



**Decolourisation of Methylene Blue using  
Activated Carbon from Coffee Residue  
as a Low Cost Adsorbent**

by

**Nur Ismah Izzati binti Ismail**

A report submitted in fulfillment of the requirements for the degree of  
Bachelor of Applied Science (Sustainable Science) with Honours

**FACULTY OF EARTH SCIENCE  
UNIVERSITI MALAYSIA KELANTAN**

2017

## DECLARATION

I, Nur Ismah Izzati binti Ismail with matric number E13A363, under the Faculty of Earth Science, undertaking Sustainable Science declares that this thesis entitled “Decolourisation of Methylene Blue using Ativated Carbon from Coffee Residue as a Low Cost Adsorbent” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : \_\_\_\_\_

Name : \_\_\_\_\_

Date : \_\_\_\_\_

## ACKNOWLEDGEMENT

As for the completion of this Final Year Project report, I would like to express my gratitude to Universiti Malaysia Kelantan to provide me this platform to experience myself in conducting laboratory experiments, polishing my soft skills and having the need of a good project management. Moreover, what it is meant to have the ability and skills needed in order to succeed in life.

Besides that, I would like to thank my esteemed project supervisor Dr. Rozidaini Bt Mohd Ghazi for her valuable guidance and advices that shown me the right orders in completing this task at every stage with success.

I would like to appreciate the hospitality given by Ruby Café as to provide the coffee residues needed to run the experiments for this project study.

Nonetheless, I would like to thank my classmates for the support and cooperation given to excel in this task by sharing our knowledge and thrust. They are my reason to thrive harder in life and challenge myself to become better.

Last but not least, I would certainly give my foremost appreciation to my family that back me up from time to time. They are the reason for my joy and motivation of my hard work including making this task a much smoother and meaningful journey. They assist me in critical thinking and better decision making in life.

## TABLE OF CONTENTS

<b>Content</b>	<b>Page</b>
<b>TITLE</b>	<b>i</b>
<b>DECLARATION</b>	<b>ii</b>
<b>ACKNOWLEDGEMENT</b>	<b>iii</b>
<b>TABLE OF CONTENTS</b>	<b>iv</b>
<b>LIST OF TABLES</b>	<b>vii</b>
<b>LIST OF FIGURES</b>	<b>viii</b>
<b>LIST OF ABBREVIATIONS</b>	<b>ix</b>
<b>LIST OF SYMBOLS</b>	<b>x</b>
<b>ABSTRACT</b>	<b>xi</b>
<b>ABSTRAK</b>	<b>xii</b>
<b>CHAPTER 1 INTRODUCTION</b>	
1.1 Background of Study	1
1.2 Problem Statement	3
1.3 Objectives	4
1.4 Significance of Study	4
<b>CHAPTER 2 LITERATURE REVIEW</b>	
2.1 Industrial Wastewater	5
2.2 Textile Effluents	7
2.3 Methylene Blue	14

2.4	Low Cost Adsorbent	16
2.5	Agricultural Waste	23
<b>CHAPTER 3 MATERIALS AND METHODS</b>		
3.1	Collection of samples	27
3.1.1	Adsorbent – coffee residues (CR)	27
3.1.2	Adsorbate – methylene blue (MB)	27
3.2	Preparation of activated carbon	28
3.3	Preparation of methylene blue	30
3.4	Adsorption of methylene blue	31
	using activated carbon	
3.4.1	Optimization of activated carbon samples	32
3.4.2	Optimization of contact time	33
3.4.3	Optimization of activated carbon dosage	33
<b>CHAPTER 4 RESULTS AND DISCUSSION</b>		
4.1	Introduction	34
4.2	Calibration curve	34
4.3	Dye removal by adsorption	36
4.3.1	Removal by different activated carbon samples	36
4.3.2	Removal by different contact time	38
4.3.3	Removal by different activated carbon dosage	40

## **CHAPTER 5 CONCLUSION AND RECOMMENDATIONS**

5.1	Conclusion	42
5.2	Recommendations for future research	43
	<b>REFERENCES</b>	<b>45</b>
	<b>APPENDIX A</b>	<b>51</b>
	<b>APPENDIX B</b>	<b>52</b>



## LIST OF TABLES

NO.		Page
2.1	Major Polluting Industries and Nature of Pollutant	5
2.2	Classification of dyes according to colour index (C.I) application	9
2.3	Advantages and advantages of physical and chemical methods of dye removal from industrial effluent	18
3.1	Characterization of AC samples	29
3.2	Parameters set up for adsorption of MB	32

UNIVERSITI  
MALAYSIA  
KELANTAN

## LIST OF FIGURES

NO.		Page
2.1	Schematic diagram of batik process	12
2.2	Methylene blue chemical structure with its systematic name	15
2.3	Coffee residue	23
4.1	Calibration curve	35
4.2	Removal by different activated carbon samples	36
4.3	Removal by different contact time	38
4.4	Removal by different carbon dosage	40
A1	Sampling of AC produced after carbonization	51
B1	Convection oven (ED23, BINDER)	52
B2	Weighing balance (83002-S, METTLER-TOLEDO)	52
B3	Digital Muffle Furnace (FH-14, WiseTherem)	53
B4	Buchner filtration apparatus	53
B5	Hot plate stirrer (C MAG HS 7, IKA)	54
B6	pH meter (HI 2211, HANNA)	54
B7	Orbital shaker (KS 4000 i control, IKA)	55
B8	Uv-Vis spectrophotometer (GENESYS 20, ThermoScientific)	55



## LIST OF ABBREVIATIONS

AC	activated carbon
BET	Brunauer-Emmett-Teller
CAS	Chemical Abstracts Service
C.I	colour index
COD	chemical oxygen demand
CR	coffee residue
CV	crystal violet
DO	dissolve oxygen
DOE	Department of Environment
FTIR	Fourier Transform Infrared Spectrum
H <sub>3</sub> PO <sub>4</sub>	phosphoric acid
IP	isoelectric point
IUPAC	International Union of Pure and Applied Chemistry
KOH	potassium hydroxide
ZnCl <sub>2</sub>	zinc chloride
MB	methylene blue
NaOCl	sodium hypochlorite
PZC	point of zero charge
RB5	reactive black 5
SEM	Scanning Electron Microscopy
TB	toluidine blue
TDS	total dissolve solid

## LIST OF SYMBOLS

t/yr	tonne per year
nm	nanometer
°C	degree celcius
mg/L	milligram per liter (concentration)
mg/g	milligram per gram (dye uptake by gram)
mL	milliliter (volume)
Q	adsorption capacity
C <sub>i</sub>	initial dye concentration
C <sub>f</sub>	final dye concentration
g	gram
g/mol	molar mass
v	volume of adsorbate
m	mass of adsorbent
X <sub>p</sub>	impregnation percentage
λ <sub>max</sub>	maximum wavelength (adsorption)
min	minute
h	hour
rpm	revolutions per minute (shaking speed)
%	percentage
w/v	weight per volume (concentration)
π	pi

## ABSTRACT

Activated carbon derived from coffee residues was utilized in this study. Batch adsorption experiments were carried out for the removal of methylene blue cationic dye from aqueous solution using different activated carbon samples. The activated carbon samples undergone two methods which are chemical and physical activation processes. The samples are classified by their carbonization time (min) and measure of the different concentration (w/v %) of phosphoric acid as the activating agent. The impregnation percentage of 0.6% and 0.8% were applied on the coffee residue to observe its influence on the capacity adsorption of methylene blue. The adsorption process coincides with removal of dye percentage and total dye uptake equations while the factors influencing percentage removal of the adsorbate and adsorption capacity of the absorbent such as type of adsorbents, amount of adsorbents, and time of contact were investigated. The highest percentage removal and adsorption capacity are 101.1% (at dosage = 0.5 g) and 1.996 mg/g (at dosage = 0.25 g) respectively were obtained after shaken at 100 rpm, for 12 h. The results show the high efficiency of the absorbent and thus expected to be a good candidate as an absorbent for water treatment.

Keywords: coffee residues; phosphoric acid; methylene blue; activated carbon; adsorption; percentage removal.

## ABSTRAK

Karbon teraktif yang diperolehi daripada sisa kopi telah digunakan dalam kajian ini. 'Batch' eksperimen penjerapan telah dijalankan untuk penyingkiran metilena pewarna kationik biru dari larutan akueus menggunakan sampel karbon diaktifkan yang berbeza. Sampel karbon diaktifkan melalui dua kaedah yang proses pengaktifan kimia dan fizikal. Sampel diklasifikasikan oleh masa mereka karbonisasi (min) dan ukuran kepekatan yang berbeza (w/v %) daripada asid fosforik sebagai ejen pengaktif. Peratusan semaian diberi ialah 0.6% dan 0.8% telah digunakan pada sisa kopi untuk melihat pengaruhnya terhadap penjerapan kapasiti metilena biru. Proses penjerapan bertepatan dengan penyingkiran peratusan pewarna dan jumlah persamaan pengambilan pewarna manakala faktor yang mempengaruhi penyingkiran peratusan kapasiti bahan terjerap dan penjerapan penyerap seperti jenis adsorben, jumlah bahan penyerap, dan masa perhubungan telah disiasat. Penyingkiran peratusan dan kapasiti penjerapan tertinggi ialah 101.1% (pada jumlah = 0.5 g) dan 1.996 mg/g (pada jumlah = 0.25 g) masing-masing didapati selepas digoncang pada 100 rpm, selama 12 jam. Keputusan menunjukkan kecekapan yang tinggi penyerap dan dengan itu dijangka menjadi calon yang baik sebagai penyerap untuk rawatan air.

Kata kunci: sisa kopi; asid fosforik; metilena biru; karbon aktif; penjerapan; penyingkiran peratusan.

# CHAPTER 1

## INTRODUCTION

### 1.1 Background of Study

Great water pollution that occurs today is due to the generation of coloured wastewaters ever since the Industrial Revolution as to the fact that the level of dyes production has increased as their extensive use in many applications has also increased. It is known today that there are more than 100,000 dyes with different chemical structures available commercially worldwide (Allen *et al.*, 2004). The coloured dye effluents are generally contemplated to be of highly toxic to animals and plants of particular region and habitat of exposure (Isah *et al.*, 2015). Countless of related human health problems such as allergy, dermatitis, skin irritation, cancer, and mutations in humans are correlated with dye pollution from any of the water bodies (Isah *et al.*, 2015).

These industrial activities along with increase in population have been accounted for the scarce commodity of many parts of the world's fresh water supply. Fresh water demand is on the rise and this challenge has spurred many researches into finding long-lasting solution to this catastrophe by devising ways of improved purification technology, recycling and search for new water sources (Alexandro *et al.*, 2011).

Large quantities of hazardous dyes are emitted into the wastewaters, including pigments and metals that have started from dye manufacturing, textile, and pulp and paper industries. It is approximated that 2% of dyes produced every year are discharged as effluents from manufacturing operations whilst 10% are discharged from textile and associated industrial activities (Allen *et al.*, 2004). This makes

treating the contaminated water as difficult as the colours tend to persist due to its high stability to adapt in the environment even after the conventional removal processes have been done. The dye contaminations in water tend to prevent light penetration affecting the process of photosynthesis greatly (Aljeboree *et al.*, 2014).

The adsorption technique based on the transfer of pollutants from the solution to the solid phase is known as one of the efficient and general wastewater treatment method (Saleh & Gupta, 2012). Adsorption is dependent on the concentration of dye, temperature of surrounding, nature of dye, pressure exerted, and surface area of adsorbent. Whereas, the activated carbon, a widely used adsorbent in the industrial processes, is composed of microporous, homogenous structure with high surface area and shows radiation stability (Aljeboree *et al.*, 2014)

Commercial activated carbon used in surface and wastewater treatment in Malaysia mostly acquired from coal. The coal-based carbons have the advantages that can be seen in their capability to remove toxic organic compounds from industrial and municipal wastewater and potable water as well (Jibril *et al.*, 2013). Besides that, another important application of coal-based carbons is decolourisation. However, the feedstock for these carbons often made from the bituminous coals which are non-renewable resources. This has encouraged researchers to consider renewable resources such as agricultural by-products or waste as an alternative (Jibril *et al.*, 2013).

