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# **Removal of Metanil Yellow Dye from Aqueous Solution using Cassava Peel**

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degree of Bachelor of Applied Science (Bioindustrial  
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## DECLARATION

I declare that this thesis entitled “Removal of Metanil Yellow Dye from Aqueous Solution using Cassava Peel” 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.

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## TABLE OF CONTENTS

	<b>PAGE</b>
<b>DECLARATION</b>	<b>iii</b>
<b>ACKNOWLEDGEMENT</b>	<b>iv</b>
<b>TABLE OF CONTENTS</b>	<b>v</b>
<b>LIST OF TABLES</b>	<b>ix</b>
<b>LIST OF FIGURES</b>	<b>x</b>
<b>LIST OF ABBREVIATION</b>	<b>xi</b>
<b>LIST OF SYMBOLS</b>	<b>xii</b>
<b>ABSTRAK</b>	<b>xiii</b>
<b>ABSTRACT</b>	<b>xiv</b>
<b>CHAPTER 1 INTRODUCTION</b>	
1.1 Research Background	1
1.2 Problem Statement	4
1.3 Objective	5
1.4 Scope of Study	5
1.5 Significant of Study	5
<b>CHAPTER 2 LITERATURE REVIEW</b>	
2.1 Agricultural Waste	7
2.1.1 Agricultural Waste as Adsorbent	7
2.1.2 Cassava Peel as Adsorbent	8

2.2 Dye	9
2.2.1 Classification of Dye	11
2.2.2 Synthetic Dye	13
2.2.3 Anionic Dyes	13
2.2.4 Metanil Yellow	14
2.3 Technique For Dye Treatment	17
2.3.1 Biological Treatment	17
2.3.2 Chemical Treatment	19
2.3.3 Physical Treatment	20
2.4 Adsorption	21
2.5 Adsorption Isotherm	22
2.5.1 Langmuir Adsorption Isotherm Model	23
2.5.2 Freundlich Adsorption Isotherm Model	23
2.6 Factor Affecting Adsorption	24
2.6.1 Effect of Adsorbent Size	24
2.6.2 Effect of Contact Time	25
2.6.3 Effect of Dosage Of Adsorbent	25
2.6.4 Effect of pH	26
2.6.5 Effect of Initial Dye Concentration	26
<b>CHAPTER 3 MATERIALS AND METHODS</b>	
3.1 Materials	28
3.1.1 Apparatus and Equipment	28
3.1.2 Chemicals and Reagent	29

3.2 Method	29
3.2.1 Preparation of Adsorbent	29
3.2.2 Preparation of Metanil Yellow	29
3.2.3 Effect of Adsorbent Size	30
3.2.4 Effect Of Adsorbent Dosage	31
3.2.5 Effect of Initial Dye Concentration	31
3.2.6 Effect of Contact Time	31
3.2.7 Effect of pH	32
3.2.8 Characterise using FTIR	33
3.2.9 Characterise using SEM	33
<b>CHAPTER 4 RESULTS AND DISCUSSION</b>	
4.1 Characteristic of Cassava Peel	34
4.1.1 FT-IR Analysis	34
4.1.2 SEM Analysis	36
4.2 Calibration Curve	37
4.3 Effect of Adsorbent Size	38
4.4 Effect of Adsorbent Dosage	39
4.5 Effect of Initial Dye Concentration	40
4.6 Effect of Contact Time	43
4.7 Effect of pH	44
4.8 Adsorption Isotherm	46
<b>CHAPTER 5 CONCLUSION AND RECOMMENDATION</b>	

5.1 Conclusion	50
5.2 Recommendation	51
<b>REFERENCES</b>	53
<b>APPENDIX A</b>	64
<b>APPENDIX B</b>	67
<b>APPENDIX C</b>	68



## LIST OF TABLES

NO		PAGE
2.1	Previous research of cassava peel as adsorbent	9
	Previous	
2.2	Classification of synthetic dye	12
2.3	Physical and chemical properties of Metanil Yellow dye	15
2.4	Previous research of Metanil Yellow dye	16
2.5	Previous study on various method for dye removal.	20
3.1	List of buffer preparation formula	32
4.1	Infrared spectroscopy absorptions by frequency regions	36
4.2	Langmuir and Freundlich adsorption isotherm parameters for contact time and pH	46



## LIST OF FIGURES

NO		PAGE
2.1	Classification of dye	12
4.1	FT-IR spectrum for cassava peel before adsorption (a) and after adsorption (b)	35
4.2	SEM image of cassava peel before adsorption (a) and after adsorption (b)	37
4.3	Calibration curve for Metanil Yellow	38
4.4	Effect of adsorbent size on the removal of MY dye using cassava peel	39
4.5	Effect of adsorbent dosage on the removal of MY dye using cassava peel	40
4.6	Effect of initial dye concentration on the removal of MY dye using cassava peel	41
4.7	Spectrum of MY at concentration 150 mg/L (a), 200 mg/L (b), 250 mg/L (c), 300 mg/L (d) and 400 mg/L (e)	42
4.8	Effect of initial dye concentration on the removal of MY dye using cassava peel	44
4.9	Effect of pH on the removal of MY dye using cassava peel	45
4.10	Langmuir adsorption isotherm plot for contact time (a) and pH (b)	48
4.11	Freundlich adsorption isotherm plot for contact time (a) and pH (b)	49

## LIST OF ABBREVIATION

BET	Brunauer–Emmett–Teller
FT-IR	Fourier-Transform Infrared Spectroscopy
MY	Metanil Yellow
SEM	Scanning Electron Microscopy
XRF	X-ray Fluorescence

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## LIST OF SYMBOLS

%	Percentage
$Q_e$	Equilibrium concentration of dyes on the adsorbent (mg/g)
$C_E$	Equilibrium concentration of dyes in solution (mg/L)
$Q_{max}$	Monolayer capacity of adsorbent (mg/g)
$K_L$	Langmuir constant (L/mg)
$K_F$	Constant value which related to adsorption capacity (mg/g)
mg/g	Milligram per gram
mg/L	Milligram per litre
$R^2$	Correlation coefficient
mL	Millilitre
mm	Millimeter
°C	Degree Celsius
h	Hour
g	Gram
nm	Nanometre
$C_o$	Initial concentration of adsorbent
$C_e$	Final concentration of adsorbent
Rpm	Revolutions per minute
<	Less than
>	More than

## **Penyingkiran Pewarna Kuning Metanil daripada Larutan Akueus dengan Menggunakan Kulit Ubi Kayu**

### **ABSTRAK**

Bahan-bahan yang tidak digunakan dari pertanian dikenali sebagai sisa pertanian. Sisa-sisa pertanian mempunyai keupayaan untuk menyingkirkan logam dan pewarna daripada air buangan. Pada masa kini, sisa pertanian kebanyakannya digunakan dalam proses penjerapan untuk merawat air yang tercemar dari pelbagai industri seperti tekstil, lilin, farmaseutikal, dan lain-lain. Penjerapan dikenali sebagai kaedah yang berkesan untuk menyingkirkan logam, bahan cemar dan pewarna dari efluen. Kulit ubi kayu sebagai penjerap mempunyai keupayaan untuk menyingkirkan pewarna daripada larutan akueus. Tujuan utama kajian ini adalah untuk menyiasat kapasiti dan potensi penjerapan kulit ubi kayu untuk menyingkirkan pewarna Kuning Metanil. Pencirian kulit ubi kayu telah dikaji menggunakan FT-IR dan SEM. Saiz penjerap, masa sentuhan, dos bahan penjerap, kepekatan awal pewarna dan pH adalah faktor yang mempengaruhi penjerapan. Dalam kajian ini, parameter tersebut dijalankan untuk menentukan parameter optimum dan isoterma penjerapan untuk menyingkirkan pewarna Kuning Metanil dengan menggunakan kulit ubi kayu. 3 g saiz penjerap kecil (<0.125 mm) dalam 150 mg/L kepekatan awal pewarna, 8 jam masa sentuhan dan pH 8 menunjukkan peratus penyingkiran perwarna yang tinggi. Data keseimbangan adalah paling sesuai kepada isoterma Langmuir dengan kapasiti penjerapan maksimum 3.618 mg/L.

Katakunci : Kulit ubi kayu, Pewarna Kuning Metanil, Kapasiti penjerapan dan Isoterma Langmuir.

## Removal of Metanil Yellow Dye from Aqueous Solution using Cassava Peel

### ABSTRACT

Unused materials from agricultural are known as agricultural waste. This cheap and renewable agricultural waste has the ability to remove heavy metals and dyes from wastewater. Nowadays, agricultural wastes are mostly used in adsorption process to treat the polluted water from various industries like textile, tannery, candle, pharmaceutical, etc. Adsorption is known as the effective method to remove heavy metals, contaminants and dyes from the effluent. Cassava peel as a low-cost adsorbent has the ability to remove dye from aqueous solution. The main aim of this study is to investigate the potential and adsorption capacity of raw cassava peel as adsorbent for removal of Metanil Yellow dye. The characteristic of cassava peel was studied using FT-IR and SEM analysis. Adsorbent size, contact time, dosage of adsorbent, initial dye concentration and pH are the main factors that affecting adsorption. In this study, these parameters were investigated to determine the optimum parameters and adsorption isotherms for removal of Metanil Yellow dye using cassava peel. 3 g of small size adsorbent ( $< 0.125$  mm) in 150 mg/L of initial dye concentration for 8 hours at pH 8 was showed the highest percentage of dye removal. The equilibrium data was best-fitted to Langmuir isotherm with the maximum adsorption capacity was 3.618 mg/L.

Keywords : Cassava peel, Metanil Yellow, Adsorption capacity and Langmuir isotherm.

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Research Background

Water is essential for every living things and it is a basic need of life. It is very important to maintain a balance ecosystem. However, the availability and accessibility to freshwater has been proved as one of the most severe case effected in recent years (Chun, 2010).

