameters (dosage = 0.60g, speed = 200 rpm, pH = 3.0, time = 60 minutes). In figure 4.2 (a) indicates that as the initial concentration increase, the percentage removal increased until it reaches equilibrium at 400 mg/L and after that the dye uptake started to remain constant. Besides, the results for amount of dye sorbed per unit mass is continually increase by increasing of concentration of Acid Blue 25 dye as shown in figure 4.2 (b). Similar with the first parameter, experiment is repeated by using different adsorbent dosage 0.30 g and 0.80 g while remained other parameter remain constant.

The trend for repeated trials are observed and the same trend of graph has been obtained as the dosage of 0.60 g. From the graph, optimum initial concentration is at 400 mg/L where the percentage of adsorption is 92% of Acid Blue 25 dye.

From Figure 4.2 (a) and (b), we can see that the uptake of dye increases with increase in the initial dye concentration. This is might be because of the initial dye concentration provides necessary driving force to overcome the resistance to the mass transfer between the aqueous and solid phase. The increase in dye concentration diminishes the resistance and makes more contact between dye and adsorbent. Availability of dye molecules in the vicinity of adsorbent also increases while increasing the concentration, which results in high uptake of dye at higher concentration. Similar finding is also reported by Palanysamy *et al.*, (2009). However, for the adsorbent dosage 0.30 g, the amount of percentage adsorbed is decreasing after 300mg/L. This is because of when the adsorption site of the adsorbent is already saturated, backwash process will happen on the adsorbent surface. There could not uptake the amount of dye into the adsorption site. It is due to smaller mass transfer occurring since all the adsorption sites has been fully occupied.



Figure 4.2 (a): Percentage removal for the effect of initial concentration for removal of Acid Blue 25. Time = 60 min, speed = 200 rpm, pH = 3.0, C<sub>o</sub> = 80 - 500 mg/L, dosage = 0.30 - 0.80g, at room temperature.



Figure 4.2 (b): Amount of dye sorbed for the effect of initial concentration for removal of Acid Blue 25. Time = 60 min, speed = 200 rpm, pH = 3.0, C<sub>o</sub> = 80 - 500 mg/L, dosage = 0.30 - 0.80g, at room temperature.

## 4.3 Effect of pH

The pH of the aqueous solution is an important controlling parameter in the dyes sorption processes. The influence of pH on the adsorption capacity was observed over a pH range of 1 - 11 while other parameters remain constant at optimum condition for the first and second parameter which is at 0.60 g adsorbent dosage and 400 mg/L of initial concentration and speed = 200 rpm, contact time = 60 minutes and at room temperature. As can be seen at figure 4.3 (a) the maximum capacity for initial concentration 400 mg/L achieves at pH value of 2.0 and the optimum uptake of Acid Blue 25 dye is 92%. Whereas, for the amount of dye per unit mass is decreasing with the increasing of pH and can be seen in the Figure 4.3(b). Similar with other parameter above, in this parameter, method is repeated in different initial concentration in order to see the trend of the optimum pH of dried water hyacinth on the Acid Blue 25 dye. Optimum pH for different concentration is remains the same which is at pH 2.0.

With the increase of pH value, the adsorption capacity for each initial concentrations decreases. Acid Blue 25 is anionic in nature and increased adsorption in an acidic medium. Whereas, it is increased desorption in an alkaline medium showed that these dyes were held by the adsorbent, most probably by ion exchange. A similar trend was observed for desorption of congo red and procion orange by waste orange peel (Namasivayam *et al.*, 1996). At lower pH, there are excessive in H<sup>+</sup> ion while Acid Blue 25 is anionic, so adsorption rate towards the dried water hyacinth is higher. This is because, the molecules of dye anions bind at the sorption sites at the surface of sorbent. Thus, enhance the capability of the binding activity between dye anions and sorbent surface through electrostatic forces of attraction. Meanwhile, the removal of dye is low at high pH due to the excess of hydroxide ions, OH<sup>-</sup>, competing with the molecules of dye anions to bind at the sorption sites at the surface of sorbent. This statement is supported by the FTIR analysis that shows lowered absorbance after the dye uptakes from 3411.94 to 3368.89.