## 1.2 Problem Statement

Textile effluent is considered as industrial wastewater that contain hazardous chemicals and other elements that has potential toxicity risks and environmental impacts towards living organisms such as body system reflexes that can cause irritation or even more and dyes that produce coloured water preventing the process of photosynthesis and aquatic lives respiration within any aquatic ecosystems. Most of these dyes are of synthetic origin and toxic in nature with suspected carcinogenic and genotoxic effects (Daneshvar *et al.*, 2007).

There are conventional methods that have been studied from other researches to curb this problem such as sedimentation with clarification, coagulation and flocculation, chemical oxidation, filtration using membranes, adsorption, biodegradation and more. Some of these methods have shown to be potent. However, these methods have some limitations such as excess amount of chemical usage, accumulation of concentrated sludge that has serious disposal problems and inadequate effective colour reduction (Saleh & Gupta, 2012).

One of the major disadvantages of the adsorption process is the high costs of procuring commercial grade activated carbon adsorbents. This necessitates the demand for the low cost adsorbents in the treatment of textile wastewater especially in decolourisation of textile effluents. Therefore, the increasing interest in the development and application of activated carbon produced from agricultural waste is the purpose for conducting this study.

### **1.3 Objectives**

The objectives of this study are:

1. To prepare activated carbon from coffee residue as a low cost adsorbent.
2. To analyze the potential of the prepared activated carbon to decolourise the synthetic textile effluent.

### **1.4 Significance of Study**

The findings of this study will redound to the benefit of society as well as to the environment considering that treating wastewater plays an important role in promoting better living conditions, conservation of natural environment, and innovation in science and technology today. This production of adsorbent can facilitate the removal of hazardous chemicals and other elements within the aquatic ecosystems. Hence, reducing the impacts caused by industrial wastewater such as removal of coloured wastewater, increasing rate of respiration of aquatic lives, and prevention of safety and health effects on humans and other beings. Limitations of this method is reduced by lowering the amount of chemical usage into using only one activating agent and low impregnation percentage on the raw material. Increase in adsorption potentiality by optimizing the factors influencing the adsorption capacity of adsorbent. Cost-saving potential given that procuring activated carbon produced from coffee residues which are abundant and has no further modification (just washed with distilled water, then dried in an oven) except impregnation of activated carbon with the activating agent.



## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Industrial Wastewater

Industrial effluents are one of the major causes of global environmental pollution. They consist of many types since they are based on their industrial sector which each sector represents its particular combination of pollutants. The existence of dyes in the effluents is a serious concern to many forms of living organisms for their adverse effects to life. The dyes that are discharged into the environment is worrisome for both toxicological and esthetical reasons (Hameed *et al.*, 2008a).

Industries such as textile, leather, paper, plastics, etc., are some of the sources for dye effluents (Hameed *et al.*, 2008b; Ravikumar *et al.*, 2005). It is stated that more than 100,000 commercially accessible dyes with over  $7 \times 10^5$  tonnes of dyestuff produced every year (Hameed *et al.*, 2008b). Almost 2% of these dyes are discharged directly into the aquatic ecosystems which may prove detrimental to marine lives due to the presence of metals and chlorides in them (Xu *et al.*, 2008). Table 2.1 shows the major polluting industries and nature of pollutant respectively.

**Table 2.1:** Major Polluting Industries and Nature of Pollutant

<b>Major Polluting Industries</b>	<b>Nature of pollutants</b>
Cement Mills (>200 tonne/day)	Dust particles, alkali, sulfur oxides, nitrogen oxides, heavy metals, waste soil, byproduct gypsum, coal ash
Sugar	Floor washing waste, sugar cane juice, molasses
Thermal power plants	Fly ash, heavy metals, coal, oil, suspended solids
Distilleries	Glucose, polysaccharides, ethanol, glycerol, amino acids, proteins, caramels, high concentration of salts, organic matter, sulfates
Fertilizers	Organics, ammonia, nitrate, phosphorus, fluoride, cadmium/other heavy metals, and suspended solids
Petroleum/Petrochemicals	Oil, acid, soda sludge, hydrogen sulfide, lead sludge, hydrocarbons, spent filter clay, ethylene glycol, 1,4-dioxane
Mining industries	Heavy metals like copper, lead, zinc, mercury, cadmium oxide, calcium oxide, sodium oxide, barium oxide, cuprous oxide, zinc oxide, sulfates, chlorine, lithium oxide, manganese oxide, magnesium oxide, silica, gypsum, hydroxides, carbonates, cyanide, sulfur
Integrated iron and steel	Ammonia, cyanide, benzene, naphthalene, anthracene, phenol, cresol, heavy metals
Pulp and high quality paper	High concentration of chemicals such as sodium hydroxide, sodium carbonate, sodium sulfide, bisulfide, elemental chlorine, chlorine dioxide, calcium oxide, hydrochloric acid, organic halides, toxic pollutants, lime mud, wood processing residuals, traces of heavy metals, pathogens
Tanneries	Organics, heavy metals such as chromium, ammoniacal nitrogen, acids, salts, sulfides, suspended solids, dyes, fats, oil

Pharmaceuticals	Polycyclic aromatic hydrocarbons, arsenic trioxide, chlorambucil, epinephrine, cyclophosphamide, nicotine, daunomycin, nitroglycerin, melphalan, physostigmine, physostigmine salicylate, streptozotocin, warfarin over 0.3%, uracil mustard, halogenated/ nonhalogenated solvents, organic chemicals, sludge and tars, heavy metals, test animal remains
Dye and dye intermediates/textiles	Complex mixture of salts, acids, heavy metals, organochlorine-based pesticides, pigments, dyes, Polycyclic aromatic hydrocarbons
Pesticides	Volatile aromatics, halomethanes, cyanides, haloethers, heavy metals, chlorinated ethane, phthalates, Polycyclic aromatic hydrocarbons

(Source: Ranade & Bhandari, 2014)

## 2.2 Textile Effluents

Many industries like the textile industry used dyes to colour their products. This activity producing wastewater containing organics with a strong colour, where in the dyeing processes the percentage of dye lost in wastewater is 50% of the dye because of the low levels of dye-fiber fixation (Adegoke & Bello, 2015).

Discharge of these dyes in to effluents affects the people who may use these effluents for living purposes such as washing, bathing and drinking (Adegoke & Bello, 2015). Therefore, it is very crucial to clarify the water quality and its status, especially when even just 1.0 mg/L of dye concentration in drinking water could impart a significant colour, making it unsuitable for human consumption (Adegoke & Bello, 2015).

Real textile wastewater is a mixture of dyes, organic compounds, heavy metals, total dissolved solids, surfactants, salts, chlorinated compounds, chemical oxygen demand and biological oxygen demand (Adegoke & Bello, 2015). Therefore, some studies tested the agricultural wastes as adsorbents for these pollutants. For example, Hameed and Ahmad (2009) studied the reduction of colour and COD using

bamboo activated carbon, and they found that the maximum reduction of colour and COD were 91.84% and 75.21%, respectively.

Dye molecules consists of two key components: the chromophores, which are largely responsible for producing the colour, and the auxochromes, which not only supplement the chromophore but also render the molecule soluble in water and enhance its affinity (to attach) toward the fibers (Adegoke & Bello, 2015). Dyes may be classified in several ways, according to chemical constitution, application class, and end use. Dyes are here classified according to how they are used in the dyeing process. Main dyes are grouped as acid dyes, basic dyes, direct dyes, mordant dyes, vat dyes, reactive dyes, disperse dyes, azo dyes, and sulphur dyes. Typical dyes used in textile dyeing operations are given in Table 2.2 (Adegoke & Bello, 2015).

Apart from being a major contributor to Malaysia's economy development, batik industries also contribute large amounts of effluents with a high concentration of pollutants which required extensive treatment before discharging into the environment. The Kelantan Department of Environment (DOE), stated in the study conducted by Noor & Rohasliney (2011), has found that the batik industry in the state has the lowest level of compliance with the department's law and regulations.

Khairuddin Mohamad Idris as the department's director, said that the study conducted by Noor & Rohasliney (2011), revealed that between January and September 2010, the batik industry in Kelantan only recorded 5% level of compliance compared to other manufacturing industries. The study conducted revealed that chemical oxygen demand (COD) value is between 700 – 4900 mg/L which is higher than the acceptable condition and was positively correlated with temperature and pH, and was negatively correlated with dissolve oxygen (DO) and total dissolve solid (TDS).

**Table 2.2:** Classification of dyes according to colour index (C.I) application.

Class	Principal substrates	Method of application	Chemical Types	Examples
Acid	Nylon, wool, silk, paper, inks, and leather	Usually from neutral to acidic dye baths	Azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso	Acid Yellow 36
Azoic components and compositions	Cotton, rayon, cellulose acetate and polyester	Fibre impregnated with coupling component and treated with a solution of stabilized diazonium salt	Azo	Bluish red azoic dye
Basic	Paper, polyacrylonitrile, modified nylon, polyester and inks	Applied from acidic dye baths	Cyanine, hemicyanine, diazahemicyanine, diphenylmethane, triarylmethane, azo, azine, xanthene, acridine, oxazine and anthraquinone	Basic brown, methylene blue
Direct	Cotton, rayon, paper, leather and nylon	Applied from neutral or slightly alkaline baths containing additional electrolyte	Azo, phthalocyanine, stilbene, and oxazine	Direct orange 26
Disperse	Polyester, polyamide, acetate, acrylic and plastic	Fine aqueous dispersion often applied by high temperature / pressure or lower temperature carrier methods; dye may be padded on cloth and baked on or thermofixed	Azo, anthraquinone, styryl, nitro, and benzodifuranone	Disperse yellow 3, Disperse Red 4, and Disperse Blue 27
Flourescent Brighteners	Soaps and detergents, and all fibers, oils, paints and plastics	From solution, dispersion or suspension in a mass	Stilbene, pyrazoles, coumarin, and Naphthalimides	4,4'-bis (ethoxycarbonylvin yl) stilbene
Food, drug, And cosmetic	Foods, drugs, and cosmetics	-	Azo, anthraquinone, carotenoid and triarylmethane	Food Yellow 4, Tartrazine
Mordant	Wool, leather, and anodized aluminium	Applied in conjunction with Cr salts	Azo and anthraquinone	Mordant red 11
Oxidation Bases	Hair, fur, and cotton	Aromatic amines and phenols oxidized on the substrate	Aniline black and indeterminate structures	-

Reactive	Cotton, wool, silk, and nylon	Reactive site on dye reacts with functional group on fiber to bind dye covalently under influence of heat and pH (alkaline)	Azo, anthraquinone, phthalocyanine, formazan, oxazine and basic	Reactive blue 5
Solvent	Plastics, gasoline, varnishes, lacquers, stains, inks, fats, oils, Waxes	Dissolution in the substrate	Azo, Triphenylmetane, anthraquinone, and phthalocyanine	-
Sulphur	Cotton and rayon	Aromatic substrate vatted with sodium sulphide and reoxidized to insoluble sulphur containing products on fibre	Indeterminate structures	-
Vat	Cotton, rayon and wool	Water-insoluble dyes solubilized by reducing with sodium hydrogen sulphite, then exhausted on fibre and reoxidized	Anthraquinone (including Polycyclic quinines) and Indigoids	Vat Blue 4 (Indanthrene).