Many industries like textile, pharmaceuticals, tannery, food, etc., involved in the consumption of dyes to impart colour to their products. Among these industries, textile industry consumes the largest quantity of dyes (Akinola and Umar, 2015). Each and everyone try to seek attention with colourful and fashionable clothes. However, they fail to look the negative effects which ended up causing harm to the environment. Dyes cause severe problems to environment. According to theory, if the concentration of dye and exposure time of dye in the water bodies are high, then it can create chronic effects on exposed organisms. Basically, dye has ability to absorb and reflect the sunlight. Thus, it blocks the sunlight from entering the water bodies. This phenomena affects the photosynthesis activity of algae in the water and creates imbalance food chain. Moreover, Vandevivere et al. (1998), mentioned that the presence of dyes in water

bodies are highly visible. This is because of their brilliance. Vandevivere et al. (1998), also stated that the dyes in the industrial waste water should be removed before the wastewater released into the environment. However, the problem is dyes are really difficult to remove from industrial waste water because they are not easily degradable (Isik and Sponza, 2006). Besides, dyes have high thermal and photo stability and this characteristic help them to remain in the environment for extended period of time. Many dyes and their breakdown products are carcinogenic, mutagenic and toxic to life. Dyes are mostly introduced into the environment through industrial effluents.

Dye is a coloured molecule which is used to give colour to many substrates like fabric, textile material, plastic, paper and waxes. Normally, dye used in liquid form (solution) due to its capability of being fixed to a fabric. Dyes must have property like soluble in water. This is because solution form of dye is easy to be absorbed and retained by the fabrics, paper, waxes and plastics. It also must be able to withstand exposure of sunlight and washing whether its dry washing or wet washing.

Metanil Yellow with a molecular formula of  $C_{18}H_{14}N_3NaO_3S$  is known as an acid dyes. Basically, acid dyes are brightest class of dyes and are applied widely in industries (Supaka et al., 2001) like dye, textile, paper and plastics industries to colour their products. However, Metanil Yellow is an extremely valuable textile dye because it revolutionized the textile industry. At the same time, natural dyes can be used to colour the textile product but the problem is the natural dyes offered a fairly limited colour palette and many stains faded easily upon washing and exposure to light. Even some aniline dyes were limited by the need to use a substance called mordant to fix the dye permanently to the textile fiber (Miller and Travis, 1993). This thing required an extra

step to the dyeing process and increases the production cost. However, this brilliant yellow dye which known as Metanil Yellow did not require a mordant to stain textile fibers and it did not fade that much easily. This is why the Metanil Yellow categories as an extremely valuable textile dye.

Even though the Metanil Yellow dye is very essential for the industries, it also give some negative impacts to the environment. Metanil Yellow dye categorised as a harmful textile dye because it cause an allergic reaction and it easily metabolise to benzidine, a human carcinogen. It not only degrade the water quality but it also cause damage to skin, kidney, liver and reproductive system in human (Shaban et al. 2017a ; Gupta et al. 2006).

Synthetic dyes such as Metanil Yellow are very difficult to remove from effluents. This is because of the complex aromatic structure. Actually, physical-chemical methods like ion exchange, chemical precipitation, reverse osmosis and oxidation can be used to treat the contaminated wastewater (water with Metanil Yellow) from industries (Han and Ding, 2008). However, the application of these techniques has been restricted due to high energy consumption and expensive synthetic chemicals (Blackburn and Richard, 2004). Moreover, these methods generate large amount of toxic sludge and are ineffective at lower concentrations of dye.

Adsorption is the most widely used technique for the removal of dyes (Allena et al., 2004). According to Vijaya and Sandhya (2003), the physical adsorption is an effective, potential and economic method for treatment of industrial waste discharge like removal of dye from wastewater. It producing high quality with desired standard



treated effluents which is totally safe for disposal. Moreover, it has become popular because of its simplicity, low cost and the availability of wide range of adsorbents.

## 1.2 Problem Statement

Textile industry known as the major consumers of dye stuffs. It is also produce large volumes of wastewater to the environment and this situation lead to water pollution if the untreated synthetic dyes are dispose directly to the water bodies. Recent studies shows that 10 to 15 percent of the dyes are discharge in the form of effluents from the textile industries. Synthetic dyes like Metanil Yellow have harmful impact to the environment and human health. This is because synthetic dyes are made up of chemical compounds like sodium chloride, toluene, benzene even mercury (Bacher, 2014).

Moreover, the removal of synthetic dye from wastewater is really difficult and hard to treat with conventional treatment methods. This is due to its complex aromatic structure. Biological oxidation and chemical precipitation process are effective and economic if and only the concentration of the dye is high. Pei et al. (2011), proved that low cost agricultural by-products are best solution for waste water treatment. In other word, agricultural waste have a potential to be used as adsorbent for the removal of dye. In addition, it also give rise to waste minimisation.

### 1.3 Objective

The objectives of this study are :

- i. To investigate the potential of cassava peel as adsorbent for removal of Metanil Yellow dye.
- ii. To determine the optimum parameters and adsorption isotherms for removal of Metanil Yellow dye using cassava peel as a low-cost adsorbent.
- iii. To characterise cassava peel adsorbents using Scanning Electron Microscope (SEM) and Fourier-transform infrared spectroscopy (FTIR).

### 1.4 Scope of Study

Cassava peel was obtained from Muar, Johor. The physical and chemical properties of cassava peel was studied by using Scanning Electron Microscope (SEM) and Fourier-transform infrared spectroscopy (FTIR). Other than that, five types of parameters such as effect of adsorbent size, adsorbent dosage, contact time, effect of pH and the initial dye concentration were studied in this research to determine the optimum parameters for the removal of Metanil Yellow dye.

### 1.5 Significant of Study

The result of this research will help the industries that using dye as their main material especially the textile industry and also give positive impact to the environment. This is because it will reduce the amount of dye in the waste effluent which will dispose to the water bodies. At the same time, this research will give some useful information

and new idea to the textile industries and environmental organizations. Moreover, this research also help to add value to the cassava peel which is known as waste product. The cassava peel has functional groups like groups of free hydroxyl groups (-OH) and carboxyl (-CO<sub>2</sub>H). The functional groups make the peel effective to remove dyes and toxic metals. In addition, cassava peel is low cost adsorbent.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Agricultural Waste

Agricultural waste is waste that produced from agricultural operations. The remain or unused substance or material from agricultural operations labeled as waste because of the economical and efficient uses of those materials are not been identified. So, these wastes are simply disposed by burning in field. Although, burning is one of the way to dispose agricultural wastes but still it has some negative impact to the environment. Burning of waste is discouraged by many people because it brings negative effect to the environment, ecology and human health. Nowadays, agricultural wastes are recognized as having economic value (Haggar, 2007).

##### 2.1.1 Agricultural waste as adsorbent

Nowadays, agricultural solid wastes are used as adsorbent to remove heavy metal and dye from wastewater. This is because adsorbent from agricultural solid waste showed high adsorption capacity (Noeline et al, 2005) and it helped to remove the waste properly from wastewater. Besides that, agricultural wastes are renewable, cheap and

available in large amounts compared to other materials which used as adsorbents. The reason for agricultural wastes become better adsorbent than other material is it use minimum process and this helps to reduce the production costs. It also helps to reduce the energy cost which associated with thermal treatment (Franca et al., 2009).

### **2.1.2 Cassava peel as adsorbent**

Cassava (*Manihot esculenta Crantz*) is major staple food in many tropical countries. Basically, processing of cassava generate huge amount of waste. It can create serious environmental problems if it not dispose properly. In Ghana, a survey was conducted on cassava processing. According to that survey, it found that 28% of the cassava peel become agricultural waste during garri production (powdery material). The peels are heaped in refuse dump. This activity affects the vegetation and soil around the heaps of cassava peels. This is due to biological and chemical reactions which took place midst of the continuously fermenting peels, soil and the surrounding vegetation (Ubalua, 2007). So, to overcome this problem, cassava peels can be used as a renewable adsorbents toward removal of water pollutants.

Cassava peel can be used as adsorbent because it has functional groups like hydroxide (-OH), carboxyl (-CO<sub>2</sub>H) and compounds such as pectin, cellulose and lignin. The functional groups and compounds make the peel effective to remove dyes and toxic metals. In addition, cassava peel is low cost adsorbent. Usually, the skin is disposed as waste since it does not have any economic value. It has been reported that the skin has the ability to remove Co<sup>2+</sup>, Cr<sup>2+</sup> and V<sup>2+</sup> from aqueous solution (Daniel et al., 2016) while the cassava peel activated carbon has been used for zinc ion removal

(Ezemokwe et al., 2018). Table 2.1 shows cassava peel that have been used as adsorbent for removal of dyes and heavy metals.