Figure 4.3 (a): Percentage removal for the effect of pH for removal of Acid Blue 25. Time = 60 min, speed = 200 rpm, pH = 1.0 - 11.0, C<sub>o</sub> = 300 - 500 mg/L, dosage = 0.60 g, at room temperature.



Figure 4.3 (b): Amount of dye sorbed for the effect of pH for removal of Acid Blue 25. Time = 60 min, speed = 200 rpm, pH = 1.0 - 11.0, C<sub>o</sub> = 300 - 500 mg/L, dosage = 0.60 g, at room temperature.

## 4.4 Effect of contact time

Effect of contact time is another important parameter that influences the adsorption rate of Acid Blue 25 dye in the dried water hyacinth. This parameter is identified by using optimum condition of another 3 parameter which at 0.60 g adsorbent dosage, 400 mg/L initial concentration, and pH 2 while the other parameter is remain constant at 200 rpm speeds and room temperature. The contact time range for this experiment is within 10 - 120 minutes. Figure 4.4 shows the result of this trial where (a) indicate the percentage dye removal and (b) is the sorption equilibrium per mass. It can be explained clearly that the dye uptake increase with the increasing of time contact between the dye and adsorbent until it reached equilibrium at 100 minutes. Further experiment on time contact results in constant value of removal which is at 92%. Another two trials were repeated by using different initial concentration which is 300 mg/L and also 500 mg/L. The outcome from the other trials is similar with the first trials.

The rate of adsorption is higher in the beginning, where at the first 50 minutes of interactions, which due to large available surface area of the dried water hyacinth. After that, the capacity of the adsorbent fully occupied which is at equilibrium state or it is become saturated, the rate of uptake is getting slower from the exterior to the interior sites of the adsorbent particles similar trend found in the B.H.Hameed *et al.*, (2008). If this experiments is proceed, desorption process will take over than the adsorption. This is due the interactions between dried water hyacinth and dyes is relating slow.



Figure 4.4 (a): Percentage removal for the effect of contact time for removal of Acid Blue 25. Time = 10 - 120 min, speed = 200 rpm, pH = 2.0,  $C_0 = 300 - 500$  mg/L, dosage = 0.60 g, at room temperature.



Figure 4.4 (b): Amount of dye sorbed for the effect of contact time for removal of Acid Blue 25. Time = 10 - 120 min, speed = 200 rpm, pH = 2.0,  $C_0 = 300 - 500$  mg/L, dosage = 0.60 g, at room temperature.

#### 4.5 Kinetics of the adsorption process

Pseudo – second-order illustrates the adsorption kinetic of Acid Blue 25. It is to indicate whether it is agreed very well to the experimental data or not. The second-order kinetic model is express as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$
(4.10)

where  $k_2$  is the pseudo-second-order rate constant (g/mg.min);  $q_e$  the quantity of dye adsorbed at equilibrium (mg/g);  $q_t$  the quantity of dye adsorbed at time t (mg/g) and t is the time (min).

Figure 4.5 shows the removal rate of Acid Blue 25 was very fast during the initial stages of the adsorption processes, especially for initial dye concentration of 400mg/L. However, the adsorption equilibrium was reached at 100 min for all three concentrations tested. Furthermore, the data fitted well the second order kinetic model ( $R^2 > 0.999$ ) for every line. Besides, the calculated q<sub>e</sub> values agree very well with the experimental data listed in table 4.1. Similar kinetic results were reported in the removal of the diazo dye reactive black 5 by sunflower seed shells and mandarin peelings by J.F.Osma *et al.*, (2007).

**Table 4.1:** Pseudo-second-order adsorption rate constants and calculated and experimental q<sub>e</sub> values for different initial concentration of Acid Blue 25 at pH 2.

Acid Blue 25 (mg/L)	K <sub>2</sub> (g/mg.min)	q <sub>e</sub> calc (mg/g)	q <sub>e</sub> exp (mg/g)	R²
300	0.1936	22.42	22.72	0.999
400	0.2048	30.25	31.25	1
500	0.0025	60.37	40	0.999



Figure 4.5: Pseudo-second- order adsorption kitetics of Acid Blue 25 at pH 2 and different initial Acid Blue 25 concentrations.