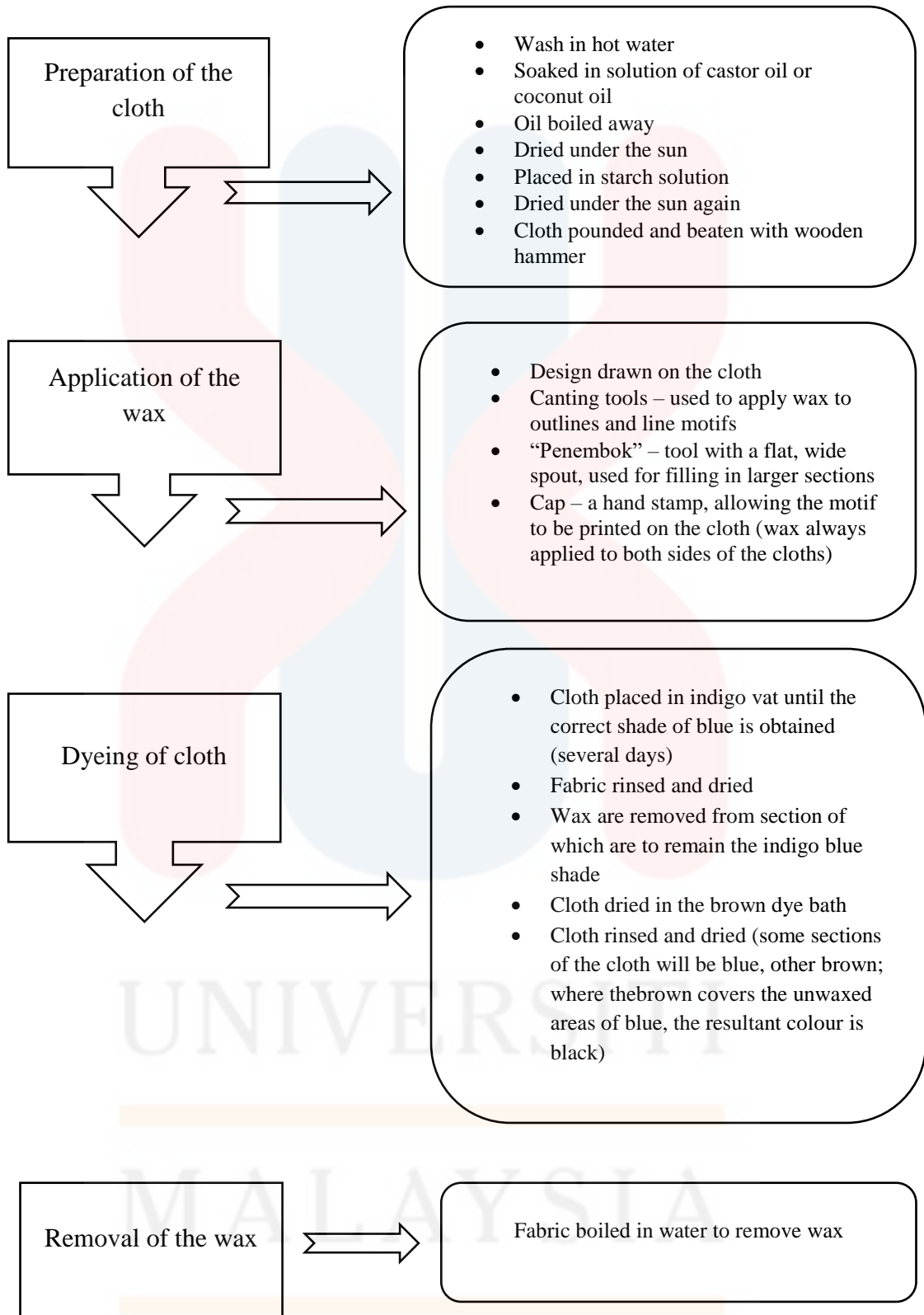
(Source: Slokar & Majcen, 1998)

Evaluation and discussion on the peril situation caused by the textile industry within Malaysia, more specifically focused in Kelantan state, where the study conducted by Noor & Rohasliney (2011), obtained that the effluents discharged by the sampling stations by the five factories within the study display extensive COD level to the receiving stream or drainage may hinder dissolve of oxygen and forge anaerobic condition. Under anaerobic condition, fetid smelling compound such as hydrogen sulfides may be generated. Biological activity will subsequently be afflicted notably in the receiving stream.

This shows batik products will commit in the continuation of more effluent with high COD value and creating it as one of the main sources of severe pollution in Malaysia. This preliminary finding should be a starting point to find an appealing application for the treatment of liquid effluents in local industries such as batik industry. Therefore, awareness education of batik effluent pollution to the batik industry entrepreneurs and manufacturers is essential especially emphasized on the importance of clean practices in the production of batik (Noor & Rohasliney, 2011).

This textile industry consumes heavy amount of water and chemicals during their wet processing. Wastewaters from the batik building mostly discharged after minimal or no pretreatment into the adjoining water channels, streams and estuaries. Figure 2.1 shows the process of batik textile that proves the usage of such chemicals used by the industry and thus, need to be monitored and analyzed to reduce the water pollution (Ahmad *et al.*, 2002).





**Figure 2.1:** Schematic diagram of batik process. (Source: Belfer, 1972).



Dyeing process uses both organic and inorganic synthetic dye that available in variety of colours. It is first pulled through a chemical agent that helps the dye to bond to the cloth. The dye reacts with the chemical agent to produce the final colour. Chemical substance such as ludigol is added into dilute dye to get a brighter and more vibrant colour (Ahmad *et al.*, 2002). Sodium alginate is used to thicken the dye for screening, printing, painting or to control spreading (Siti Zainon, 1986). Many additives are used, such as salts and surfactants, which can either accelerate or retard dye adsorption processes (Kyzas, 2012a).

Most of the batik producers use reactive dye as the colouring substance and the plain fabrics are imported from China, India, and Japan. By using pencil and stencil, variety of design can be applied on the fabrics. It is normally done by the skilled designer who is in-charge of producing new and attractive design from time to time. The design and colour combination are very important to have a good market value. Usually, the design is based on nature such as flowers, trees, and sceneries. These dyes are very stable and decomposed only at temperature higher than 200°C (Ahmad *et al.*, 2002).

### 2.3 Methylene Blue

Methylene blue (abbreviated hereafter as MB) has a pH value of 3 in water (10000 mg/L) at 25 °C and has a molecular formula of  $C_{16}H_{18}N_3SCl$  and is a cationic dye. Figure 2.2 shows the molecular structure of MB and its systematic name. MB has broad applications such as colorants for paper, hair and cotton; and strainers for medicinal surgery. However, MB has been indicated to induce retching, stun, cyanosis, jaundice, and tissue necrosis in humans (Thakur *et al.*, 2016).

MB also been accounted for eye burns which may be affiliated for permanent injury to the human eyes including other living creatures. By inhalation can impel short periods of rapid or difficult breathing as well as ingestion of this compound rise a burning sensation and arouse nausea, vomiting and methemoglobinemia (Ghosh & Bhattacharrya, 2002).

MB is a positively charged dye with the estimated dimensions of 1.43 nm × 0.61 nm × 0.4 nm and its adsorption by AC is very susceptible to solution pH. Studies revealed that the higher the solution pH, the more the MB molecules on AC surface (Wang *et al.*, 2005).

Nonetheless, MB is a member of basic class of dyes and a heterocyclic aromatic chemical component which dominated the global market of dyestuffs with a share of around 70% (Hirata *et al.*, 2012). This dye falls under azo dye type which is characterized by the presence of at least one azo bond (-N=N-) bearing aromatic rings (Soares *et al.*, 2002). Many researches have done investigating its physicochemical properties and its functions in different fields such as in chemistry and even biology. MB has also been utilized as an optical oxygen sensor in industrial food sector (Jamal & Tabbara, 2012).

MB spruces face-to-face dimers in dilute solutions, and aggregates when it is at a higher concentration. This dye is reactive to alterations in polarity in the surrounding environment. Not to mention, MB has its medicinal values and is a component of a frequently prescribed urinary analgesic/anti-infective/anti-spasmodic drug as well as able to donate or receive protons. This demonstrates that MB has potential redox properties (Priyantha *et al.*, 2015).



**Figure 2.2:** Methylene blue chemical structure with its systematic (IUPAC) name.  
(Source: Thakur *et. al*, 2016).

## 2.4 Low Cost Adsorbent

A usual effluent treatment is generally divided into preliminary, primary, secondary, and tertiary stages (Mishra & Tripathy, 1993). The preliminary stage includes equalization and neutralization. The primary stage involves screening, sedimentation, flotation, and flocculation. The secondary stage reduces the organic load and facilitates the physical/chemical separation (biological oxidation), while the tertiary stage is adjusted on decolourisation (O'Neill *et al.*, 1999). In the latter stage, to minimize the concentration of colour in effluents, the adsorption onto activated carbon is widely used (Al-Degs *et al.*, 2009). The adsorption application is done either in a single mode, especially for dyes removal from synthetic wastewaters, or in a combination mode for total cleaning of real dyeing wastewaters.

The treatment of wastewater containing soluble dyes thus requires complete removal followed by secure disposal (Ravikumar *et al.*, 2005). The most commonly used methods for colour removal include chemical precipitation, ion exchange, reverse osmosis, ozonation and solvent extraction. However, these methods have their downsides such as high capital cost and operational costs or secondary sludge disposal problem (Ravikumar *et al.*, 2005).

Chemical and electrochemical oxidations, coagulation are mainly not feasible on industries conducted in large scale. In contrary, adsorption technique is by far the most versatile and widely used due to its high applicability associated to its high porosity, rapid adsorption, and thermal stability (Hesas *et al.*, 2013).

The most common adsorbent materials are: alumina silica (Josefa & Oliveira, 2003), metal hydroxides (Wu and Tseng, 2006) and activated carbon (Malik *et al.*, 2002). Adsorption by activated carbon is worthy to mentioned amongst all considering its ease of processing and ability to adsorb a large variety of adsorbate (Rafatullah *et al.*, 2010).

By the study conducted by Crini (2006), it was reported in details the main low-cost and non-conventional adsorbents for dyes removal (natural materials, biosorbents, waste materials from industry and agriculture). Some of the reported adsorbents include clay materials (bentonite, kaolinite), zeolites, siliceous material (silica beads, alunite, perlite), agricultural wastes (bagasse pith, maize cob, rice husk and coconut shells), industrial waste products (waste carbon slurries and metal hydroxide sludge), biosorbents (chitosan beads, peat and biomass) and others (starch, cyclodextrin and cotton).

It is stated that these activated carbons contain adsorption behaviour and have many important applications in water treatment such as filtration and purification (Valdés *et al.*, 2002), catalysts (Gomes *et al.*, 2010), hydrogen storage (Lee *et al.*, 2007), supercapacitors (Fang *et al.*, 2005), and so on.

Adsorption technique although has been proven to be a promising way to treat effluents, giving significant benefits over more conventional process especially from an energetic and environmental point of view (Ravikumar *et al.*, 2005).

Table 2.3 shows the advantages and disadvantages of physical and chemical methods of dye removal from industrial effluents.

**Table 2.3:** Advantages and disadvantages of physical and chemical methods of dye removal from industrial effluent.

Physical/chemical method	Advantages	Disadvantages
Fenton's reagent	Effective decolourisation of both soluble and insoluble dyes	Sludge generation
Ozonation	Applied in gaseous state: no alteration of volume	Short half-life (20 min)
Photochemical	No sludge production	Formation of by-product NaOCl
NaOCl	Initiates and accelerates azo-bond cleavage	Release of aromatic amine
Cucubituril	Good sorption capacity for various dyes	High cost
Electrochemical destruction	Breakdown compounds are non-hazardous	High cost of electricity
Activated carbon	Good removal of wide variety	Very expensive of dyes
Peat	Good adsorbent due to cellular structure	Specific surface area for adsorption are lower than activated carbon
Wood chips	Good sorption capacity for acid dyes	Requires long retention times
Silica gels	Effective for basic dye removal	Side reactions prevent commercial application
Membrane filtration	Remove all dye types	Concentrated sludge production
Ion exchange	Regeneration: no adsorbent loss	Not effective for all dyes
Irradiation	Effective oxidation at laboratory scale	Requires a lot of dissolved O <sub>2</sub>
Electrokinetic coagulation	Economically feasible	High sludge production

(Source: Robinson *et al.*, 2001)

Activated carbon is defined by its amphoteric materials which consists of both acidic and basic surface functional groups on their surface. Therefore, the adsorbent often display positively or negatively charged character depending on the solution pH. This phenomenon can also be seen in other conventional method stated in study by Nora & Suhaimi (2009), found that isoelectric point (IP) is approximately pH 4.2 where the membrane charge is near zero (Allègre *et al.*, (2006); Szoke *et al.*,

(2002)). Below this value, membrane is positively charged and above it, the membrane is negatively charged. This finding also been supported by Xu and Lebrun, (1999) also gives the same result where at pH 4 to 8, reactive black 5 (RB5) rejection increased as pH increased.