Table 2.1 : Previous research of cassava peel as adsorbent

Adsorbent	Adsorbate	Adsorption Capacity (mg/g)	Reference
Cassava Peel	Dyes and metal ions	Not Stated	(Rajeshwari et al.,2001)
Cassava Peel Activated Carbon	Zinc, Zn <sup>2+</sup>	4.8 mg/g	(Ezemokwe et al., 2018)
Cassava Peel Activated Carbon	Hexovalent Chromium, Cr(VI)	79.37 mg/g	(Vasudevan et al., 2016)
Fermented cassava peel activated carbon and unfermented cassava peel activated carbon	Oil Refinery Wastewater Metal ion of Pb <sup>2+</sup>	Fermented cassava peel activated carbon : 1.09 mg/g Unfermented cassava peel activated carbon : 0.98 mg/g	(Kigho et al., 2016)
Cassava Peel	Cobalt, Co <sup>2+</sup> Chromium, Cr <sup>2+</sup> Vanadium, V <sup>2+</sup>	Co <sup>2+</sup> : 19.85 mg/g Cr <sup>2+</sup> : 20.72 mg/g V <sup>2+</sup> : 25.17 mg/g	(Simate et al., 2015)
Cassava Peel Activated Carbon	Cadmium, Cd <sup>2+</sup> Lead, Pb <sup>2+</sup> Chromium, Cr <sup>2+</sup>	Cd <sup>2+</sup> : 19.34 mg/g Pb <sup>2+</sup> : 42.46 mg/g Cr <sup>2+</sup> : 43.97 mg/g	(Daniel and Affonso, 2016)
Cassava Peel	Copper, Cu <sup>2+</sup> Zinc, Zn <sup>2+</sup>	Cu <sup>2+</sup> : 4.38 mg/g Zn <sup>2+</sup> : 5.21 mg/g	(Daniel and Affonso, 2015)

## 2.2 Dye

Dye is chemical compound and will be connected themselves on the surface or object to impart its colour (Yagub et al., 2014). Besides, it is also important and widely

used in the industry of leather, textile, plastic, paper, pharmaceutical and food industry (Wang et al., 2015). Dye can be divided into two categories. They are natural dye and synthetic dye. Natural dye are extracted from the sources of plants, animal, and mineral. The application of natural dye is only in the earlier textile industry. However, when the population and industrial activities increase, the application of natural dye in the industry are less because it fail to achieve industrial demand (Ngulube et al., 2017). Moreover, natural dyes offered a fairly limited colour palette and many stains faded easily upon washing and exposure to light. Even some aniline dyes were limited by the need to use a substance called mordant to fix the dye permanently to the textile fiber (Miller and Travis, 1993). So, to overcome this problems, synthetic dye have been introduced and it almost completely replaced the natural dye in the fabrics and textile industry. There are several types of synthetic dyes like basic, acid, reactive, direct, disperse and vat dye which are used in numerous type of industry. These types of dyes are soluble in the water except for disperse and vat dye because it contain traces of metal like chromium, copper, zinc, lead and cobalt (Gupta, 2003).

Dyes are being widely used in the textile industry for the production of variety colour of cloths. Besides, high intensity colour of dye is important to make sure the marketable in the commercial industries. Therefore, the colour must be able to retain for a long time and do not fade away with time. However, the intensity of the colour is depend on the strong of the radiation adsorption in the visible region (Ngulube et al., 2017).

In contrast, dyes are mutagenic, teratogenic and carcinogenic which is very harmful to the aquatic lives (Wang et al., 2015) and approximately 10% to 15% of dyes

are wasted in effluent during the process of dyeing. This will reduce the quality of water and also affect the food chain of the aquatic animals. Other than that, it also affect the pH of water body, concentration of oxygen, biological oxygen demand (BOD), and chemical oxygen demand (COD). Besides that, dyes also can be very harmful to the human as it can cause dysfunction of kidney, reproductive system, liver, brain and central nervous system (Kadirvelu et al., 2003). In addition, azo dye is toxic because it contain toxic amine in the effluent while reactive dye is water soluble and about 5% to 10% will go in the dye bath which give highly colour in the water and will cause serious problem to the environment (Yagub et al., 2014).

### **2.2.1 Classification of Dye**

There are several ways to classify commercial dyes. It can be classified according to its colour, structure and application system. However, the classification of dye always be made based on the application system due to its complexities of colour nomenclature from chemical structure system. Besides that, classification of dye based on the structure have its own advantage and have been widely used and most preferable by the chemist. The advantages are it can be readily identified the dye group and also having characteristics properties. However, the classification of dye based on application is advantageous before considering the method based on the structure due to complexities of dye nomenclature (Gupta and Suhas, 2009). Besides that, dye also can be divided into two parts which is chromophore and auxochromes. Chromophore is the part which produces the colour while auxochromes is the part which indicates the intensity of the colour of dye (Ngulube et al., 2017). The classification of dye is summarised in Figure 2.1 and Table 2.2.



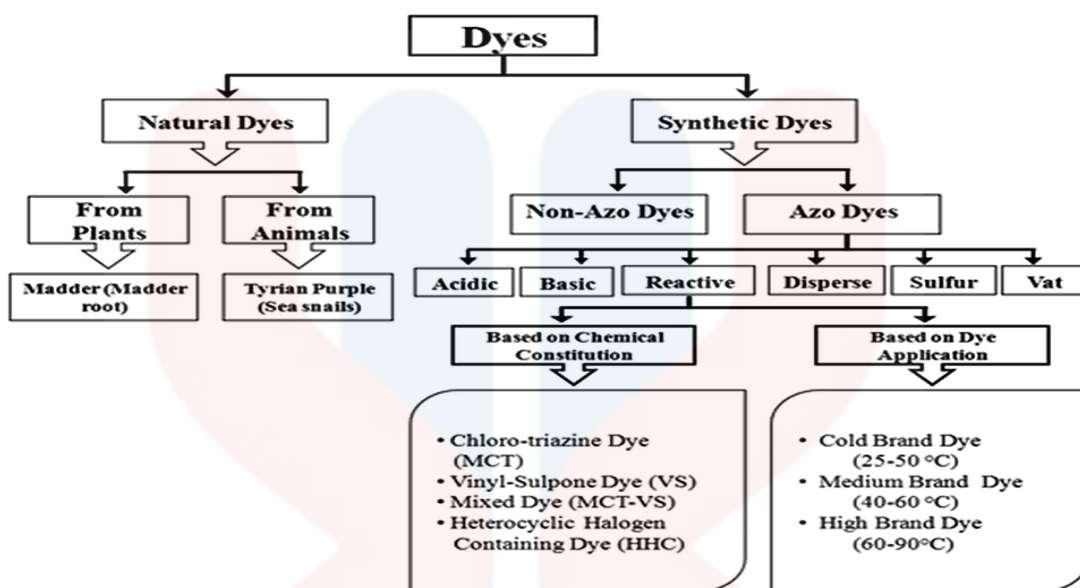


Figure 2.1: Classification of dye (Yagub et al., 2014)

Table 2.2: Classification of synthetic dye

Class	Principle Substrate	Principle chemical class	Solubility in the water
Reactive dye	Cotton	Azo, metallised azo, phthalocyanine, anthraquinone	Soluble
Disperse dye	Polyester, electronic photography	Non-ionic	Insoluble
Direct dye	Cotton, regenerated cellulose	Anionic, poly-azo	Soluble
Vat dye	Cellulose fibres	Indigoids, anthraquinone	Soluble leuco salt Insoluble
Sulphur dye	Cotton	Sulphur dye	Soluble
Cationic or basic dye	Paper, polyacrylo nitril, polyester	Triarylmethane	Soluble
Acid dye	Nylon, silk, wool, leather, paper, ink-jets	-	Soluble
Solvent dye	Plastic, gasoline, oil, waxes	Azo, anthraquinone	Insoluble

Source : Ngulube et al., (2017)

### 2.2.2 Synthetic Dyes

Synthetic dyes are mainly sourced from petrochemicals and used for large scale dyeing operations. Dyes are simply defined as chemicals which binding with a material and give distinct colour to them (Velmurugan et al., 2011 ; Al-Degs et al., 2007). A dye molecule normally contains two major components; chromophores and auxochromes. Chromophores are responsible for colour upon absorption of ultraviolet-visible electromagnetic radiation while auxochromes enable the dye to bind onto fibres (Gupta and Suhas, 2009). The main types of dyes applied in textile dyeing are basic dyes, acid dyes, reactive dyes, direct dyes, disperse dyes, sulfur dyes, vat dyes, azo dyes and mordant dyes (Salleh et al., 2011 ; Demirbas, 2009).

According to their structure, dyes can be classified as anionic or cationic. Anionic dyes carry a net negative charge in aqueous media. This is due to the presence of sulphate ( $\text{SO}^{3-}$ ) groups in it. On the other hand, cationic dyes carry a net positive charge in aqueous media. This is because of the presence of protonated amine or sulphur groups (Velmurugan et al., 2011; Al-Degs et al., 2007).

### 2.2.3 Anionic Dyes

The distinguishing feature of anionic or acid dye is their water solubility and ionic substituents (Salleh et al., 2011). They depend on a negative ion and include a variety of dyes such as direct dyes, anionic azo dyes and reactive dyes (Hunger, 2003; Tyagi et al., 2002). Acid dyes are mainly used with wool, silk, polyamide, modified acrylic and polypropylene fibres. The presence of aromatic and sulphonic groups makes

acid dyes harmful to humans and other microorganisms (Attia et al., 2006). Examples of anionic dyes include Metanil Yellow, Indigo Carmine and Red Reactive 141. Metanil Yellow removal from wastewater has been modeled by Kumarasamy and Chellapandian (2013), on mesoporous aluminophosphate molecular sieves, on chemically cross-linked chitosan beads by Ming and Gua (2005), and on waste materials by Gupta et al. (2016).

#### **2.2.4 Metanil Yellow**

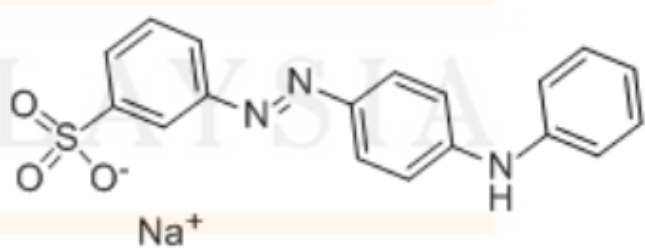
Metanil Yellow dye which categorized as a synthetic azo dye is actually an acid dye (anionic dye) which applied on wool, nylon, silk, paper, ink, aluminum, detergent, wood, fur, cosmetics, and as biological stain. Basically, acid dyes are brightest class of dyes and are applied widely in industries (Supaka et al., 2004) like dye, textile, paper and plastics industries to colour their products. However, Metanil Yellow is an extremely valuable textile dye because it revolutionized the textile industry. Metanil Yellow is highly water soluble diazo dye and it is having colour of yellowish-orange. It is also have strong affinity to cellulose fibre which is widely use in the textile industry (Bhoi, 2010). Besides that, it is actually derivative from the benzidine and naphthoic acid and metabolize to carcinogenic product (Banat and Al-Asheh, 2005). Metanil Yellow is also an acid base indicator and the absorption characteristic is depend on the pH and the nature of the solvent environment (Mera and Davies, 2006).