#### 4.6 Adsorption Isotherms

## 4.6.1 Langmuir isotherm

The Langmuir isotherm was used for its ability to explain the experimental results. The derivation of the Langmuir isotherm is based on the assumption of ideal monolayer adsorption on a homogenous surface. Once a dye molecule occupies a site, no further adsorption can take place at that site. The Langmuir adsorption isotherm has been successfully used to explain the dye removal by using hazelnut shells and wood sawdust (F.Ferrero., 2007). The Langmuir isotherm was expressed as:

$$\boldsymbol{q}_{\boldsymbol{e}} = \frac{K_L \boldsymbol{q}_m \boldsymbol{C}_{\boldsymbol{e}}}{1 + K_L \boldsymbol{C}_{\boldsymbol{e}}} \tag{4.20}$$

where  $q_e$  is the equilibrium adsorption capacity (mg/g),  $q_m$  the maximum amount of dye adsorbed (mg/g) corresponding to monolayer coverage,  $K_L$  the Langmuir constant (L/mg) and  $C_e$  is the equilibrium concentration of dye in bulk solution (mg/L).

Figure 4.6 fitted the Langmuir equation, accordingly to the data which also confirmed by the high value of  $R^2$  which is 0.876. This verifies that the sorption of AB25 on dried water hyacinth. Table 4.2 indicates that the computed maximum amount of B25 adsorbed (q<sub>m</sub>) of which is 83.33 mg/g. this value was similar with the value found by J.F.Osma *et al.*, (2007) in the removal of reactive black 5.

Furthermore, in order to see whether this experimental is favourable, the dimensionless separation factor  $R_L$  is identified.  $R_L$  can be expressed as:

$$R_L = \frac{1}{1 + K_L C_o} \tag{4.30}$$

where  $C_o$  is the initial concentration of Acid Blue 25. The value of  $R_L$  indicates the shape of the isotherm to be either unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favourable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ). The  $R_L$  values between 0 and 1 indicate favourable adsorption. As shown in figure 4.7, the value of  $R_L$  is between 0.001998 - 0.004989. It is shows that the adsorption process is favourable.

**Table 4.2:** Langmuir isotherm constant for Acid Blue 25 sorption on dried water hyacinth at adsorbent dosage 0.40g (initial concentration: 300, 400, 500 mg/L)

$C_e(mg/L)$	q <sub>e</sub> (mg/g)	$C_e/q_e$	$q_m(mg/g)$	K <sub>L</sub>	$R^2$
29.17021	33.85372	0.861654			
33.23404	45.84574	0.72491	83.33	0.028235	0.876
66.91489	54.13564	1.23606			



Figure 4.6: Langmuir isotherm plots for Acid Blue 25 sorption on dried water hyacinth



Figure 4.7: Separation factor for Acid Blue 25 sorption on dried water hyacinth.

#### 4.6.2 Freundlich isotherm

The freundlich isotherm is an empirical model that considers heterogeneous adsorptive energies on the adsorbent surface. It is express by the following equation:

$$\boldsymbol{q}_{\boldsymbol{e}} = \boldsymbol{K}_{\boldsymbol{F}} \boldsymbol{C}_{\boldsymbol{e}}^{1/n} \tag{4.40}$$

where  $q_e \text{ (mg g}^{-1}\text{)}$  is the amount of dye adsorbed at equilibrium, Ce (mg L<sup>-1</sup>) the dye concentration at equilibrium and K<sub>F</sub> and n are the Freundlich constants for the system, which are indicators of adsorption capacity and intensity, respectively.