Additionally, attraction of activated carbon with anionic or cationic materials is primarily affiliated with the surface characteristic. More negatively charged surfaces are gained at higher pH values and this favours the intake of more cationic groups due to decreased electrostatic repulsion between dye (i.e. methylene blue) and activated carbon surface and vice versa (Wang *et al.*, 2005).

Whereas, the activated carbon surface represents larger amounts of carboxylic groups after modification which improves the surface in terms of hydrophilic character. Hence, carboxylic groups are to blame for the adsorption of water molecules through hydrogen bonding and the adsorption of MB on the acid treated activated carbon samples significantly increased. In contrast, the carbonyl groups on the carbon surface are well-known as strong donors in behalf of their high dipole moments. Formation of acidic groups on the AC surface depends on the acid concentration and the total acidity decreased after a certain value of the activating agent used (Gokce & Aktas, 2014).

Activated carbon is being used as a promising adsorbent for its high efficiency. In order to increase the adsorption capacity of the adsorbent, researchers have followed different activation methods to increase the effectiveness of the activation process. Activation methods involve physical activation such as carbonization of material and chemical activation such as using chemical activating agents (Adegoke & Bello, 2015).



These processes govern the development of activated carbons with a variety of surface area, pore volume, and pore size distribution by modifying the conditions of the carbonization process. The effects of the processes can be seen by the textural properties of the activated carbon and the ability to adsorb large number of dyes (Abdulkarim *et al.*, 2002).

The physical activation process is often performed in two stage which involving pyrolysis at high temperature to decompose the hydrogenated matter and activation under flow of gas (i.e. nitrogen) for opening the porous structure of activated carbon (Rios *et al.*, 2006). In the study conducted by Gonzalez *et al.*, (1997), one of the advantages of physical activation over chemical activation is the potential in pyrolysis optimization step that is accountable for the growth of higher porosity in structure and larger active surface sites.

Likewise, chemical activation has some advantages over physical activation method when a lignocellulosic material is especially used as raw material. Besides that, yield is relatively high in this chemical activation process. The process is more economical compared to physical activation where the activation requires lower temperature (Karatepe *et al.*, 2012).

Among the diverse activating agents for chemical activation, the use of phosphoric acid is preferred recently contemplate to some environmental and economic apprehensions (Guo & Rockstraw, 2007). Molina-Sabio and Rodriguez-Reinoso (2004), reported that KOH produces only widening of the microporosity to more heterogeneous micropores, whereas  $ZnCl_2$  develops both wide micropores and low mesopores and  $H_3PO_4$  large mesopores and even macropores.



Increased in the concentration of the phosphoric acid (abbreviated hereafter as  $H_3PO_4$ ) also increase highly microporous attributes of activated carbon transforms it to another form, where the mesopores are also dominant in the overall pore size distribution after a specific concentration for a given activation condition. After the given concentration,  $H_3PO_4$  concentration may force to change the nature of the pore size developments from micropores to higher pores due to the possible changes in phosphorous materials and/or higher phosphorus contents that will interact with lignocellulosic materials during both impregnation and activation stages. It is also considered that several polyphosphoric acids have different molecular sizes, should have played a role in porosity development (Karatepe *et al.*, 2012).

Nonetheless, the incline in price of carbon may results in higher economic spending for Malaysia. Therefore, alternate adsorbents with equivalent potential of AC are current thrust area of research (Ravikumar *et al.*, 2005). Activated carbon is undoubtedly considered as universal adsorbent for effluent treatment and is commonly used for the removal of various pollutants from water (Bhatnagar *et al.*, 2010). Yet, it has been found that various low-cost adsorbents developed from different origins show little or poor sorption potential for the removal of aquatic pollutants as compared to commercial activated carbon, but it is also promising in terms of economic and ecological way of treating wastewater that can be done by most people using wastes (e.g. agricultural wastes).

In the study performed by Kyzas, (2012a), the higher dye uptakes will be seen in acidic pH-region. This is explained by the acidic nature of reactive dyes (this type of dyes contains sulfonate groups, acidic pH values, the surface of activated carbon (abbreviated hereafter as AC) from coffee residue (abbreviated hereafter as CR) can be easily charged positive due to the excess of  $H^+$  groups within the

solution. Hence, the positively charged sites of CR can interact with the negative sulfonate groups of reactive dyes, forming a strong bond between adsorbent and dye. The dye removal percentage at even pH = 10 could be attributed to a combination of decreased electrostatic and other interactions, as van der Waals forces, hydrogen bonding and  $\pi$ - $\pi$  interactions. In the case of reactive dye removal, where the adsorption is strongly pH-dependent, the dominated interactions are influenced by the pH value of solution. Strong electrostatic forces are dominated in acidic pH and even hydrophobic dye-dye or dye-adsorbent interactions in the whole pH range.

It is expected that the rate of dye removal within an effluent (real textile wastewater) should be rapid at the blooming stage of the contact. This will be decelerated until it reaches equilibrium. The fact is supported by that a large number of surface sites are reachable for adsorption causes prompt adsorption at the early stage. After an interval of time, the repulsion between the solute molecules of the solid and bulk phases make it took a long time to reach constant due to the residual surface sites are complicated to be occupied. The excess of impurities and dye auxiliaries restricts the swift removal of dye molecules and their binding onto AC surface (Kyzas, 2012a).

The composition of CR was also determined by Kyzas (2012a), that it made up of 44% water, 12% protein, 14% lipids, 25% carbohydrates and 5% ash. The morphology of CR according to SEM micrographs taken in that study represent clear distinct CR surface that was not smooth yet rough and complex which made up of large number of cavities. These cavities were then characterized as channels onto the CR surface instead of pores. The CR obtained in this study can be seen in Figure 2.3.



**Figure 2.3:** Coffee residue

## 2.5 Agricultural Waste

Available abundantly, high biosorption capacity, cost effectiveness and renewability are the important factors making agricultural wastes as economical alternatives for water treatment and waste remediation (Bhatnagar *et al.*, 2010).

In addition, the rise in demand for environmental protection each year influences the vast usage of activated carbon in the industry for purification, separation and recovery processes these past years. Other research been done using any inexpensive materials such as agricultural wastes which include nutshell (Guo & Rockstraw, 2007), hazelnut shell (Karatepe *et al.*, 2012), apple peel (Hesas *et al.*, 2013), date pits (Jeguirim *et al.*, 2014), tamarind seed (Babu & Gupta, 2009), olive stone (Hazzaa & Hussein, 2015), coffee bean and grounds (Kyzas, 2012a), tea waste (Gokce & Aktas, 2014), sugarcane bagasse (Karunarathne & Amarasinghe, 2013),

coconut shell (Aljeboree *et al.*, 2014), with a high carbon content can be used as a raw material for the production of activated carbon.

In recent past, the coffee industry has experienced continuous commodity growth as coffee (is a popular brewed drink prepared from roasted bean) has become one of the highest demands of drink consumed by millions of people around the world. The aftermath is the incline amount of spent coffee grounds, which are the solid residues obtained during the processing of coffee powder, where the roasted and grinding coffee is introduced into percolators in countercurrent treatment with the pressurized hot water to extract the favours (soluble materials) in the soluble or instant coffee manufacturing factory that have been generated worldwide to an estimation of 6,000,000 t/yr (Musatto *et al.*, 2011).

The final solid product, an insoluble residue (a slurry containing spent coffee grounds) is screw pressed. The residue weighs approximately 50% of the total input mass of coffee feedstock, representing an important organic resource from the coffee-derived products processor (Lamine *et al.*, 2014).

However, there is inadequacy of literature corresponding with the possible application of coffee residues as adsorbents (i.e., for metals), and in exact, as dye adsorbents (Kyzas, 2012a). In this project, the use of coffee residues (CR) are considered due to limited research has been conducted than other agricultural wastes but also have the amount of capability as other agricultural wastes (mentioned previously) to adsorb dyes within wastewater.

This residue used in this study was easily obtained from Ruby Café where the café operated in Universiti Malaysia Kelantan Jeli Campus. Here, the students make their own profits through selling their products made from agricultural materials such as cocoa beans and coffee beans. When the coffee beans have fully utilized, the

coffee residues are abundant as wastes which is another reason for this project to choose coffee residues as raw materials.

Other advantages of choosing coffee residue is because of its natural properties, the coffee residue exhibited a large pore size. Firstly, the reduction in waste disposal of coffee residue is also a suitable factor to choose CR. An alternative to prohibit the disposal of these wastes would be its use in the preparation or production of material of higher value, transforming the waste into raw materials used for water treatment (Moreno-Pirajan & Giraldo, 2012).

Moreover, as mentioned by Reffas *et al.*, (2010) the adsorption of dye is administered by dispersive interactions between the porous volume of the AC (CR was used) which is reachable to the dye molecule comparatively to the adsorbate (MB was used) size porous volume of materials. Based on its molecular size, this dye can be included in a sphere of minimum diameters  $\sim 2.1$  nm. The results gained by Reffas *et al.*, (2010) shows that the high mesopores structure content of AC generated from CR is highly suitable precursor to adsorb MB.

Lastly, the potential of adsorption of dyes are also recognised by studies conducted by other researches. Hameed *et al.*, (2014) that gained maximum adsorption capacity for two basic dyes of toluidine blue (TB) and crystal violet (CV), was found to be as high as 142.5 mg/g for TB and 125 mg/g for CV, which makes CR a prospective adsorbent for the removal of basic dyes from aqueous solution.

Another example can be taken from the study conducted by Kyzas *et al.*, (2012b) have studied and used coffee residues as low-cost adsorbents for the removal of dyes (reactive and basic) from single-component aqueous solutions and gained that the calculated maximum adsorption capacities for the reactive dye at 25°C were 179 mg/g (pH=2) and 295 mg/g for the basic one (pH=10).



The breakthrough of other Kyzas (2012a) study reported that mainly mechanism of the adsorption of dye onto the adsorbent comprises of different procedures. For instance, the dye molecule transportation from the bulk solution to the adsorbent surface; adsorption on the particle surface; and dye movement within the adsorbent particles.

Nevertheless, Kyzas (2012a) also reported that the use of the CR as adsorbents displayed several complexities due to the specific characteristics of the agricultural waste (i.e. the presence of complexing chemical groups). Some reactions occurred and the possible adsorption mechanism was diffculted because it is implicated that the presence of different interactions. Besides, a wide range of chemical structures, pH, and salt concentrations often add to the complication. Some of the reported interactions include physical adsorption, hydrogen bonding, electrostatic interactions, coordination/chelation, acid-base interactions, complexation, hydrophobic interactions, ion-exchange and precipitation.

## CHAPTER 3

### MATERIALS AND METHODS

#### 3.1 Collection of Samples

##### 3.1.1 Adsorbent – Coffee Residues (CR)

The low-cost adsorbents used were agricultural wastes and was collected at Ruby Café which is located at Universiti Malaysia Kelantan Jeli Campus. The CR was activated with phosphoric acid ( $H_3PO_4$ ) to further improve their adsorptive ability, washed with distilled water to remove dirt and colour, and dried at 105 °C for 5 h in a convection oven (ED23, BINDER).

##### 3.1.2 Adsorbate – Methylene Blue (MB)

Methylene blue; can also be known as Basic blue 9, Swiss Blue, Chromosmon, or Methylthionium chloride. MB, a cationic dye, is a compound that consist of dark green crystals or crystalline powder (solid form) that have a 319.851 g/mol of molecular weight. The solutions in liquid form have a deep blue colour. MB has CAS Number of 61-73-4. For this study, 1 g of MB powder was collected from the laboratory material and apparatus store in the Universiti Malaysia Kelantan Jeli Campus.

### 3.2 Preparation of Activated Carbon

Coffee residues were washed and cleaned with distilled water to remove dirt, and dried at 105°C for 5 hours in the oven. Next, the raw materials were activated with phosphoric acid (H<sub>3</sub>PO<sub>4</sub>, 30% and 40% w/v) overnight.