Metanil Yellow dye with a molecular formula of  $C_{18}H_{14}N_3NaO_3S$  has the ability to be turn into red colour in the extreme acidic solution due to the binding of cation to the unshared electron pair which cause the resonance changes (Mera and Davies, 2006). It also known to be soluble in the water and ethanol and very slightly soluble in acetone

(Ahmedi et al, 2015). In addition, Metanil Yellow which categorized as a synthetic dye is very difficult to remove due to their complex aromatic structure. This complex aromatic structure gives them thermal, optical and physico-chemical stability (Han and Ding, 2008).

Moreover, Metanil Yellow is dangerous when ingested and unsafe when inhaled or contacts the eyes (Isiuku and Onyema, 2017). Toxicity data declared that oral feeding or intra-peritoneal and intra-testicular administration of Metanil Yellow in animals produces testicular lesions, causing seminiferous tubules to suffer damage, reducing the rate of spermatogenesis. Actually, Metanil Yellow is not mutagenic but it has the ability to change the gene expression. (Gupta et al., 2003). Government of India banned this Metanil Yellow under the PFA Act (1954). This is because the same dye has found to be carcinogenic in human. Table 2.3 shows the properties of Metanil Yellow dye and Table 2.4 shows the types of adsorbents that has been used for the removal of Metanil Yellow dye from aqueous solution.

Table 2.3 : Physical and Chemical Properties of Metanil Yellow dye

Physical and Chemical Properties of Metanil Yellow dye	
<b>Chemical structure</b>	
<b>CA Index name</b>	3-[(4-anilinophenyl)diazenyl] benzenesulfonate
<b>Dye class</b>	Azo
<b>Molecular formula</b>	C <sub>18</sub> H <sub>14</sub> N <sub>3</sub> NaO <sub>3</sub> S

<b>Molecular weight</b>	375.38 g/mol
<b>pH range</b>	Red (1.2) to yellow (3.2)
<b>Melting point</b>	> 250°C
<b>Solubility</b>	25 g/L
<b>Appearance</b>	Orange-yellowish
<b>Industrial application</b>	Textiles, fiber-optic sensor, highlighters, plastics, waxes, papers, cosmetics, and food storage.
<b>Absorption</b>	434 nm

Table 2.4 : Previous research of Metanil Yellow dye

<b>Adsorbent</b>	<b>Adsorption Capacity (mg/g)</b>	<b>Reference</b>
Mesoporous Aluminophosphate Molecular Sieves	75 mg/g	(Kumarasamy et al., 2013)
Chemically cross-linked Chitosan Beads	1334 mg/g	(Ming and Gua, 2005)
Electrochemical technique Platinum and Steel Electrode	Not Stated	(Jain et al., 2009)
Activated Carbon from <i>Gmelina aborea</i> ( <i>G.aborea</i> ) Bark	2.53 mg/g	(Isiuku, and Oneyema, 2017)
Kenaf, Banana stem and Sugarcane bagasse	Banana : 68.48 mg/g Kenaf : 67.87 mg/g Sugarcane bagasse : 68.19 mg/g	(Abid et al., 2012)
Carbon Slurry Waste	248 mg/g	(Gupta et al., 2016)
Chemically Activated Carbon. (H <sub>3</sub> PO <sub>4</sub> activated carbon and NaOH activated carbon)	H <sub>3</sub> NO <sub>4</sub> activated carbon : 1186 mg/g NaOH activated carbon : 890 mg/g	(Isiuku and Michael, 2013)
Positively charge-modified Nylon 66 Membrane	Not Stated	(Srini Raghavan, (2007)

## 2.3 Technique for Dye Treatment

Wastewater which contain dye and pigment are mostly generated by the industry with high in colour and also organic content. There is about 10, 000 different commercial dye and pigment are release and exist in the water body. Besides that, about  $7 \times 10^5$  tons are produced annually world-wide (Gomez et al., 2007). Furthermore, it also should be noted that the contamination of drinking water by dye at even concentration of 1.0 mg/L may be impart significant colour and consequently could affect the human health which is totally unfit for human consumption or daily use (Garg et al., 2004). Therefore, the effluent of dye caught the attention because most of dye degradation and product is harmful to the aquatic animals and human health due to its toxicological properties which cause major problem (Deniz and Ersanli, 2016).

There are many way in treating dye effluent such as membrane separation, electrochemical and advanced biological process. The advancement in scientific technique of dye removal have split the technique into three categories which are biological treatment, chemical treatment and physical treatment.

### 2.3.1 Biological Treatment

Biological treatment is the process involvement of microorganisms which play the crucial role in mineralisation of biopolymer and xenobiotic compound. Besides that, biological treatment can be broadly divided into three process which is aerobic process, anaerobic process and combination of both aerobic and anaerobic process (Rai et al., 2005). This method of treatment include removal of colour by *Sphingomonas*, white rod

fungi, *pseudomonas strains*, and microbial cultures (Hassan, 2016). This biological treatment offers considerable advantageous which is relatively inexpensive and end product mineralisation is not being toxic.

In aerobic condition, the enzyme will be secreted by the bacteria presence in the wastewater to break down the organic compound (Rai et al., 2005). However, specific strain is required by aerobic bacterial strain for dye decolourisation which show that a strict ability on a specific dye structure (Husain, 2006). Furthermore, there are several group of dye which can be decolourise by the fungal such as azo and triphenyl-methane dye. However, there are one species of fungi which have ability to decolourise wide range of dye; that is *Phanerochaete chrysosporium* (Panswad and Luangdilok, 2000). During the process of removal of dye, some factors like concentration of pollutants, dye stuff concentration, initial pH and temperature of the effluent may affect the decolourisation process (Christie, 2007).

In anaerobic condition, the type of dye which have widely been degrading is synthetic dye. Furthermore, anaerobic pre-treatment is more cheaper compared to the aerobic as expensive aeration and bulking sludge also could be prevent. Besides that, there are some advantageous of anaerobic process where dye can be decolourise with efficient and cheap removal of BOD level, no foaming problem with the surfactant, high pH effluent can be acidified and degradation of refractory organics can be initiated (Liu, 2007).

The combination of the aerobic and anaerobic process are carried out to get better colour remediation. Besides that, this combination treatment have advantage of

complete mineralisation system which is achieved due to synergistic action by different organism (Gupta and Suhas, 2009).

### 2.3.2 Chemical Treatment

There are several treatment involved in the chemical wastewater treatment such as precipitation, flocculation, coagulation, floatation and filtration, electro-kinetic coagulation, oxidation method, irradiation or electrochemical process (Hassan, 2016). The effectiveness of chemical treatment is depends on the interaction between the contaminant and the chemical used in the water (Iqbal and Bhatti, 2014). The presence of the chemical is to help the separation process and also neutralise the detrimental effect which is cause by the pollutant (Mohan et al., 2002).

Furthermore, in a chemical treatment, coagulating or flocculating agents are used as robust way for the removal of colour in the water body. Chemical treatment involves the addition agent like aluminium ( $\text{Al}^{3+}$ ), Calcium ( $\text{Ca}^{2+}$ ), or Ferric ( $\text{Fe}^{3+}$ ) ions to the effluent dye and induce flocculation. This agent use to improve the process and sometimes combination of two agents will be further enhanced the process. Besides that, this process is economically feasible but sometimes it may need high cost due to the use of chemical added in the process. However, this process is not effective for the removal or certain type of dye like azo, reactive, acid, and basic dye (Gupta and Suhas, 2009). Besides, this technique also will create a lot of sludge after use which can be lead to the sludge disposal problem. Moreover, secondary pollution might be occur due to the too much uses of chemical for the removal of colour (Kharub, 2012).



### 2.3.3 Physical Treatment

Physical treatment involves the process of adsorption technique and membrane filtration (reverse osmosis, electro-dialysis, nanofiltration). However, there are some disadvantage of using membrane filtration process such as limited life time, problem of membrane fouling and also the cost of periodic replacement. However, in comparison to biological, chemical or physical method, adsorption process is an efficient and effective in removing the contaminant and decolour the water sources (Kharub, 2012).

Adsorption is a technique where it offer the attractive alternative method for the colour removal in the wastewater where the adsorbent is inexpensive, locally available, require less pre-treatment step before use (Crini, 2006). Table 2.5 show some previous study on methods used for dye removal.