To determine the constants K<sub>F</sub> and n the linear form of the equation is used:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{4.50}$$

The plot of ln  $q_e$  versus ln Ce (Figure 4.8) is employed to generate the intercept  $K_F$  and the slope 1/n. The values of  $K_F$ , n, the experimental and the calculated  $q_e$  (mg g<sup>-1</sup>) values and the linear regression correlation (R<sup>2</sup>) for Freundlich are given in the table 4.3. From the figure 4.8, The Freundlich constant,  $K_F$  increased with increase in temperature. The value of n shown in table 4.3 is greater than 1.0 indicating the adsorption Acid Blue 25 on to dried water hyacinth is favourable. There is no remarkable difference in the correlation coefficient between Freundlich and Langmuir models. The adsorption isotherm data fits reasonably well for both Langmuir and Freundlich models.

**Table 4.3:** Freundlich isotherm constant for Acid Blue 25 sorption on dried water hyacinth at adsorbent dosage 0.40g (initial concentration: 300, 400, 500 mg/L)

Acid Blue 25 (mg/L)	q <sub>e</sub> calc (mg/g)	q <sub>e</sub> exp (mg/g)	K <sub>F</sub>	n	$R^2$
300	37.79522	37.63692			
400	40.02765	40.34195	8.5677	2.2727	0.999
500	54.46197	54.4919			



Figure 4.8: Freundlich isotherm plots for Acid Blue 25 sorption on dried water hyacinth

#### 4.7 FTIR analysis

FTIR analysis is done twice during the research. Firstly is before the reaction with the dyes. Secondly is after uptake at optimum condition for all the parameters. FTIR is commonly used in order to see the functional groups of adsorbents. In simple words it is as a method of characterization of dried water hyacinth before and after the experiment. Figure 4.9 shows the adsorption peak of several compounds that found on the dried water hyacinth. The adsorption site indicated maximum wave number at 3200 cm<sup>-1</sup> to 3400 cm<sup>-1</sup>, representing stretching of –OH groups. Furthermore absorption peaks around 3300 cm<sup>-1</sup> to 3600 cm<sup>-1</sup> represent the presence of NH<sub>2</sub> which is the amine group (P.N palanisamy *et al.*, 2009). The stretching at 1618 cm<sup>-1</sup> is represents C - C bending. Whereas for the C – H bending approximately at 2900 cm<sup>-1</sup> and for C –O is around 1200 cm<sup>-1</sup>.

However after running the experiments at optimum conditions for all the parameters, we can see the FTIR analysis on Figure 4.10. The peak is became lowered and some parts of it is becoming straight line. It is convinced that the adsorption process between dried water hyacinth and Acid Blue 25 occurs.



Figure 4.9: The FTIR analysis of dried water hyacinth before dye uptake



Figure 4.10: The FTIR analysis of dried water hyacinth after dye uptake

#### **CHAPTER 5**

## **CONCLUSIONS AND RECOMMENDATIONS**

#### 5.1 Conclusions

All the data and analysis done in this study is fulfilling the objectives of the study which is to study the removal of Acid Blue 25 from aqueous solution. The removal of Acid Blue 25 by using dried water hyacinth is enhanced by manipulating the initial concentration of Acid Blue 25, such as adsorbent dosage, pH and also contact time at the optimum conditions. The optimum conditions for all the parameters are 400 mg/L of initial concentration, 0.60g dosage, pH 2 and also 100 minutes of time contact.

In order to verify the experimental data on the adsorption process, pseudosecond-order analysi, Langmuir and freundlich isotherm were performed. Data that analyze by using pseudo-second-order is used for the comparison between  $q_e$  calculated and  $q_e$  experimental which is at high value of  $R^2$  (0.999). Furthermore, the calculated  $q_e$ values agree very well with the experimental data with low value of error. So it is shows that, this study is verified using pseudo-second-order for the kinetics of the adsorption process.

Besides, for the Langmuir isotherm, it is used to explain the ability of dried water hyacinth in this experiment. For the first analysis, the value of  $q_m$ , the maximum amount of dye adsorbed is 83.33 mg/g and the value of K<sub>L</sub>, the Langmuir constant is 0.028235 L/mg. Whereas the value of R<sup>2</sup> is 0.876. Moreover, for second analysis on separation

factor or  $R_L$  is on the range between 0.001998 - 0.004989 which is shows that the adsorption process is favourable.