Then, the CR was carbonized for certain holding time (5, 10, 30, 60 min), at 300°C using digital muffle furnace (FH14, WiseTherm) and allowed cooling. Hence, the AC produced was made of 8 samples known as A, B, C, D, E, F, G, H differentiate by their time of carbonization (whether 5, 10, 30 or 60 min and concentration of H<sub>3</sub>PO<sub>4</sub> by 30% or 40% w/v).

The impregnation percentage ( $X_p$ ) of chemical activation was also defined as the ratio of the weight (g) of H<sub>3</sub>PO<sub>4</sub> (70.4 g and 94 g for 30% w/v and 40% w/v of H<sub>3</sub>PO<sub>4</sub> respectively) to the weight of raw material (120 g for each  $X_p$  of dried CR). The impregnated samples were kept for 24 h before undergoing the carbonization process. The  $X_p$  was determined according to the following Eq. 1:

$$X_p = \frac{\text{weight of H}_3\text{PO}_4}{\text{weight of CR to be activated}} \quad (1)$$



The preparation and characterization of samples are shown in Table 3.1:

**Table 3.1:** AC samples based on characterization

AC samples	Characterization				
	Temperature (°C)	Holding time (min)	Concentration of H <sub>3</sub> PO <sub>4</sub> (% w/v)	Impregnation percentage (X <sub>p</sub> )	Impregnation ratio
A	300	5	30	0.6	7:12
B	300	5	40	0.8	9:12
C	300	10	30	0.6	7:12
D	300	10	40	0.8	9:12
E	300	30	30	0.6	7:12
F	300	30	40	0.8	9:12
G	300	60	30	0.6	7:12
H	300	60	40	0.8	9:12

The AC was cleaned with hot distilled water (using Buchner filtration set with 1-stage vacuum pump) to reach the pH of 6 (using the pH meter (HI2211, HANNA)) to get rid of the excess of H<sub>3</sub>PO<sub>4</sub>. The heating of distilled water was to increase the removal of impurities within untreated AC samples after undergoing the carbonization stage. The process was using a hot plate (C-MAG HS 7, IKA) and then, the treated AC samples were oven dried for 110<sup>0</sup>C for an hour each sample.

### 3.3 Preparation of Methylene Blue

Meanwhile, the methylene blue dye was analyzed of their absorbance to determine their concentrations using UV-Vis spectrophotometer (GENESYS 20, Thermo Scientific) at 670 nm as  $\lambda_{\text{max}}$  of MB.

The synthetic textile effluent of only MB was made by preparing a stock solution of 1000 mg/L of dye by adding 1 g of MB powder into 1000 mL of distilled water. The stock solution was kept in a 1000 mL reagent bottle to avoid degradation. A calibration curve of MB was achieved by preparing 100 mg/L of MB from the stock solution. Then, the initial concentrations of dilution were prepared from 0, 2, 4, 6, 8, 10, and 12 mg/L of MB by using Eq. (2).

$$M_1V_1 = M_2V_2 \quad (2)$$

where  $M_1$  is the initial concentration of solution (mg/L),  $V_1$  is the unknown volume of solution to be added into distilled water (mL),  $M_2$  is the final concentration of solution (mg/L), and  $V_2$  is the known volume of mixture wanted between solution and distilled water (mL).

When the absorbance of each dilution was obtained, the calibration curve was formed which also shows the equation (later refer as Eq. (3)) and the  $R^2$  value on chart.

$$y = 0.1606x \quad (3)$$

### 3.4 Adsorption of Methylene Blue using Activated Carbon

MB adsorption experiments were performed using batch methods. This study was carried out by adding 0.5 g of AC into a series of 250 mL conical flask containing 50 mL solution of MB with concentration 10 mg/L. The synthetic textile effluent was treated with the AC by adsorption process where the percentage removal of dye by the activated carbon were determined using Eq. (4) and the amount of total dye uptake will be determined using Eq. (5).

$$\text{Removal (\%)} = [(C_i - C_f) / C_i] \times 100 \quad (4)$$

where  $C_i$  and  $C_f$  are the initial and final dye concentrations (mg/L) respectively.

Amount of the adsorption capacity by each different parameter was investigated to improve better understanding of produced AC from CR. Adsorption capacity can also be known as dye uptake by AC which is defined as the mass of MB adsorbed per unit mass of adsorbent.

$$Q = \frac{(C_i - C_f)V}{m} \quad (5)$$

where  $m$  (g) is the mass of adsorbent;  $V$  (L) the volume of adsorbate;  $C_i$  and  $C_f$  (mg/L) are the initial and final dye concentrations in the liquid phase, respectively.

UNIVERSITI  
MALAYSIA

KELANTAN

In this experiment, various experimental conditions are summarized in Table 3.1 shown:

**Table 3.2:** Parameters set up for adsorption of MB

Parameters							
	AC Sample	Concentration dye (mg/L)	Adsorbent dosage (g)	Temperature (°C)	Agitation rate (rpm)	Time (h)	pH
Optimisation of AC samples	A-H	10	0.50	24	100	1	6
Optimisation of contact time	H	10	0.50	24	100	1-12	6
Optimisation of AC dosage	H	10	0.25-2.00	24	100	12	6

#### 3.4.1 Optimization of Activated Carbon Samples

From the 8 samples of AC produced, the highest percentage removal of MB by one of those samples was determined. Each sample was taken for 0.5 g of weight using weighing balance (83002-S, Mettler-Toledo) to be added into a standardized initial concentration of 10 mg/L of MB each. The time was set for an hour and were shaken at 100 rpm using an orbital shaker at room temperature (KS 4000 i control, IKA).

After an hour, the absorbance of each samples was taken using the spectrophotometer. The final concentrations for those samples were determined by using Eq. (3), the percentage removals were calculated using Eq. (4), and the adsorption capacities of AC were identified using Eq. (5).

### 3.4.2 Optimization of Contact Time

After determining the best AC among the 8 samples, it was selected to achieve 100 percent removal of MB for optimum contact time of 1, 2, 4, 6, 8, 10 and 12 h at room temperature with maintaining the agitation rate and temperature. The best AC sample was taken for 0.5 g of weight to be added into a standardization of initial concentrations of 10 mg/L of MB for each time set.

After an hour, the absorbance of each samples was taken using the spectrophotometer. The final concentrations for those samples are determined by using Eq. (3), the percentage removals were calculated using Eq. (4), and the adsorption capacities of AC were identified using Eq. (5). This method was repeated for 2 until 12 h of contact time in the orbital shaker.

### 3.4.3 Optimization of Activated Carbon Dosage

As the effective time of contact was determined, it was considered to analyse the optimization of carbon dosage for 0.25, 0.50, 1.00, 1.50 and 2.00 g. The best AC sample was taken for 0.25 g of weight to be added into a standardized initial concentration of 10 mg/L of MB. The temperature and agitation rate were kept constant. This method procedure was repeated for 0.50 until 2.00 g of carbon dosage.

After finished shaking, the absorbance of each samples was taken using the spectrophotometer. The final concentrations for those samples were determined by using Eq. (3), the percentage removals were calculated using Eq. (4), and the adsorption capacities of AC were identified using Eq. (5).

## CHAPTER 4

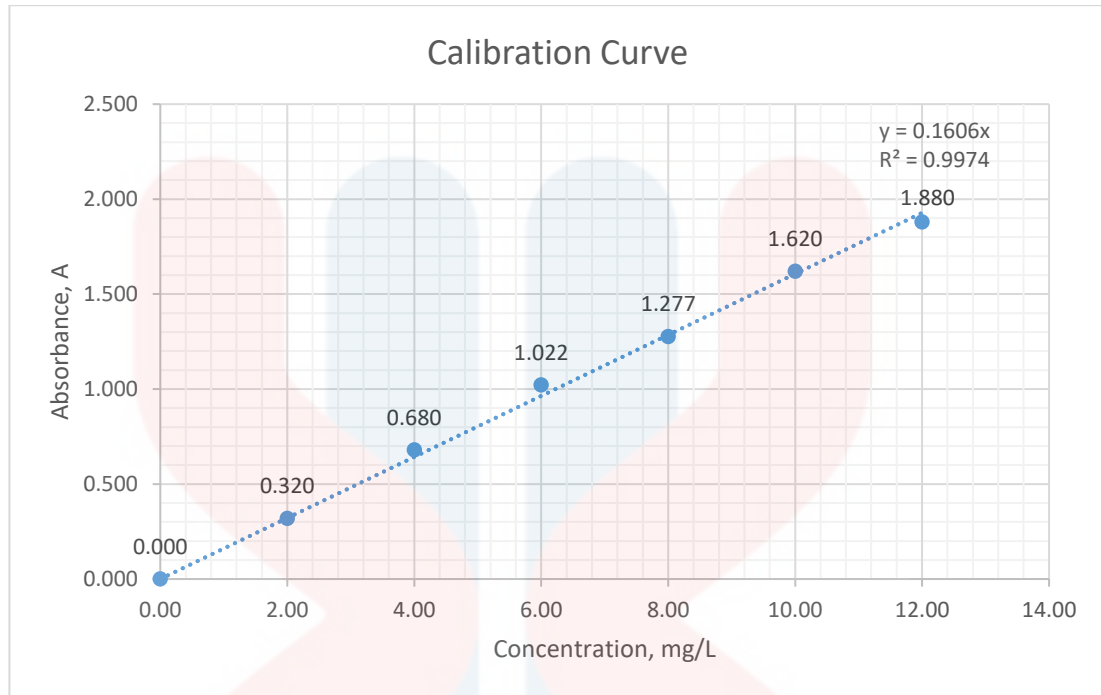
### RESULTS AND DISCUSSION

#### 4.1 Introduction

The objectives of this study are achieved by using agricultural waste as an economical way to produce low cost adsorbent and the decolourisation of MB was analyzed by determining the percentage of dye removal in different parameters used; different types of AC samples that has been developed; the contact time of adsorption MB onto the AC; and the effects of varying the dosage of AC used onto the synthetic dye. The final concentrations, percentage removal by adsorption, and adsorption capacity of dye uptake by the different parameters used in this study. The data extracted from the results obtained was calculated, compared, tabulated and charted.

#### 4.2 Calibration Curve

A calibration curve of the MB dye is formed as shown in Fig. 4.1, to assist in achieving the wanted R-squared value and equation (refer as Eq. (2)) of curve to determine final concentrations obtained by adsorption. In other words, the percentage of MB removal can be calculated by the equation obtained from the curve (Eq. (4)).



**Figure 4.1:** Calibration curve of methylene blue

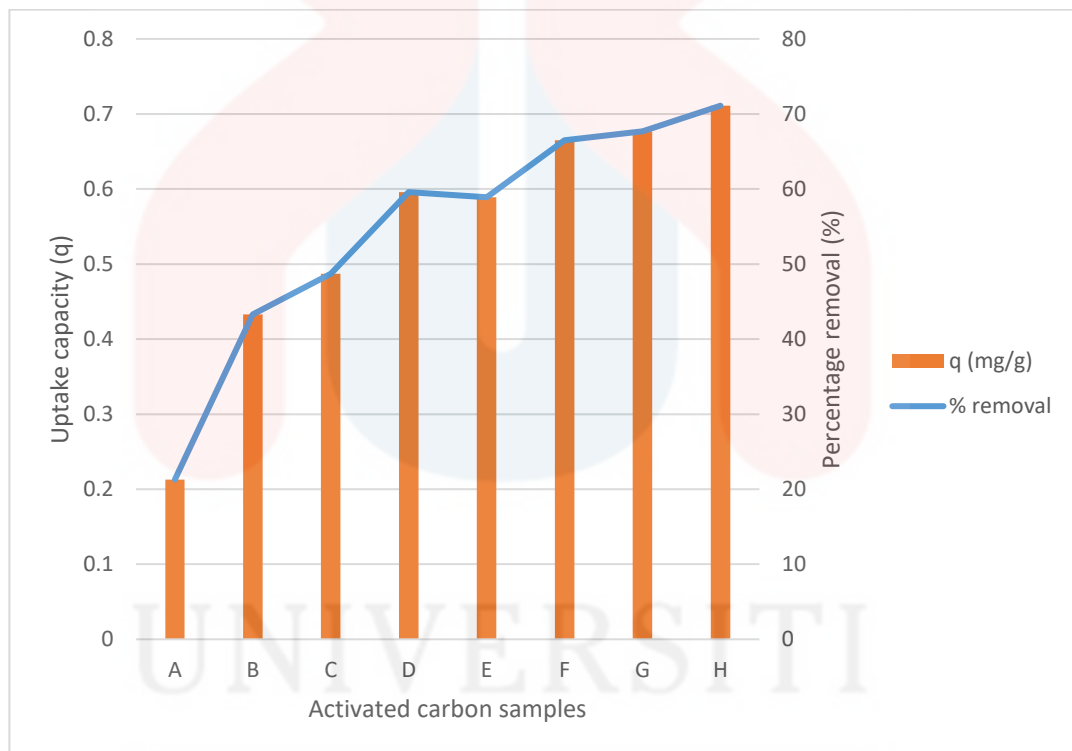
The results show that the increase in concentrations also increase in the amount of absorbance. The  $R^2$  value obtained is 0.9974 (shows the high efficiency of the absorbent and thus expected to be a good candidate as an absorbent for water treatment) and the equation obtained is  $y = 0.1606x$  (refer as Eq. (3)). The y-value resembles the absorbance taken by using spectrophotometer and the x-value is the final concentration obtained for that sample.