Table 2.5: Some previous studies on various method for dye removal

Technique	Dye	Result (removal efficiency)	References
<b>Chemical oxidation</b>	Azo dye Reactive Black 5	40 %	(Turgey et al., 2011)
<b>Coagulation Flocculation</b>	Acid Blue 92	99 %	(Kornaros and Lyberatos, 2006 ; Szygula et al., 2009)
<b>Adsorption</b>	Vertigo Blue 49, Orange DNA 13	Vertigo Blue 49: 11.57 mg/g Orange DNA 13: 4.54 mg/g	(Gupta et al., 2017)
<b>Trickling filter</b>	Organic dye	30% - 60%	(Szygula et al., 2009 ; Kornaros & Lyberatos, 2006)
<b>Biological decolourisation (Bacterium <i>Pseudomonas luteola</i>)</b>	Reactive azo dye (red G, RBP)	Red G: 37% RBP: 93%	(Rai et al., 2005)

## 2.4 Adsorption

Adsorption is one of the important separation process and it is also known as surface process. Adsorption can be defined as an exothermic process where the atom, ion or molecules of liquid, dissolved solid or gas can be collected on the surface of another substance. It is unlike absorption which a substance diffuses into another substance. The main reason for adsorption occur is the imbalance of forces between surface of materials. This situation give rise to formation of bonds like hydrogen bonds, Van der Waals bond, covalent and ionic bonds between the adsorbents and adsorbate (Bhoi, 2010). Basically, adsorbent is a thing or substance that used to adsorb solute molecules from a liquid or gas. On the other hand, adsorbate is a substance that adsorbed on surface of adsorbent by adsorption. In simple sentence, it can be defined as sticking of particles to a surface. The sticking can be either permanent or temporary. Normally, adsorption process can be differentiated based on the type of forces between the adsorbate and the adsorbent. According to this statement, adsorption processes can be classified as physical adsorption and chemical adsorption (Aharoni and Ungarish, 1977).

Physical adsorption or also can call as physisorption is one type of adsorption which occurs when the particles in contact with a solid or liquid surface. It occurs quickly and can form multilayers. Physical adsorption begins with monolayer and then forms multilayer until the pores are filled with adsorbate (Gupta et al., 2004). This situation explain that the maximum capacity of a porous adsorbent depends more on the pore volume than the surface area. However, chemical adsorption which is also known as chemisorption is a type of adsorption that allows the formation of monolayer with the

help of formation of chemical bond between the adsorbate and adsorbent (Dhanakumar et al., 2007). In other word, chemical adsorption required chemical bond formation between adsorbent and adsorbate. This is because chemisorption is a chemical process which associate with activation energy with it.

In reality, most of the commercial adsorbents depend on physical adsorption than chemical adsorption (Laasri et al., 2007). This is because physical adsorption can occur under suitable temperature and pressure but chemical adsorption only take place if the adsorbate and adsorbent are able to form chemical bond between them. Other than that, physically adsorbed molecules are easy to remove but chemically adsorbed molecules are difficult to remove. At the same time, chemisorption required activation energy while physisorption does not required activation energy.

## **2.5 Adsorption Isotherm**

Adsorption isotherm model is invaluable curve which represent or describe the process of releasing and mobility of the substances from aqueous porous media or aquatic environment to a solid phase with constant of pH and temperature. Besides, this model is use to know the ratio or the amount of the adsorbed and the amount of the remaining which is known as adsorption equilibrium (Foo and Hameed, 2010). The analysis of isotherm data is important to know which model is suit to present in the different isotherm model for design purpose (Hameed and Ahmad, 2009). There are many type of adsorption isotherm model such as Langmuir, Freundlich, Brunauer Emmett Teller, and Redlich Peterson (Foo and Hameed, 2010). However, the most widely use are Langmuir and Freundlich isotherm model.

### 2.5.1 Langmuir Adsorption Isotherm Model

This model assume that process of adsorption is monolayer adsorption and can be expressed by the following equation:

$$C_E / Q_e = (1/Q_{\max}K_L) + (C_E/Q_{\max}) \quad (2.1)$$

Where,  $Q_e$  is the equilibrium concentration of dyes on the adsorbent (mg/g),  $C_E$  is the equilibrium concentration of dyes in solution (mg/L),  $Q_{\max}$  is the monolayer capacity of adsorbent (mg/g) and  $K_L$  is the Langmuir adsorption constant. The Langmuir constant  $K_L$  is a measure of the affinity between adsorbate and adsorbent and  $1/K_L$  value gives half maximum adsorption (Hameed and Ahmad, 2009). Plot of  $C_E/Q_e$  vs  $C_E$  is a straight line with slope  $1/Q_{\max}$  and intercept  $1/Q_{\max}K_L$ . This model assume that the process of adsorption is occur on the homogenous surface of adsorbent of identical site which is available and energetic with each side carry the same amount of molecules to avoid interaction between the adsorbate (Qada et al., 2006). However, the maximum adsorption is occur when the surface is covered with the monolayer of adsorbate (Ahmad, 2006).

### 2.5.2 Freundlich Adsorption Isotherm Model

Freundlich model is the earliest model that is describing the non-ideal and reversible adsorption which is not restricted to the formation of monolayer. Besides, this model can be applied to the multilayer adsorption which does not have equal distribution of heat and affinity. This model is used in the heterogeneous system

especially for organic compound, highly interaction between the activated carbon and molecular sieve. The range to measure the adsorption intensity or surface heterogeneity is 0 to 1 where the closest value to 0 is more homogenous (Foo and Hameed, 2010).

This model can be expressed in following relation:

$$\log(q_e) = \log(K_F) + \frac{1}{n}\log(C_E) \quad (2.2)$$

Where  $q_e$  (mg/g) represent equilibrium dye concentration onto the adsorbent,  $C_E$  (mg/L) is equilibrium dye concentration onto the solution,  $K_F$  (mg/g)  $(L/g)^{1/n}$  is the constant of Freundlich and  $n$  is the heterogeneity factor. The value of the Freundlich constant and  $1/n$  obtained from the intercept and slope of straight line  $\log q_e$  versus  $\log C_E$  (Ahmad, 2006).

## 2.6 Factor Affecting Adsorption

Dye adsorption can be affected by various factors like adsorbent size, contact time, dosage of adsorbent, pH and initial dye concentration. These factors optimisation can be referred to be applied on full scale treatment process for eliminating dye.

### 2.6.1 Effect of Adsorbent Size

Adsorbent size is a significant parameter which affecting the adsorption process. The smaller the particle diameter, the faster the rate of adsorption. According to Abramian and El-Rassy (2009), the particle size has no influence on the equilibrium loading capacity. Nunez et al. (2007), noted an inverse dependence of the rate on the

mean particle diameter. Smaller particle size reduce internal diffusion and mass transfer limitation to the penetration of the adsorbate inside the adsorbent. This situation lead hand to achieve equilibrium more easily and nearly full adsorption capability can be attained.

### **2.6.2 Effect of Contact Time**

According to theory, the dye removal rate increases as the contact time increases to a certain extent. Barathi and Ramesh (2013), reported that further increase in contact time will not increase the uptake of dye on adsorbent due to the deposition of dyes on the available adsorption site on adsorbent. At this point, the amount of dye desorbing form the adsorbent is in a state of dynamic equilibrium with the amount of dye being adsorbed onto the adsorbent. The time required to achieve this condition is called the equilibrium time and the amount of dye adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions (Mohd Salleh et al., 2012). Contact time between adsorbent and adsorbate significantly affecting the performance of dye removal (El-Sayed et al., 2014).

### **2.6.3 Effect of Dosage of Adsorbent**

Another parameter that affects the dye removal rate is adsorbent dosage. It helps to determine the adsorbent's capacity for a given amount of adsorbate at the operating conditions. In general, the dye removal rate increases as the adsorbent dosage increases. This is because increase of adsorbent dosage will increase the amount of sorption site at the adsorbent surface. It will result on the increase of dye removal percentage

(Adeyemo et al., 2015). In order to study the effect of adsorbent dose on the adsorption process, it can be carried out by preparing adsorbent-adsorbate solution with different amount of adsorbents added to fixed initial dye concentration then shaken together until reach the equilibrium time (Mohd Salleh et al., 2011).

#### **2.6.4 Effect of pH**

The pH factor is very important for dye adsorption in the adsorption process. A medium pH will control the electrostatic charges magnitude which are imparted by ionized dye molecules and resulting the adsorption rate vary with the pH of the medium used (Etim et al., 2012). Generally, dye removal percentage for anionic dye will increase at a low pH, while decrement in dye removal percentage for ionic dyes adsorption. In contrast, cationic dye adsorption preferred for high solution of pH but as for anionic dye adsorption the efficiency will be lower (Bharathi and Ramesh, 2013). As surface charge density decreases with an rising of pH, the electrostatic repulsion between the positively charged dye and adsorbent surface is lowered, which may result in an increment in the adsorption extent (Yilmaz et al., 2010).

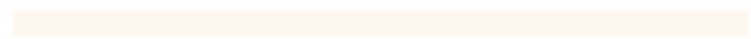
#### **2.6.5 Effect of Initial Dye Concentration**

Initial dye concentration is one of the important factor in adsorption process. The dye removal rate increases when the initial dye concentration increases to certain extent. The effect of initial dye concentration can be conducted by preparing adsorbent-adsorbate solution with different initial dye concentration using fixed adsorbent dosage

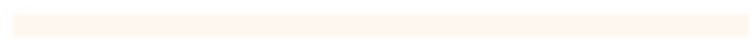
and contact time (Mohd Salleh et al., 2011). The effect of increment in initial dye concentration will increase the adsorbent loading capacity (Adeyemo et al., 2015).



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## CHAPTER 3

### MATERIALS AND METHODS

#### 3.1 Materials

Cassava peel that was used in this study was obtained from Muar, Johor.

##### 3.1.1 Apparatus and Equipment

The apparatus that was used in this study are oven, air- tight zipper bag, siever, conical flask (250 mL), volumetric flask (500 mL), beaker (100 mL and 250 mL), media bottle (500 mL), measuring cylinder (10 mL and 50 mL), hot plate and stirrer, pipette, pipette tips, pH meter, glass rod, spatula, gloves, dropper and aluminium foil.

Equipment that used in this study are Scanning Electron Microscope (SEM), Fourier-Transform Infrared Spectroscopy (FTIR), weighing balance, and UV Spectrophotometer.

### 3.1.2 Chemicals and Reagent

Chemicals and reagent required for this research are Metanil Yellow ( $C_{18}H_{14}N_3NaO_3S$ ), sodium hydroxide (NaOH), hydrochloric acid (HCl), citric acid, sodium citrate, Borax and distilled water.