Freundlich isotherm is commonly just the same as the Langmuir isotherm. As for the freundlich isotherm, is an empirical model that considers heterogeneous adsorptive energies on the adsorbent surface. In these experiments is favourable since the value of nis more than 1. So, this study is verified for pseudo-second-order kinetic analysis and also Langmuir and freundlich isotherm.

## 5.2 **Recommendations**

In this study, experiments were performing in the batch reaction process. In order to scale up this experiment, it should be continued by running it in an adsorption column. Since, nowadays concern of the environment is relating high among the society. So, by performing in industrial scale experiments, it will help much on the environmental problems around the world.

Furthermore, during the experiment, there is no analysis on the Scanning Electrostatic Microscopic (SEM). By doing these analysis, the structure of dried water hyacinth on both before and after dye uptake can be observed. Moreover, by doing SEM analysis, it will be identified whether the dried water hyacinth is a good adsorbent or not.

Besides, for optimizing the experiment to solve the real world's environmental problems, these experiments can be performed by using the wastewater that comes from the industries such as textiles industries. Since the Acid Blue 25 is commonly used in textiles industries.

#### REFERENCES

- Abdelhamid. A.M., Gabr A.A., 1991. Evaluation of water hyacinth as feed for ruminants. *Archives of Animal Nutrition (Archiv fuer Tiererna "hrung)* 41 (7/8), 745–756.
- Arami. M, Nargess. Y.L, Niyaz. M. M., Evaluation of the adsorption kinetics and equilibrium for the potential removal of acid dyes using a biosorbent. *Journal of Chemical Engineering* 139 (2008) 2–10
- Aweke G, 1993. The water hyacinth (*Eichhornia crassipes*) in Ethiopia. *Bulletin des* se'ances. Acade'mie royale des Sciences d'outremer, Brussels 39 (3), 399–404.
- Aydin. H, Baysal G, 2006., Adsorption of acid dyes in aqueous solutions by shells of bittim (*Pistacia khinjuk* Stocks). *Journal of desalination* (196) 248–259.
- Bansal, R.C., Goyal, M., 2005. Activated Carbon Adsorption. Taylor & Francis Group, Boca Raton.
- Bolenz S., Omran H., Gierschner K., 1990. Treatments of water hyacinth tissue to obtain useful products, *Journal of Biological Wastes* 33 (4), 263–274.
- Chen, B.N., Hui, C.W., McKay, G., 2001. Film-pore diffusion modeling and contact time optimization for the adsorption of dyestuffs on pith, *Journal of Chem. Eng.* 84, 77–94.
- Cheng R., Oub S., Li M., Li Y., Xiang B., 2009. Ethylenediamine modified starch as biosorbent for acid dyes, *Journal of Hazardous Materials* 172 (2009) 1665–1670

- Cheremisinoff, N.P., 2002. Handbook of Water and Wastewater Treatment Technologies.Butterworth-Heinemann, Boston.
- El Zawahry M.M, Kamel M.M., 2001. Removal of azo and anthraquinone dyes from aqueous solutions by Eichhornia Crassipes, *Journal of Water Research* 38 (2004) 2967–2972.
- El-Khaiary M. I., 2006. Kinetics and mechanism of adsorption of methylene blue from aqueous solution by nitric-acid treated water-hyacinth, *Journal of Hazardous Materials* 147 (2007) 28–36.
- Ferrero F., 2007. Dye removal by low cost adsorbents: hazelnut shells in comparison with wood sawdust, *Journal of Hazard. Mater* 142, 144–152.
- Ghodbane H., Hamdaoui O., 2009. Intensification of sonochemical decolorization of anthraquinonic dye Acid Blue 25 using carbon tetrachloride, *Journal of Ultrasonics Sonochemistry* 16 (2009) 455–461
- Gunarson C.C., Petersen C.M., 2007. Water hyacinth as a resource in agriculture and energy production: A literature review, *Journal of waste management* 27 (2007)117-129
- Gupta V.K., Carrott P.J.M., Ribeiro Carrott, M.M.L., Suhas, 2009 Low cost adsorbents: growing approach to wastewater treatment – a review. Crit. Rev. Env. Sci. Technol., in press.
- Gupta V.K., Suhas , 2008. Application of low-cost adsorbents for dye removal A review, *Journal of Environmental Management* 90 (2009) 2313–2342.
- Hameed .B.H., (2008). Spent tea leaves: A new non-conventional and low-cost adsorbent for removal of basic dye from aqueous solutions. *Journal of Hazardous Materials*.