This curve produced by using the initial concentration of 100 mg/L and the final concentrations are already set from 0 until 12 mg/L (as shown in Fig. 4.1). Therefore, the absorbance gained from each concentration is determined thus gaining the calibration curve of the MB. The equation used to dilute the dye according to the wanted concentrations is by using Eq. (2).

### 4.3 Dye Removal by Adsorption

#### 4.3.1 Removal by Different Activated Carbon Samples

The production of 8 AC samples are to compare the highest removal between them based on their characteristics on time of carbonization (5, 10, 30 and 60 min) and concentration of  $H_3PO_4$  (30% or 40% w/v). The results are shown in Fig. 4.2, where the blue line represents percentage removal of dye whereas the orange bar represents the adsorption capacity of AC.



**Figure 4.2:** Removal by different activated carbon samples

The results gained (blue line) that H sample of AC removed the highest percentage of dye within the solution by 71% compared to the other AC samples followed by G, F, E, D, C, B and lastly A. The H sample was made from 60 min of carbonization period that has been soaked with 40% w/v concentration of  $H_3PO_4$ .



This increment in carbonization holding time increases MB adsorption was estimated to give better activation of the AC which has been achieved causing the pores to increase in size, opening previously inaccessible pores, formation of new ones, thus promoting higher available space for sorption of dye. In addition, the  $H_3PO_4$  reacting within the internal cellulose structure is assumed to induce a depolymerization leading to enhancement of pore volume (Reffas *et al.*, 2010).

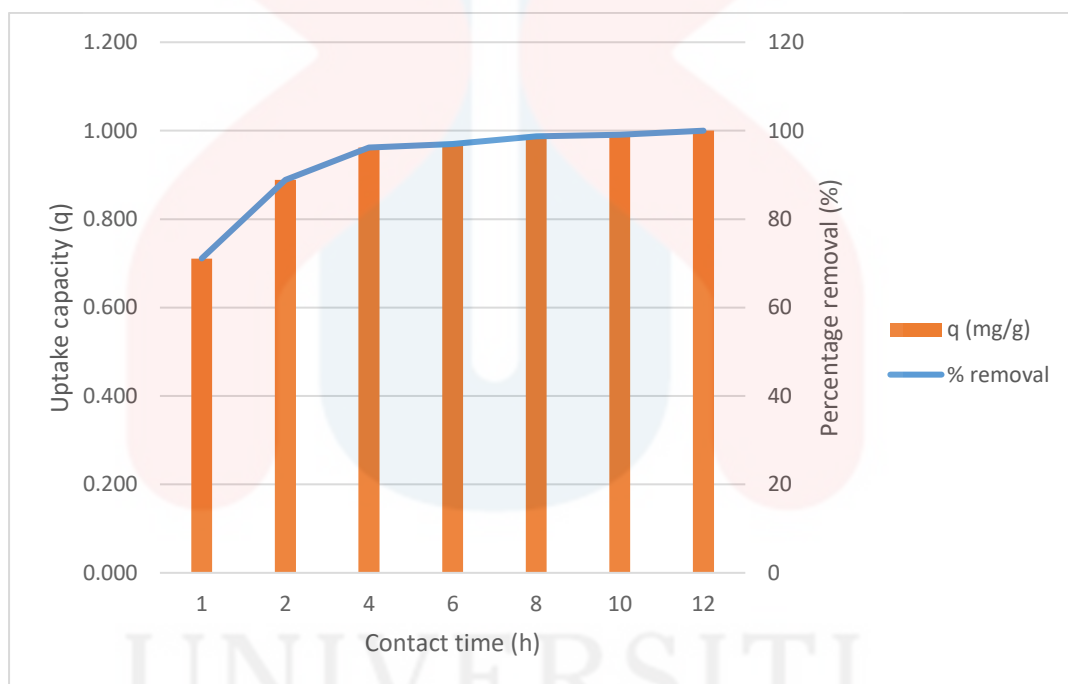
Besides, the  $X_p$  of the AC samples showed important effects towards the pattern of MB adsorption onto the AC. The  $X_p = 0.6\%$  produce lower removal results than the AC produced from  $X_p = 0.8\%$ . This may due to the inclined maximum surface area of AC by rising the impregnation ratio in AC production during chemical activation process. The impregnation ratio has strongly impelled the development of the porosity (Moreno-Pirajan & Giraldo, 2012).

With increasing chemical ratio from 7 to 9, the surface areas and total pore volumes of the activated carbon may also increase. The increased in porosity with  $X_p$  can be attributed to the release of tars from the cross-linked framework generated by treatment of the chemical agents. Both surface pyrolysis and interior etching process may have occurred simultaneously during the preparation of AC. Therefore, creating a global volume expansion of the AC (Moreno-Pirajan & Giraldo, 2012).

The results (orange bar) obtained shown in Fig. 4.2, gained that different AC samples gave out different amount of adsorption capacity values. As expected, the highest adsorption capacity was gained by H which is 0.711 mg/g in one hour of contact time set. By these results, it was expected that higher mesopores content are present in sample D, E, F, G and H which promote higher intake ( $> 0.5$  mg/g) of dye by the ACs.

### 4.3.2 Removal by Different Contact Time

As H (AC sample) was considered for the entire batch experiments and other parameters such as agitation rate, temperature and carbon dosage were kept constant to test the removal by contact time needed to achieve a full (100%) removal of MB within the solution. The results shown in Fig.4.3, shows that rapid removal of MB within 2 h of contact time yet gradually slows down after. It was gained that the amount of time taken is 12 h of contact time to remove overall MB.



**Figure 4.3:** Removal by different contact time

It is explained by Kyzas (2012), that a large number of surface sites were only accessible for adsorption causes rapid adsorption at the early stage of contact. After a lapse of time, it took longer time to reach equilibrium (full MB removal) due to the remaining surface sites are difficult to be occupied. Other reason was due to the excess of impurities and dye auxiliaries prevents the fast removal of dye molecules and their binding onto the surface of the AC.

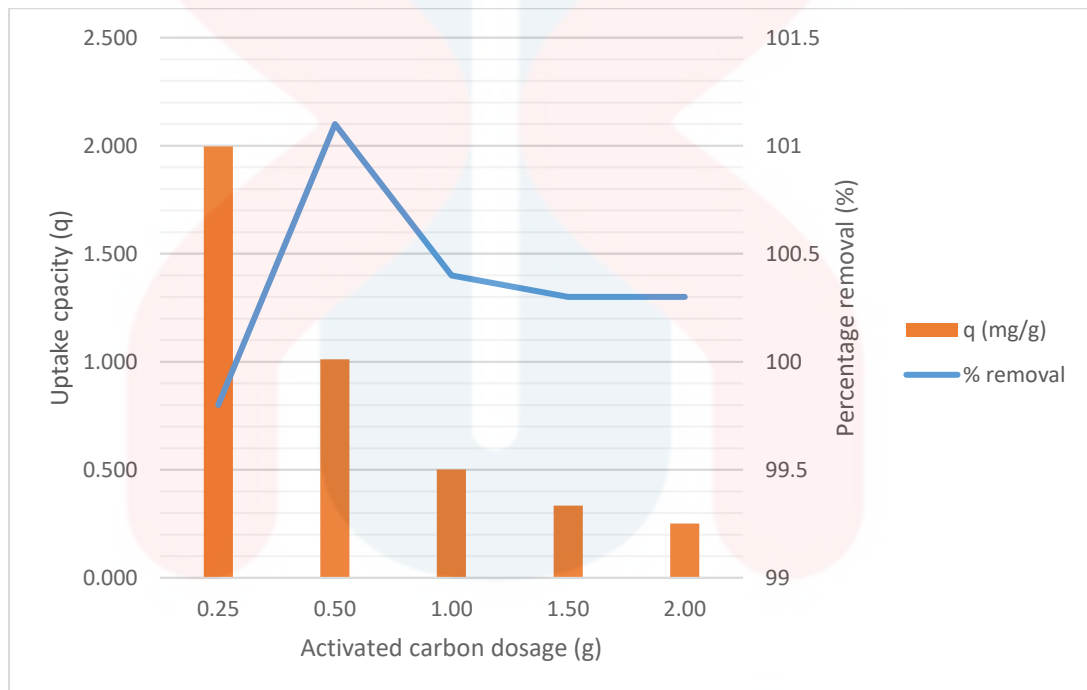
By these results (blue line), it was expected that higher time of contact encourage competitive dye adsorption onto the AC surface and pressured the residual MB to be adsorbed further into the internal pores and cavities presence within the AC (Kyzas, 2012a). When the time reached 12 h, it was observed that the gradient has achieved an equilibrium stage where it will not increase in steepness of percentage removal line for further adsorption. This was expected due to the nature of the adsorbent used and the declining in available adsorption sites as intraparticle diffusion becomes predominant and slow pore diffusion of MB into the bulk of the AC (Babu & Gupta, 2009).

Results in Fig. 4.3 (based on orange bar) indicated the gradual increase in MB uptake in first 2 h indicated that there are available active adsorption sites of the AC before it is fully accumulated by the MB. In scientific terms, the results were responsible by the reduced in electrostatic and dispersion forces cause lowered adsorption of MB over time. The formation of surface oxygen groups in adsorption, led to weakening of dispersion forces due to extraction of electrons from the  $\pi$  band of aromatic groups of MB on the basal plane of AC (Gokce & Aktas, 2014).

Therefore, the optimum contact time was 12 h to reach 100% removal of MB by the CR with adsorption capacity of 1.000 mg/g at 0.5 g of dosage shaken at 100 rpm.

### 4.3.3 Removal by Different Activated Carbon Dosage

The aqueous suspensions containing different amounts of the adsorbent were let to equilibrate for 12 h under agitation (100 rpm) at room temperature and then the samples were collected and filtered (Kyzas, 2012a). The results shown in Fig. 4.4 (blue line), that to decolourise 10 mg/L of MB, the carbon dosage of 0.50 g was already sufficient to obtain 100% removal.



**Figure 4.4:** Removal by different of carbon dosage

Therefore, increasing the carbon dosage led to the increase in dye removal within the solution. This was because the surface area of AC has been increased giving greater active sites for MB adsorption. However, as observed in Fig. 4.4 (blue line), the percentage removal of MB increased very fast at low dosage up to a point, after which the increase in the dosage did not increase the % removal significantly. This may be due to the decline rate of further ions exchange, hydrogen bonding and  $\pi$ - $\pi$  interactions occur within the solution (between AC and MB) (Kyzas, 2012a).

The presence of higher amount positive amino groups on MB may favours its adsorption onto AC, which was provided by increment of AC dosage (Labaran & Vohra, 2016).