## 3.2 METHOD

### 3.2.1 Preparation of adsorbent

Cassava peel was used as an adsorbent and it was obtained from Muar, Johor. Cassava peel was rinsed by using the distilled water to remove the suspended impurities. Then, it was allowed to dry under sunlight for 48 hours. Then, it was cut into small pieces and dried in oven at  $85^{\circ}C$  until a constant mass obtained in order to remove the moisture content. Next, the dried sample was blended into powder form and sieved to the particle sizes of 0.125, 0.300 and 0.700 mm. Then, the sample was stored in air-tight zipper bag.

### 3.2.2 Preparation of adsorbate (Metanil Yellow dye)

A Metanil Yellow stock solution was prepared by dissolving 0.5 g in 500 mL of distilled water to produce a concentration of 1000 mg/L using a 500 mL volumetric flask. Serial dilutions was made by diluting the Metanil Yellow stock solution in accurate proportions using distilled water. For the construction of calibration curve, a few series of Metanil Yellow concentrations prepared in the range of 0.5 - 20 mg/L by

diluting the prepared stock solution with distilled water. Then, various concentrations of Metanil Yellow were measured using a UV spectrophotometer (Thermo Scientific, Gynesis 20) at 434 nm wavelength (Somasekhara Reddy and Nirmala, 2012).

### 3.2.3 Effect of adsorbent size

Adsorbent (cassava peel) was sieved by using sieve machine in various sizes such as 0.125 mm, 0.300 mm and 0.710 mm. A mixture of 150 mL of 100 mg/L Metanil Yellow solution and 2 g of adsorbent with different sizes were agitated with the speed of 150 rpm for 10 minutes at room temperature to perform the adsorption process. Then, the mixture of adsorbent - adsorbate was left for 24 hours to obtain the equilibrium. After 24 hours, the samples were filtered by using filter papers. The filtrates were measured using UV spectrophotometer at 434 nm wavelength. The filtrates measured 3 times in the UV spectrophotometer to get an accurate reading and converted them into average reading. Then, the percentage removal of Metanil Yellow was calculated by using the following equation.

**Dye removal in percentage :-**

$$\text{Percentage removal (\%)} = \frac{(C_0 - C_e) \times 100}{C_0}$$

$C_0$

(3.1)

where,  $C_0$  is the initial concentration of Metanil Yellow in solution (mg/L) and  $C_e$  is the final concentration of Metanil Yellow in solution (mg/L).

### **3.2.4 Effect of adsorbent dosage**

Adsorbent size with the highest percentage of dye removal (0.125 mm) was chosen as the optimum value and was used for this study and for the subsequent parameters. Different dosage of the adsorbents was prepared such as 0.5 g, 1.0 g, 2.0 g, 3.0 g, 4.0 g, 5.0 g, 6.0 g and 7.0 g in 150 mL at concentration of 100 mg/L of dye solution. The mixtures was agitated at 150 rpm for 10 minutes at room temperature and left for 24 hours to reach the equilibrium. After 24 hours, the samples were filtered and the filtrates were measured by using UV spectrophotometer at 434 nm.

### **3.2.5 Effect of initial concentration on adsorption**

The optimum size (0.125 mm) and dosage of the adsorbent (3 g) was fixed to study the effect of initial dye concentrations on adsorption. The effect of initial dye concentration was studied at concentration of Metanil Yellow from 30 mg/L to 400 mg/L. The mixture was agitated at 150 rpm for 10 minutes under room temperature and the mixture was left until obtain the equilibrium for 24 hours. After 24 hours, the samples were filtered and the filtrates were measured by using UV spectrophotometer at 434 nm.

### **3.2.6 Effect of contact time**

The contact time between dye and adsorbent was studied at optimum size of adsorbent (0.125 mm), adsorbent dosage (3g) and initial dye concentration (150mg/L). These parameters were kept fixed for the subsequent parameters. The volume of the dye

used was maintained at 150 mL and the effect of contact time was studied using different of contact time from 30 minutes to 24 hours (result was obtained for every 4 hours). The mixture was agitated at 150 rpm for 10 minutes under room temperature. The conical flasks were labeled and left untouched according to the time stated. The mixture of dye and the adsorbent were filtered according to the allocated time. The filtrates were measured by using UV spectrophotometer at 434 nm.

### 3.2.7 Effect of pH

Buffer were prepared manually according to following formula as shown in Table 3.1. The buffer stored in reagent bottles.

Table 3.1: List of buffer preparation formula

pH	Chemicals
3 - 6	0.1 M Citric acid / 0.1 M Sodium citrate
7 - 8	0.1 M Potassium dihydrogen phosphate / 0.1 M Sodium hydroxide
9	0.025 M Borax / 0.1 M Hydrochloric acid
10	0.025 M Borax / 0.1 M Sodium hydroxide

All the chemicals were dissolved in distilled water to make up to the required amount. The pH meter was used to measure the pH for each of the prepared buffers. The effect of pH was studied by using the optimum adsorbent size (0.125 mm), dosage (3g), initial dye concentration (150 mg/L) and contact time (8 hours). The mixture was marked up until 150 mL with buffer instead of distilled water. The pH value was in the range of pH 3 to pH 10. The mixture was agitated at 150 rpm for 10 minutes under room

temperature. The mixture were filtered by using filter paper and the filtrates were measured by using UV spectrophotometer at 434 nm.

### **3.2.8 Characterise using FTIR**

0.1 g of cassava peel before and after adsorption were analyzed using FTIR to identify the functional groups that available on the surface of the cassava peel.

### **3.2.9 Characterise using SEM**

0.1 g of cassava peel before and after adsorption were analyzed using Joel JSM-IT100 SEM to examine the surface morphology of cassava peel before and after adsorption.

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Characteristic of cassava peel

##### 4.1.1 FT-IR Analysis

Analysing the chemical structure of an adsorbent is importance because it improves the understanding on adsorption process. The FT-IR spectra of cassava peel before and after adsorption of Metanil Yellow (MY) were carried out to gain better understanding into the functional groups available on the surface of the cassava peel. The FT-IR spectra measured within the range of  $500 - 4000 \text{ cm}^{-1}$ . The spectrum for cassava peel before and after adsorption were recorded as shown in Figure 4.1 respectively.

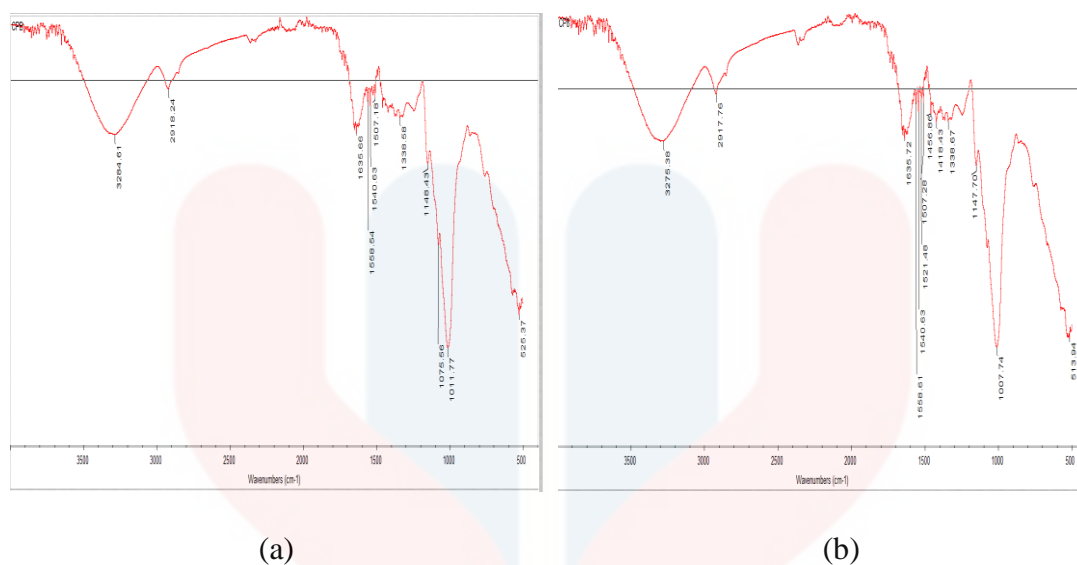


Figure 4.1 : FT-IR spectrum for cassava peel before adsorption (a) and after adsorption (b)

From Figure 4.1 (a), it was discovered that the FT-IR spectrum showed strong broad band at  $3284.61\text{ cm}^{-1}$ , which was due to O-H stretching of free alcohol while the sharp band observed at  $2918.24\text{ cm}^{-1}$  indicated the presence of N-H stretching of amine salt. The band observed at  $1635.61\text{ cm}^{-1}$  was an indication of medium C=C stretching of alkene while the band at  $1558.54\text{ cm}^{-1}$  and  $1540.63\text{ cm}^{-1}$  was found to be attributed to strong N-O stretching of nitro compound. The bands at  $1338.67\text{ cm}^{-1}$  and  $1148.43\text{ cm}^{-1}$  were due to strong S=O stretching of sulfone. The band which appeared at  $1075.56\text{ cm}^{-1}$  were assigned to strong C-O stretching of alkyl aryl ether while the band at  $1011.77\text{ cm}^{-1}$  may be indicated the presence of lignin (Guo et al., 2008).