- Ho Y. S. and McKay G., 1998. Kinetic models for the sorption of dye from aqueous solution by wood, *Institution of Chemical Engineers Trans IChemE*, Vol 76, (B) 183-191.
- Hsueh C.C, Chen B.Y, Chia-Y Y, 2009. Understanding effects of chemical structure on azo dye decolorization characteristics by *Aeromonas hydrophila, Journal of Hazardous Materials*
- Hunger K., 2003. Industrial Dyes: Chemistry, Properties, Applications. Wiley-VCH,
- Juang R.-S, Wu F.C, Tseng R.-L, 2002. Characterization and use of activated carbons prepared from bagasses for liquid-phase adsorption, *Colloids Surf* A 201, 191–199.
- Lee. B., 1979. Insects for controlling water weeds. Rural-Research (105), 25–29.
- Low K. S., Lee C. K. and Tan K. K., 1995. Biosorption of basic dyes by dried Water Hyacinth, *Journal of Bioresource Technology* 52 (1995) 79-83.
- Malik A., 2007. Environmental challenge vis a vis opportunity: The case of water hyacinth, *Journal of Environment International* 33 (2007) 122–138
- McKay, G., El-Geundi, M., Nassar, M.M., 1996. Equilibrium studies for the adsorption of dyes on bagasse pith, *Adsorpt. Sci. Technol* 15, 251–270.
- Namasivayam C., Prabha D. and Kumutha M., 1996. Removal of Direct Red and Acid Brilliant Blue by Adsorption on to Banana Pith, *Journal of Bioresource Technology* 64 (1998) 77-79.
- Osma J.F., Saravia V., Toca-Herrera L.J., Rodrigueze Couto S., 2007. Sunflower seed shells: A novel and effective low cost adsorbent for the removal of diazo dye Reactive Black 5 from aqueous solutions, *Journal of Hazardous Materials* 147 (2007) 900 905

- Palanisamy P.N., Sivakumar P., 2009. Kinetic and isotherm studies of the adsorption of Acid Blue 92 using a low-cost non-conventional activated carbon, *Journal of Desalination* 249 (2009) 388–397
- Poddar K., Mandal L., Banerjee G.C., 1991. Studies on water hyacinth (Eichhornia crassipes) Chemical composition of the plant and water from different habitats. *Journal of Indian Veterinary* 68, 833–837.
- Sadik W.A., 2007. Decolourization of an azo dye by heterogeneous photocatalysis, *Trans IChemE* 85 (B6) 515–520.
- Selvam K., Swaminathan K., Chae K. S, 2002. Decolourization of azo dyes and a dye industry effluent by a white rot fungus Thelephora sp, *Journal of Bioresource Technology* 88 (2003) 115–119.
- Sivaraj R., Namasivayam C., Kadirvelu K., 2001. Orange peel as an adsorbent in the removal of Acid violet 17 (acid dye) from aqueous solutions, *Journal of Waste Management* 21 (2001) 105-110 Weinheim; [Cambridge].
- Wilson JR., Holst N., Rees M.. Determinants and patterns of population growth in water hyacinth. Aquat Bot 2005;81:51–67.
- Zheng J.C., Feng H.M., Lam H.W., Sing P. K. Lam, Y.W.Ding, H.Q. Yu, Removal of Cu(II) in aqueous media by biosorption using water hyacinth roots as a biosorbent material, *Journal of Hazardous Materials* 171 (2009) 780–785