The role played by differentiating the AC dosage onto the amount rate of dye adsorption (orange bar) is shown in Fig. 4.3 above. The optimum parameter for contact time remained the same (12 h). It was observed that adding the adsorbent dosage concurs the reduction of dye uptake within the solutions. The maximum value gained by 0.25 g was 1.996 mg/g, and the minimum value gained by 2.00 g of AC was 0.251 mg/g.

The decreased in adsorption capacity with increasing carbon dosage may have been due to greater adsorption sites for dyes and the use of low dye concentration over high amount of AC used. If the AC dosage is lowered by keeping the MB concentration constant, the amount of MB adsorbed per unit mass of adsorbent increases. This indicated that the incline in AC dosage may result from unsaturated adsorbent sites during the process causing the decline in adsorption capacity (Babu & Gupta, 2014).

Therefore, 0.5 g showed the optimum MB removal by 101.1% and 0.25 g showed highest MB uptake by 1.996 mg/g shaken at 100 rpm for 12 h.

## CHAPTER 5

### CONCLUSION AND RECOMMENDATIONS

#### 5.1 Conclusion

The conclusions made upon this study, is where the objectives of study are successfully achieved. The first objective was reached as activated carbon from coffee residues as among the lignocellulosic renewable materials can be considered as competitive precursor in the preparation of activated carbons and are a promising product that required low cost of production with only a small amount of acid needed (approximately 164.4 mL).

By the results obtained, the second objective of study was obtained when a good AC from CR to fully decolourise MB dye was achieved by 60 min at 300°C of carbonization impregnated with 40% w/v of H<sub>3</sub>PO<sub>4</sub> with impregnation percentage 0.8% at 0.5 g dosage and 12 h of contact time shaken at 100 rpm.

The higher activating agent concentration and longer holding time applied on the CR is observed to influence better removal of MB. The higher impregnation percentage are shown to be potent for producing good activated carbon. The optimum contact time are observed to be as long as 12 h to reach full removal of MB and amount of AC as low as 0.25 g gain adsorption capacity of as high as 1.996 mg/g respectively. Increasing the AC dosage led to the increase in percentage dye removal as high as 101.1% yet reduce the adsorption capacity of activated carbon due to greater adsorption sites for dyes and the use of low dye concentration over high amount of AC used.

## 5.2 Recommendations for Future Research

Throughout this study, there are a few recommendations of experimental methods that can be carry out for future research. Other researches may analyze a deeper and better result by characterizing the activated carbon by following such methods as Brunauer-Emmett-Teller (BET) equation to analyze the specific surface area, pore volume, and the distribution of pore size of the activated carbon.

The point of zero charge (PZC) can be evaluated according to titration procedures. The dye concentration can also be expressed in ADMI units to obtain a direct application to the legislation limits apart from using concentration units in mg/L or ppm.

Sequential adsorption-desorption cycles can be done using the same adsorbents to determine the potential reusability of the adsorbents. This may result in gaining some scientific information of AC degradation rate.

Other than that, the activated carbon can be prepared by the pyrolysis of coffee residues at different carbonization temperatures and adding the stream of gas flow such as nitrogen to analyze the opening of pore structure and distribution within the activated carbon.

In addition, different impregnation ratios on the porous development can be investigated by conducting adsorption isotherm modelling. Adsorption isotherm can be used to describe the interactions of adsorbate with adsorbent at equilibrium. Adsorption equilibrium data can be modelled with three isotherm models: Langmuir (four linearized expressions), Freundlich, and Tempkin models.



The activating agent can be varied to compare and gain optimum result such as using zinc chloride or potassium hydroxide. However, for carbonization process, it is reported that using excessive microwave/heating energy could burn the carbon, destroying the pore structure and henceforth lowering the adsorption onto the AC. Thus, it is important to prepare optimization of parameters including carbonization activation temperature (Foo & Hameed, 2012).

Besides that, Fourier Transform Infrared Spectrum (FTIR) analysis and Boehm titration method can be conducted in the characterization process to identify the functional group of the activated carbon. This can habilitate the adsorption process to occur.

Other research studies can be done with comparing the adsorption isotherms of different dyes with a commercial activated carbon. The research can be brought further down into dyes of different types/groups. The effect of temperature on equilibrium can be analyzed using isotherms curves. The change in the surrounding temperature of process from 25 to 65 °C may play role in the increase of the dye uptake (adsorption capacity) (Kyzas, 2012a).

Lastly, the porosity and morphological structure of the activated carbon can be analyzed and studied by using Scanning Electron Microscopy (SEM) as SEM image are closely defining the physical appearances outlined by the activated carbon. It can be used to examine the particles on their individual structure and giving the information of the molecular arrangement of the activated carbon.

## REFERENCES

- Abdulkarim, M. A., Darwish, N. A., Magdy, Y. M., Dwaidar, A., (2002). Adsorption of phenolic compounds and methylene blue onto activated carbon prepared from date fruit puits. *Journal of Life Science Engineering*, 2, 161-165.
- Adegoke, K. A., & Bello, O. S., (2015). Dye sequestration using agricultural wastes as adsorbents. *Water Resources and Industry*, 12, 8-24.
- Ahmad, A. L., Harris, W. A., Syafiie, Seng, O. B., (2002). Removal of dye from wastewater of textile industry using membrane technology. *Jurnal Teknologi*, 36, 31-44.
- Al-Degs, Y. S., Khraisheh, M. A. M., Allen, S. J., Ahmad, M. N., (2009). Adsorption characteristics of reactive dyes in columns of activated carbon. *Journal of Hazardous Materials*, 165, 944–949.
- Alexandro, M. M., Cazetta, V. A. L., Kunita, M. H., Silva, T. L., Almeida, V. C., (2011). Adsorption of methylene blue on activated carbon produced from flamboyant pods (*Delonix regia*): Study of adsorption isotherms and kinetic models. *Chemical Engineering Journal*, 168, 722-730.
- Allègre, C., Moulin, P., Maisseu, M., Charbit, F., (2006). Treatment and reuse of reactive dyeing effluents. *Journal of Membrane Science*, 269(1-2), 15-34.
- Aljeboree, A. M., Alshirifi, A. N., Alkaim, A. F., (2014). Kinetics and equilibrium study for the adsorption of the textile dyes on coconut shell activated carbon. *Arabian Journal of Chemistry*, 7, 101-108.
- Allen, J. S., Mckay, G., Porter, J. F., (2004). Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems. *Journal of Colloid and Interface Science*, 280, 322-333.
- Babu, B. V., & Gupta, S., (2014). Utilization of waste product (tamarind seeds) for the removal of Cr(VI) from aqueous solutions: Equilibrium, kinetics, and regeneration studies. *Journal of Environmental Management*, 90, 3013-3022.
- Belfer, N., (1972). Designing in batik and tie dye. Davis Publication Inc., Massachusetts.
- Bhatnagar, A., Vilar, V. J. P., Botelho, C. M. S., Boaventura, R. A. R., (2010). Coconut-based biosorbents for water treatment — A review of the recent literature. *Advances in Colloid and Interface Science*, 160, 1–15.
- Crini, G., (2006). Non-conventional low-cost adsorbents for dye removal: A review. *Bioresource Technology*, 97, 1061–1085.
- Daneshvar, N., Ayazloo, M., Khataee, A. R., Pourhassan, M., (2007). Biological decolourization of dye solution containing Malachite Green by microalgae *Cosmarium* sp. *Bioresource Technology*, 98, 1176–1182.

- Fang, B., Wei, Y.-Z., Suzuki, K., Kumagai, M., (2005). Surface modification of carbonaceous materials for EDLCs application. *Electrochimica acta*, 50, 3616-3621.
- Foo, K. Y., & Hameed, B. H., (2011). Preparation and characterization of activated carbon from sunflower seed oil residue via microwave assisted  $K_2CO_3$  activation. *Bioresource Technology*, 102, 9794-9799.
- Ghosh, D., & Bhattacharyya, K. G., (2002). Adsorption of methylene blue on kaolinite. *Applied Clay Science*, 20, 259-300.
- Gokce, Y., & Aktas, Z., (2014). Nitric acid modification of activated carbon produced from waste tea and adsorption of methylene blue and phenol. *Applied Surface Science*, 313, 352–359.
- Gomes, H. T., Miranda, S. M., Sampaio, M. J., Silva, A. M., Faria, J. L., (2010). Activated carbons treated with sulphuric acid: Catalysts for catalytic wet peroxide oxidation. *Catalysis Today*, 151, 153-158.
- Gonzalez, M. T., Rodriguez-Reinoso, F., Garcia, A. N., Marcilla, A., (1997).  $CO_2$  activation of olive stones carbonized under different experimental conditions. *Carbon*, 35, 159-165.
- Guo, Y., & Rockstraw, D. A., (2007). Physicochemical properties of carbons prepared from pecan shell by phosphoric acid activation. *Bioresource Technology*, 98, 1513-1521.
- Hameed, B. H., Mahmoud, D. K., Ahmad, A. L., (2008a). Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: Coconut (*Cocos nucifera*) bunch waste. *Journal of Hazardous Materials*, 158, 65-72.
- Hameed, B. H., Tan, I. A. W., Ahmad, A. L., (2008b). Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: Equilibrium, kinetic and thermodynamic studies. *Journal of Hazardous Materials*, 154, 337-346.
- Hameed, B. H., & Ahmad, A. A., (2009). Reduction of COD and colour of dyeing effluent from a cotton textile mill by adsorption onto bamboo-based activated carbon. *Journal of Hazardous Materials*, 172, 1538–1543.
- Hameed, B. H., Lafi, R., Fradj, A., Hafiane, A., (2014). Coffee waste as a potential adsorbent for the removal of basic dyes from aqueous solution. *Korean Journal of Chemical Engineering*, 31(12), 2198-2206.
- Hazzaa, R., & Hussein, M., (2015). Adsorption of cationic dye from aqueous solution onto activated carbon prepared from olive stones. *Environmental Technology & Innovation*, 4, 36–51.
- Hesas, R. H., Arami-Niya, A., Ashri, W. M. W. D., Sahu, J. N., (2013). Preparation and characterization of activated carbon from apple waste by microwave-assisted phosphoric acid activation: methylene blue adsorption. *Bioresources*, 8(2), 2950-2966.

- Hirata, M., Kawasaki, N., Nakamura, T., Matsumoto, K., Kabayama, M., Tamura, T., Tanada, S., (2002). Adsorption of dyes onto carbonaceous materials produced from coffee grounds by microwave treatment. *Journal of Colloid and Interface Science*, 254, 17-22.
- Isah, U. A., Abdulraheem, G., Bala. S., Muhammad, S., Abdullahi, M., (2015). Kinetics, equilibrium and thermodynamics studies of C.I. Reactive Blue 19 dye adsorption on coconut shell based activated carbon. *International Biodeterioration & Biodegradation*, 102, 265–273.
- Jamal, M. M. E., & Tabbara, M. A., (2012). A kinetic study of discoloration of methylene blue by Na<sub>2</sub>SO<sub>3</sub>, comparison with NaOH. *Journal of University of Chemical Technology and Metallurgy*, 47, 3, 275-282.
- Jeguirim, M., Belhachemia, M., Limousy, L., Addoun F., (2014). Comparison of NO<sub>2</sub> removal using date pits activated carbon and modified commercialized activated carbon via different preparation methods: Effect of porosity and surface chemistry. *Chemical Engineering Journal*, 253, 121–129.
- Jibril, M., Noraini, J., Poh, L. S., Evuti, A. M., (2013). Removal of colour from waste water using coconut shell activated carbon (CSAC) and commercial activated carbon (CAC). *Jurnal Teknologi*, 60, 15-19.
- Josefa, S. Y. M., & Oliveira, E. D., (2003). Heavy metals removal in industrial effluents by sequential adsorption treatment. *Advance Environmental Research*, 7, 263-272.
- Karatepe, N., Örküna, Y., Yavuzb, R., (2012). Influence of Temperature and Impregnation Ratio of H<sub>3</sub>PO<sub>4</sub> on the Production of Activated Carbon from Hazelnut Shell. *Acta Physica Polonica A*, 121, 277-280.
- Karunaratne, H. D. S. S., & Amarasinghe, B. M. W. P. K., (2013). Fixed bed adsorption column studies for the removal of aqueous phenol from activated carbon prepared from sugarcane bagasse. *Energy Procedia*, 34, 83-90.
- Kyzas, G. Z., (2012a). A decolorization technique with spent “Greek Coffee” grounds as zero-cost adsorbents for industrial textile wastewaters. *Material*, 5, 2069-2087.
- Kyzas, G. Z., Lazaridis, N. K., Mitropoulos, A. C., (2012b). Removal of dyes from aqueous solutions with untreated coffee residues as potential low-cost adsorbents: Equilibrium, reuse and thermodynamic approach. *Chemical Engineering Journal*, 189, 148–159.
- Labaran, B. A., & Vohra, M. S., (2016). Application of activated carbon produced from phosphoric acid-based chemical activation of oil fly ash for the removal of some charged aqueous phase dyes: role of surface charge, adsorption kinetics, and modeling. *Journal of Desalination and Water Treatment*, 57(34), 16034-16052.