The FT-IR spectrum showed visible shifts of some of the bands and appearance of some of the bands in Figure 4.1 (b). Bands at  $3284.51\text{ cm}^{-1}$ ,  $2918.24\text{ cm}^{-1}$ ,  $1635.72\text{ cm}^{-1}$ ,  $1148.43\text{ cm}^{-1}$  and  $1011.77\text{ cm}^{-1}$  (shown in (a)) were shifted to  $3275.38\text{ cm}^{-1}$ ,  $2917.76\text{ cm}^{-1}$ ,  $1635.66\text{ cm}^{-1}$ ,  $1147.70\text{ cm}^{-1}$  and  $1007.74\text{ cm}^{-1}$ , respectively, as shown in



Figure 4.1 (b). The shifts in the bands confirmed the participation of the functional groups in the adsorption of MY on cassava peel. The new bands which appeared at  $1456.86\text{ cm}^{-1}$  and  $1418.43\text{ cm}^{-1}$  were assigned to medium C-H bending of alkane. The appearances of the new bands were due to the changes in the nature of binding after the interaction with MY dye. Table 4.1 shows the list of infrared spectroscopy absorptions by frequency regions.

Table 4.1 : Infrared spectroscopy absorptions by frequency regions

3700 - 3584	medium	Sharp	O-H	stretching	alcohol
3550 - 3200	strong	Broad	O-H	stretching	alcohol
3000 - 2800	strong	Sharp	N-H	stretching	amine salt
1662 - 1626	medium	-	C=C	stretching	alkene
1550 - 1500	strong	-	N-O	stretching	nitro compound
1450 - 1375	medium	-	C-H	bending	alkane
1350 - 1300	strong	-	S=O	stretching	sulfone
1160 - 1120					
1275 - 1200	strong	-	C-O	stretching	Alky aryl ether
1075 - 1020					
1205 - 1124	strong	-	C-O	stretching	Tertiary alcohol

Source : Infrared Spectroscopy Absorption Table, (2014)

#### 4.1.2 SEM Analysis

The surface morphology of cassava peel before and after adsorption were examined using Scanning Electron Microscopy (SEM). From the SEM micrographs, the

change in surface texture and pore were clearly observed. Figure 4.2 shows the surface of cassava peel before (a) and after adsorption (b) respectively.

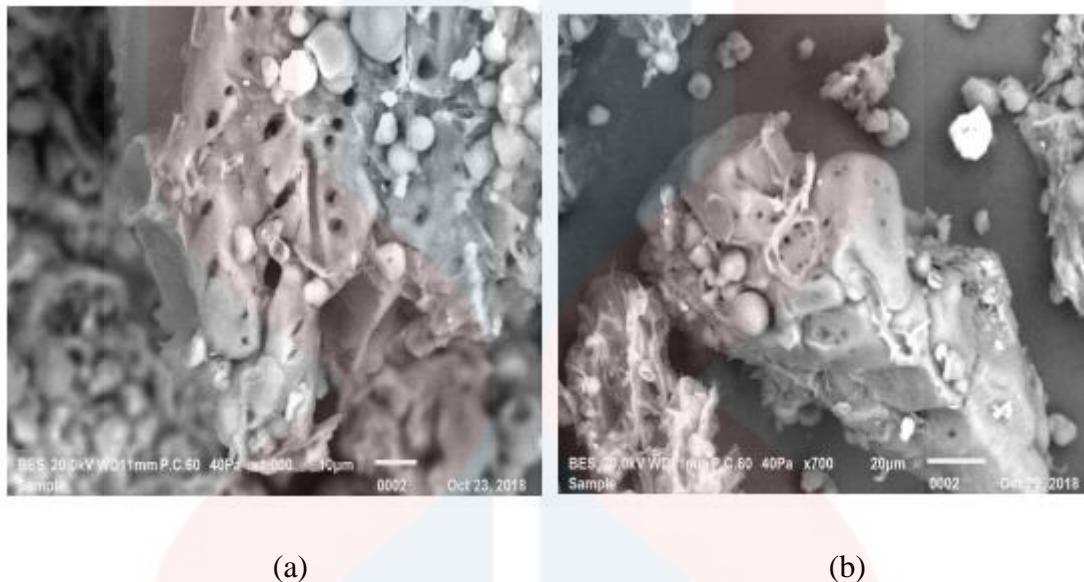


Figure 4.2 : SEM image of cassava peel before adsorption (a) and after adsorption (b)

In Figure 4.2 (a), the surface of cassava peel shows larger pore size while the surface of cassava peel in Figure 4.2 (b) shows smaller pore size. These changes due to the adsorption of the MY dye on cassava peel. The dye molecules attached on the pores and make the pores smaller as the attachment of dye molecules increase. Even, Arami et al. (2005) also observed the similar result in orange peel adsorbent. From here it can be proved that the adsorption of MY occurred on cassava peel.

## 4.2 Calibration Curve

From 1000 mg/L stock solution of MY dye, a few series of MY solutions at different concentrations (0.5 mg/L - 20 mg/L) were prepared to generate linear calibration curve. The purpose of calibration curve is to determine the final

concentration of MY dye after adsorption using cassava peel. The calibration curve for MY shown in Figure 4.3. Data for calibration curve can be obtained in Appendix A.1.

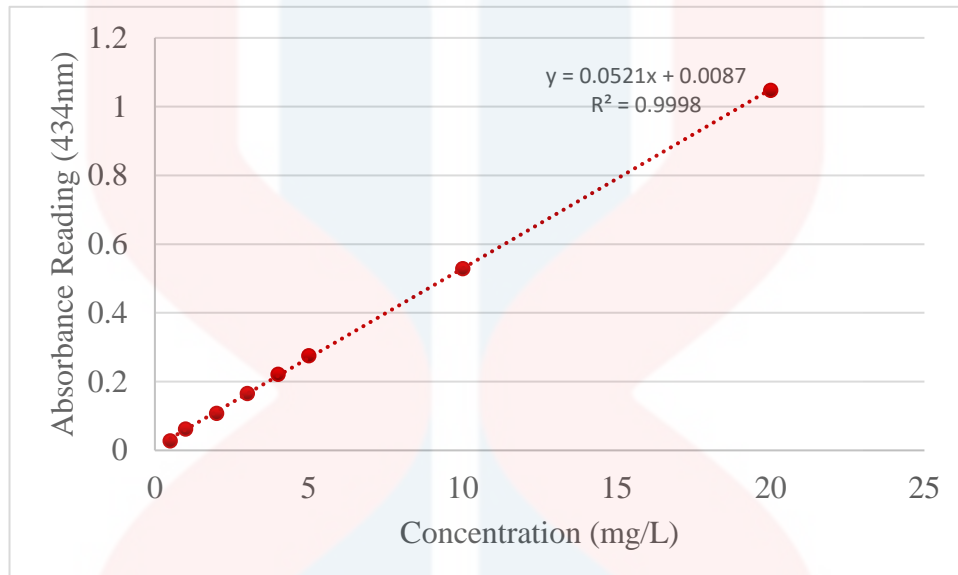


Figure 4.3 : Calibration curve for MY

### 4.3 Effect of adsorbent size

The effect of adsorbent size for MY dye can be seen from Figure 4.4. It is clear that the removal percentage of MY is decrease from 0.125 mm to 0.700 mm. This situation corresponding to Gardazi et al. (2014), who reported the smaller adsorbent size shows higher percentage of dye removal than the bigger adsorbent size. Even Abramian and El-Rassy (2009), stated that the smaller the particle size, the higher the percentage of dye removal. This is because the smaller adsorbent size has high surface area and it lead to mass transfer limitation to the penetration of the adsorbate inside the adsorbent. From the data, it was proved that < 0.125 mm was the optimum adsorbent size for this study. Data for effect of adsorbent size can be obtained in Appendix A.2.

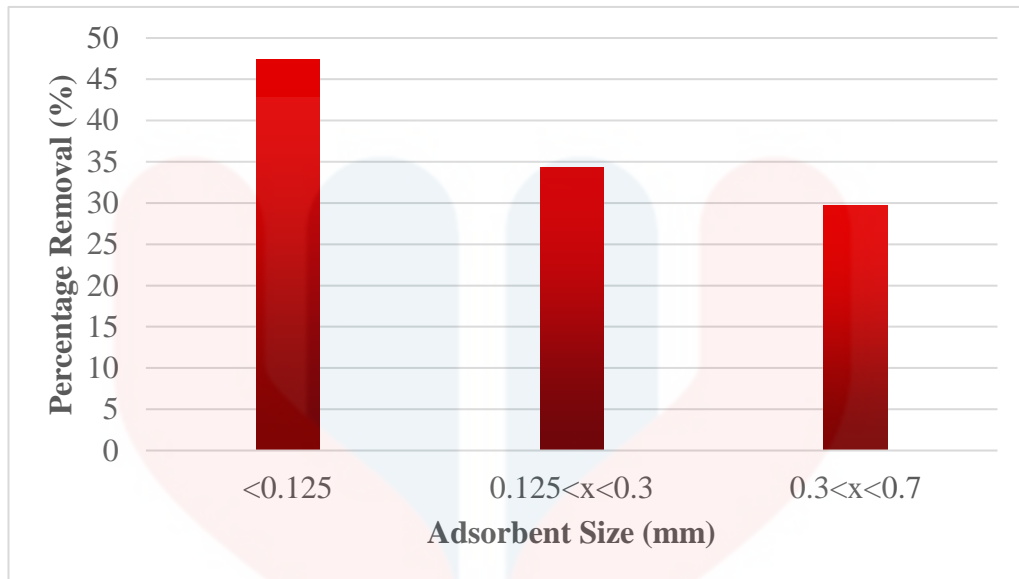


Figure 4.4 : Effect of adsorbent size on the removal of MY dye using cassava peel

#### 4.4 Effect of adsorbent dosage

The effect of adsorbent dosage on the removal of MY dye using cassava peel was shown in Figure 4.5. The data showed that the MY uptake increased from 0.5 g to 3 g and became constant beyond 3 g. The percentage of dye removal is increased as adsorbent dosage increased. This is due to the availability of more adsorbent active sites as well as greater availability of specific surfaces of the adsorbents. This result similar to Adeyemo et al. (2015), who reported that the increase in adsorbent dose increases number of active sites. When the number of active sites of adsorbent increases then the amount of MY uptake by adsorbent increases ; hence it results in higher percentage of dye removal.