# **APPENDICES A**

## EXPERIMENTAL PROCESS AND EQUIPMENTS USED



Figure A1: Collecting the water hyacinth at Gambang Lake, Pahang



Figure A2: Washing the aerial and leaf by using tap water



Figure A3: After washing air dried before drying on the oven



Figure A4: Water hyacinth before and after drying in the oven over 24-72 hours



Figure A5: Blending process by using blender



Figure A6: Dried water hyacinth



Figure A7: Acid Blue 25 before adsorption process



Figure A8: Orbital shaker



Figure A9: Refrigerated centrifuge



Figure A10: pH meter



Figure A11: Desicator



Figure A12: UV-Vis spectrophotometer



Figure A13: Fourier transform infrared

# **APPENDICES B**

## **EXPERIMENTAL DATA**

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I able KI:	Mass of	dried	water	hvacinth	during	drving
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Time (min)	Initial mass (g)	Final mass (g)	Moisture content
			(%)
1	650.0	211.1	207.91
2	211.1	63.8	230.88
3	63.8	42.5	50.12
4	42.5	42.3	0.47

Table B2: Standard curves data

Concentration,		Adsorption value				real
mg/mL	A1	A2	A3	A4	Average	OD
0.02	0.002	0.005	0.001	0.004	0.003	0.006
0.04	0.21	0.202	0.222	0.224	0.2145	0.429
0.06	0.486	0.419	0.419	0.419	0.43575	0.8715
0.08	0.681	0.677	0.678	0.678	0.6785	1.357
0.1	0.948	0.945	0.945	0.947	0.94625	1.8925

Dosage,	% Removal				
(g)	300 mg/L	400mg/L	500mg/L		
0	0	0	0		
0.1	46.11348	36.04787	33.75319		
0.2	75.24113	73.06915	55.26383		
0.3	87.38652	85.2367	79.11489		
0.4	90.2766	91.69149	86.61702		
0.5	91.11348	92.9867	90.52553		
0.6	90.89007	93.89362	92.73191		
0.7	90.89007	93.73936	94.01915		
0.8	90.60638	92.57979	91.69149		
0.9	91.1383	93.23936	92.74681		
1	91.75177	93.40957	93.85106		

Table B3: Percentage removal experimental data for the effect of adsorbent dosage

(Co=300, 400, 500 mg/L, Dose=0.10-1.0 g)

Table B4: Equilibrium adsorption data for the effect of adsorbent dosage

Dosage,		qe (mg/g)	
(g)	300 mg/L	400mg/L	500mg/L
0	0	0	0
0.1	69.1702	72.0957	84.383
0.2	56.4309	73.0691	69.08
0.3	43.6933	56.8245	65.929
0.4	33.8537	45.8457	54.136
0.5	27.334	37.1947	45.263

0.6	22.7225	31.2979	38.638
0.7	19.4764	26.7827	33.578
0.8	16.9887	23.1449	28.654
0.9	15.1897	20.7199	25.763
1	13.7628	18.6819	23.463

**Table B5:** Percentage removal experimental data for the effect of initial concentration(Dose=0.3, 0.6, 0.8 g, Co=80-500 mg/L)

Initial conc,	% Removal				
(mg/L)	0.30 g	0.60 g	0.80 g		
0	0	0	0		
80	71.0904	67.7394	69.375		
100	73.3085	73.3936	76.766		
150	83.078	85.5816	85.0071		
200	70.6649	87.4202	88.2447		
250	67.6681	83.2894	90.0638		
300	87.3865	90.6064	90.6064		
350	87.386	86.1611	91.1337		
400	85.2367	92.5798	92.5798		
500	79.1149	91.6915	91.6915		

Initial	qe, (mg/g)				
conc, (mg/L)	0.30 g	0.60 g	0.80 g		
0	0	0	0		
80	9.478723	4.515957	3.46875		
100	12.21809	6.116135	4.797872		
150	20.7695	10.6977	7.969415		
200	23.55496	14.57004	11.03059		
250	28.19504	17.35195	14.07247		
300	43.69326	22.6516	16.9887		
350	50.97518	25.13032	19.93551		
400	56.82447	30.85993	23.14495		
500	65.92908	38.20479	28.65359		