- Lamine, S. M., Ridha, C., Mahfoud, H-M., Mouad, C., Lotfi, B., Al-Dujaili, A. H., (2014). Chemical activation of an activated carbon prepared from coffee residue. *Energy Procedia*, 50, 393 – 400.
- Lee, Y. S., Kim, Y. H., Hong, J. S., Suh, J. K., Cho, G. J., (2007). The adsorption properties of surface modified activated carbon fibers for hydrogen storages. *Catalysis Today*, 120, 420-425.
- Malik, D. J., Strelko, V. Jr., Streat, M., Puziy, A. M., (2002). Characterization of novel modified active carbons and marine algal biomass for the selective adsorption of lead. *Water Research*, 36, 1527-1538.
- Mishra, G., & Tripathy, M., (1993). A critical review of the treatments for decolourization of textile effluent. *Colourage*, 40, 35–38.
- Molina-Sabio, M., & Rodriguez-Reinoso, F. (2004). Role of chemical activation in the development of carbon porosity. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 241, 15–25.
- Moreno-Pirajan, J. C., & Giraldo, L., (2012). Synthesis of activated carbon mesoporous from coffee waste and its application in adsorption zinc and mercury ions from aqueous solution. *E-Journal of Chemistry*, 9(2), 938-948.
- Mussatto, S. I., Machado, E. M. S., Martins, S., Teixeira, J. A., (2011). Production, composition, and application of coffee and its industrial residues. *Food Bioprocess Technology*, 4, 661–672.
- Noor, S. S., & Rohasliney, H., (2011). *A preliminary study on batik effluent in Kelantan state: a water quality perspective*. Paper presented at International Conference on Chemical, Biological and Environment Sciences (ICCEBS'2011), Bangkok, Thailand, 274 – 276.
- Nora, A. A., & Suhaimi, N. S., (2009). Performance Evaluation of Locally Fabricated Asymmetric Nanofiltration Membrane for Batik Industry Effluent. *World Applied Sciences*, 5, 46-52.
- O'Neill, C., Hawkes, F. R., Hawkes, D. L., Lourenço, N. D., Pinheiro, H. M., Delée, W., (1999). Colour in textile effluents—sources, measurement, discharge consents and simulation: A review. *Journal of Chemical Technology & Biotechnology*, 74, 1009–1018.
- Priyantha, N., Lim, L. B. L., Dahri, M. K., (2015). Dragon fruit skin as a potential biosorbent for the removal of methylene blue dye from aqueous solution. *International Food Research Journal*, 22, 5, 2141-2148.
- Rafatullah, M., Sulaiman, O., Hashim, R., Ahmad, A., (2010). Adsorption of methylene blue on low-cost adsorbents: A review. *Journal of Hazardous Materials*, 177, 70-80.
- Ranade, V. V., & Bhandari, V. M., (2014). Chapter 1 – Industrial Wastewater Treatment, Recycling, and Reuse: An Overview. *Industrial Wastewater Treatment, Recycling and Reuse*, 1–80. Retrieved from <http://dx.doi.org/10.1016/B978-0-08-099968-5.00001-5>

- Ravikumar, K., Deebika, B., Balu, K., (2005). Decolourization of aqueous dye solutions by a novel adsorbent: Application of statistical designs and surface plots for the optimization and regression analysis. *Journal of Hazardous Materials*, B122, 75-83.
- Reffas, A., Bernardet, V., David, B., Reinert, L., Lehocine, M.B., Dubois, M., Batische, N., Duclaux, L., (2010). Carbons prepared from coffee grounds by H<sub>3</sub>PO<sub>4</sub> activation: characterization and adsorption of methylene blue and Nylosan Red N-2RBL. *Journal of Hazardous Materials*, 175, 779-788.
- Rios, R. V. R. A., Martinez-Escandell, M., Molina-Sobia, M., Rodriguez-Reinoso, F., (2006). Carbon foam prepared by pyrolysis of olive stones under steam. *Carbon*, 44, 1448-1454.
- Robinson, T., McMullan G. G., Marchant, R., Nigam, P., (2001). Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Journal of Bioresource Technology*, 77, 247 – 255.
- Saleh, T. A., & Gupta, V. K., (2012). Column with CNT/magnesium oxide composite for lead(II) removal from water. *Environmental Science and Pollution Research*, 19(4), 1224–1228.
- Slokar, Y. M., & Majcen, A. L. M., (1998). Methods of decoloration of textile wastewaters. *Dyes and Pigments*, 37, 335–356.
- Siti Zainon, I., (1986). *Reka Bentuk Kraftangan Melayu Tradisi*. Kuala Lumpur, Malaysia: Dewan Bahasa dan Pustaka, Kementerian Pelajaran Malaysia.
- Soares, G. M. B., Amorim, M. T. P., Hrdina, R., Costa-Ferreira, (2002). Studies on the biotransformation of novel diazo dyes by laccas. *Process Biochemistry*, 37, 581-587.
- Szoke, S., Patzay, G., Weiser, L., (2002). Characteristics of thin-film nanofiltration membranes at various pH-values. *Desalination*, 151, 123-129.
- Thakur, S., Pandey, S., Arotiba, O., (2016). Development of a sodium alginate-based organic/inorganic superabsorbent composite hydrogel for adsorption of methylene blue. *Carbohydrate Polymers*, 153, 34-46.
- Valdés, H., Sánchez-Polo, M., Rivera-Utrilla, J., Zaror, C., (2002). Effect of ozone treatment on surface properties of activated carbon. *Langmuir*, 18, 2111-2116.
- Wang, S. B., Zhu, Z. H., Coomes, A., Haghseresht, F., Lu, G. Q., (2005). The physical and surface chemical characteristics of activated carbons and the adsorption of methylene blue from wastewater. *Journal of Colloid and Interface Science*, 284, 440–44.
- Wu, F-C., & Tseng, R-L., (2006). Preparation of highly porous carbon from fir wood by KOH etching and R-L., CO<sub>2</sub> gasification for adsorption of dyes and phenols from water. *Journal of Colloid and Interface Science*, 294, 21-30.

- Xu, D., Hein, S., Loo, S. L., Wang, K. (2008). The fixed-bed study of dye removal on chitosan beads at high pH. *Industrial & Engineering Chemistry Research*, 47(22), 8796–8800.
- Xu, Y., & Lebrun, R. E., (1999). Investigation of the solute separation by charged nanofiltration membrane: effect of pH, ionic strength and solute type. *Journal of Membrane Science*, 158, 93-104.





## APPENDIX A

### Activated Carbon Samples Produced

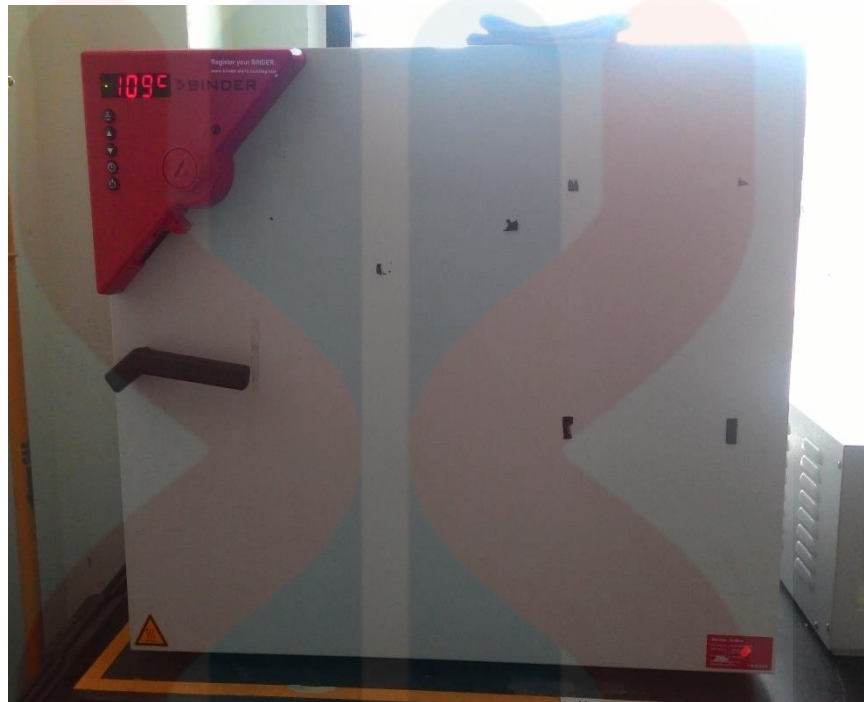


Figure A1: Sampling of AC produced after carbonization

UNIVERSITI  
MALAYSIA  
KELANTAN

## APPENDIX B

### Instrument Used to Run the Experiment



**Figure B1:** Convection oven (ED23, BINDER)



**Figure B2:** Weighing balance (83002-S, METTLER-TOLEDO)



Figure B3: Digital Muffle Furnace (FH-14, WiseTherm)

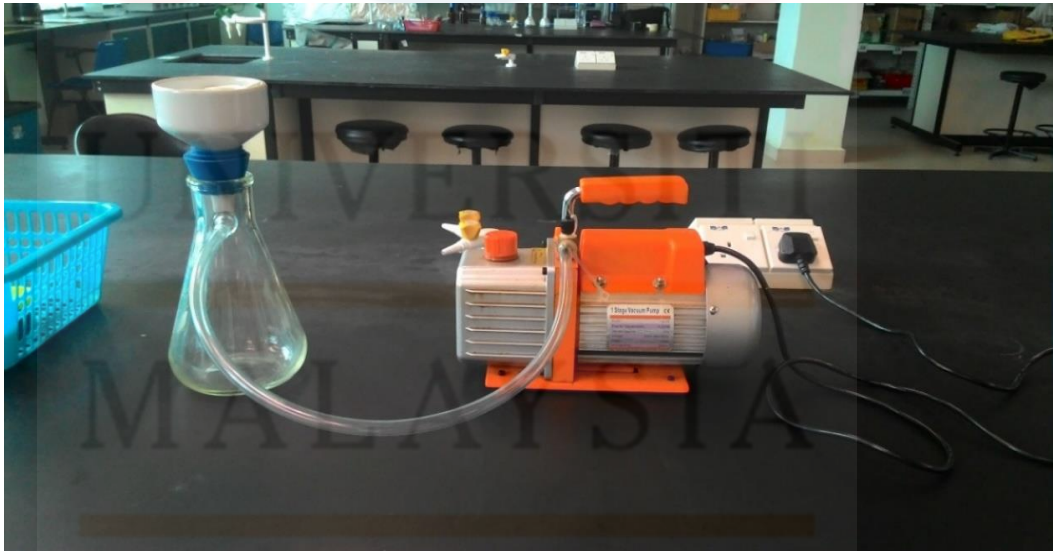


Figure B4: Buchner filtration apparatus





**Figure B5:** Hot plate stirrer (C MAG HS 7, IKA)



**Figure B6:** pH meter (HI 2211, HANNA)

KELANTAN



**Figure B7:** Orbital shaker (KS 4000 i control, IKA)



**Figure B8:** Uv-Vis spectrophotometer (GENESYS 20, ThermoScientific)