**Table B6:** Equilibrium adsorption data for the effect of initial concentration(Dose=0.3, 0.6, 0.8 g, Co=80-500 mg/L)

**Table B7:** Percentage removal experimental data for effect of pH(Co=300, 400, 500 mg/L, pH=1-11)

	Percentage removal (%)		
pН	300mg/L	400mg/L	500mg/l
0	0	0	0
1	64.4069	84.3511	87.1617
2	69.1809	92.2261	91.566
3	67.4282	88.4495	87.0319
4	63.125	80.8989	75.8213
5	56.6622	68.8138	62.817
6	50.9681	56.1809	57.0511
7	41.6862	50.2766	48.7319
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8	36.234	48.5213	43.9234
9	30.6809	46.0213	44.2426
10	29.2128	33.3085	47.9234
11	24.5319	40.6755	34.4979

**Table B8:** Equilibrium adsorption data for effect of pH(Co=300, 400, 500 mg/L, pH=1-11)

pН		qe (mg/g)	
	300mg/L	400mg/L	500mg/l
0	0	0	0
1	21.46897	28.11702	36.31738
2	23.06028	30.74202	38.15248
3	22.47606	29.48316	36.2633
4	21.04167	26.96631	31.5922
5	18.88741	22.93794	26.17376
6	16.98936	18.72695	23.77128
7	13.89539	16.75887	20.30496
8	12.07801	16.17376	18.30142
9	10.22695	15.34043	18.4344
10	9.737589	11.10284	19.96809
11	8.177305	13.55851	14.37411

Contact	Percer	ntage remova	al (%)
time, min	300 mg/L	400 mg/L	500 mg/L
0	0	0	0
10	91.06028	89.32181	87.15532
20	91.11702	90.92287	88.65106
30	91.69149	91.50266	89.20851
40	92.0461	90.97074	89.18511
50	91.37589	91.84574	91.48511
60	91.30142	91.6516	91.86383
80	91.29787	91.57713	91.63191
100	89.48582	92.09309	92.27447
120	91.54255	91.40691	92.03191

**Table B9:** Percentage removal experimental data for effect of time $(C_0=300, 400, 500 \text{ mg/L}, \text{ contact time} = 10-120)$ 

**Table B10:** Equilibrium adsorption data for effect of time(Co=300, 400, 500 mg/L, contact time = 10-120)

Contact time,		qe (mg/g)	
min	300 mg/L	400	500
		mg/L	mg/L
0	0	0	0
10	22.76507	29.77394	39.76958
20	22.77926	30.30762	39.7684
30	22.92287	30.50089	39.75643
40	23.01152	30.32358	39.74904
50	22.84397	30.61525	39.763
60	22.82535	30.55053	39.76455

00			
80	22.82447	30.52571	39.76463
100	22.37145	30.6977	39.80238
120	22.88564	30.46897	39.75953

# **APPENDICES C**

# **EXPERIMENTAL GRAPH**



Figure C1: Standard curve for AB25

### **APPENDICES D**

### PROCEDURE FOR SAMPLE ANALYSIS

#### **Procedure using UV-Vis Spectrophotometer**

- 1) Switch on the UV-Vis Spectrophotometer.
- 2) Wait until the equipment is calibrated completely.
- 3) Sample is diluted with minimum three times of dilution factor.
- 4) Place the diluted sample into the cuvette cell enough until it reaches the margin on the cell.
- 5) Choose the characteristics to be analyzed on the screen and be sure to set the maximum wavelength of the sample before analyzing.
- 6) The data can be obtained at the 'Data Display' button.

#### Procedure using Fourier Transform Infra Red

- 1) Place the smart performer and switch on the FTIR.
- 2) Click on the software EZ OMNIC on the computer.
- 3) Follow the instructions given in the software.
- 4) Before placing the sample on the plate, it must be cleaned with acetone first.
- 5) Carefully handle the smart performer and the plate because it is a sensitive

device.

- 6) Place the sample onto the cleaned plate.
- 7) Find the peaks according to the characteristics in the software.
- 8) Print out the data.

## Procedure for using refrigerated centrifuge

- 1. Place the sample into the centrifuge tubes.
- 2. Set the temperature, speeds and time by using button on the centrifuge screen.
- 3. Close the centrifuge tray by using the cap until finger tight only.
- 4. Close the cover of the centrifuge until blue lights appear.
- 5. Click start