However, the percentage of dye removal became constant beyond 3 g. This is because of the overcrowding of adsorbent particles which lead to overlapping of the adsorption sites. According to theory, with the increase in adsorbent dosage aggregation

of particles take place, as a result, efficiency and dye uptake decreases. Jianlong and Wang (2002), mentioned that overlapping of adsorbent particles can reduce the access to available surface active sites. Thus, the adsorption rate will reduce. The optimum dosage for MY dye is 3 g. Data for effect of adsorbent dosage can be obtained in Appendix A.3.

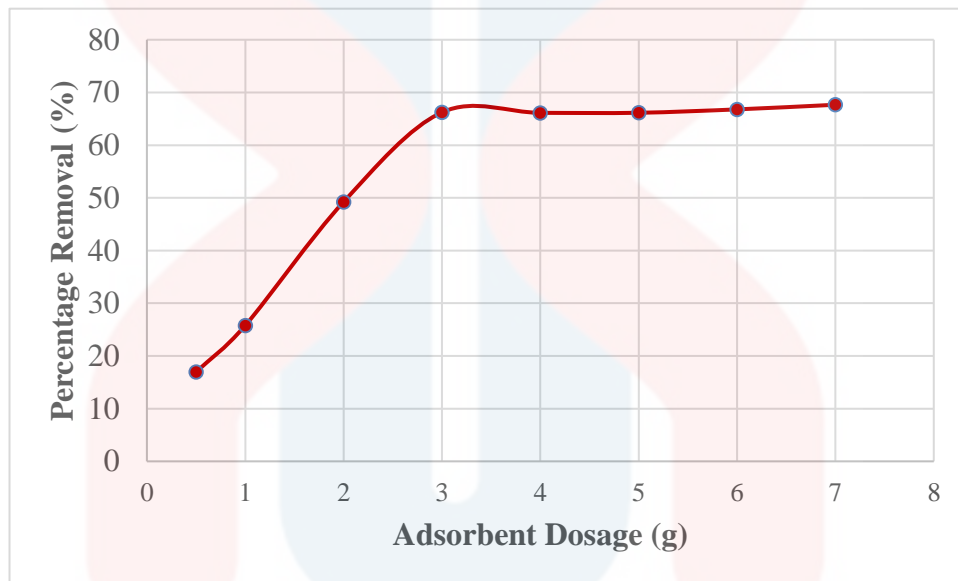


Figure 4.5 : Effect of adsorbent dosage on the removal of MY dye using cassava peel

#### 4.5 Effect of initial dye concentration

The effect of initial dye concentration for MY dye can be seen from Figure 4.6. It shows that the percentage of MY dye removal increases when the initial dye concentration increase. This is because at high dye concentration, the number of dye molecules are high and the ratio between the numbers of dye molecules to the number of available active sites is high too (Mohd Salleh et al., 2011). Moreover, the surface of adsorbent maybe not fully occupied by the MY dye. However, Bharathi and Ramesh

(2013), reported that a given mass of adsorbent material can only adsorb a fixed amount of dye. The initial MY concentration provides an important initial driving force to overcome all the mass transfer resistance between the aqueous and solid surfaces. So, the higher initial dye concentration will increase the adsorption rate. In this study, the optimum initial dye concentration is 150 mg/L. This is because at the 150 mg/L the spectrum showed a smooth curve. However, starting from 200 mg/L to 400 mg/L the spectrum does not show a smooth spectrum (see Figure 4.7). This is due to high concentration and adsorption site have fully occupied. Moreover, the limitation of instrument to detect high concentration also affected the result. Figure 4.7 shows the spectrum of MY from 150 mg/L to 400 mg/L using spectrophotometer. Data for effect of initial dye concentration can be obtained in Appendix A.4.

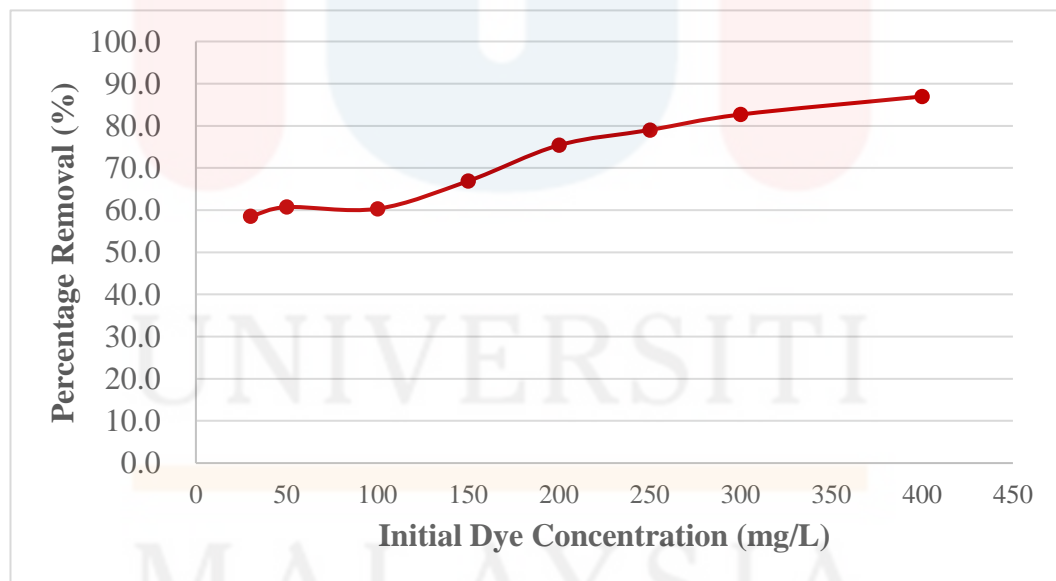
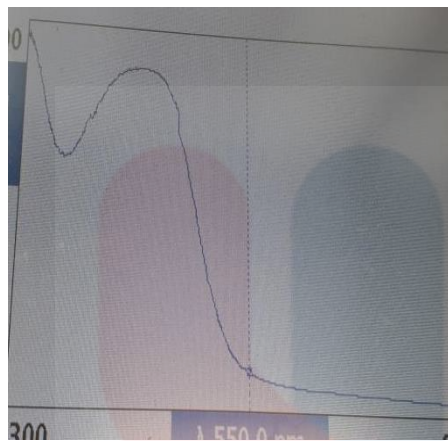
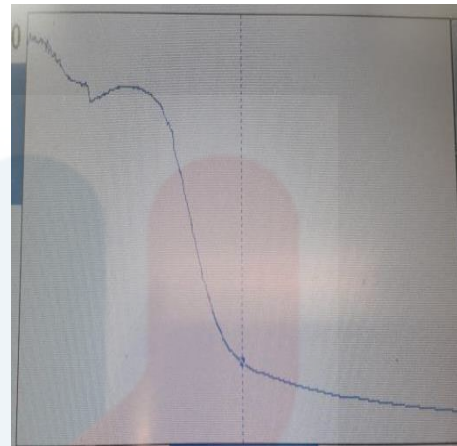


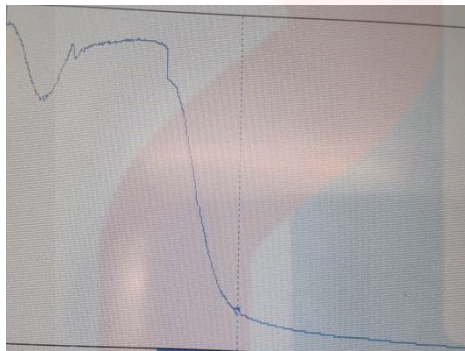
Figure 4.6 : Effect of initial dye concentration on the removal of MY dye using cassava peel



(a)



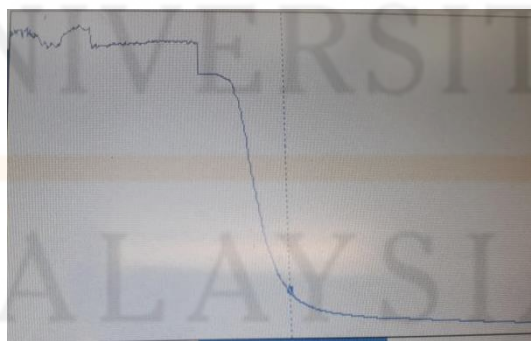
(b)



(c)



(d)



(e)

Figure 4.7 : Spectrum of MY at concentration 150 mg/L (a), 200 mg/L (b), 250 mg/L (c), 300 mg/L (d) and 400 mg/L (e)

#### 4.6 Effect of contact time

From Figure 4.8 it can be clearly seen the effect of contact time on the removal of MY dye using cassava peel. The percentage of dye removal was found to increase rapidly with time but slowed on attaining equilibrium. At the first 0.5 to 8 hours of contact time, the percentage of dye removal slowly increased. Then, at 8 to 16 hours, the percentage of dye removal was almost constant. However, after 16 hours, the percentage of dye removal was decreased. Similar observation have been made by Vieitra et al. (2012) by using macauba palm cake and cotton stalk. Even Abdullah and Teha (2012), also reported an increase in Methylene blue dye adsorption with increase in contact time.

The slow MY dye adsorption by the cassava peel in the first 0.5 to 8 hours can be attributed to the increased availability of vacant adsorption sites on the surface (Nasuha et al., 2011). After 8 hours, MY dye achieved the equilibrium state. At this point, a dynamic equilibrium state between the amount of dye desorbing from the adsorbent and that being adsorbed on the adsorbent is established. After 16 hours it started to decrease. This is because of the saturation of the active site which do not allow further adsorption to take place. In this study, the optimum contact time is 8 hours. Data for effect of contact time can be obtained in Appendix A.5.



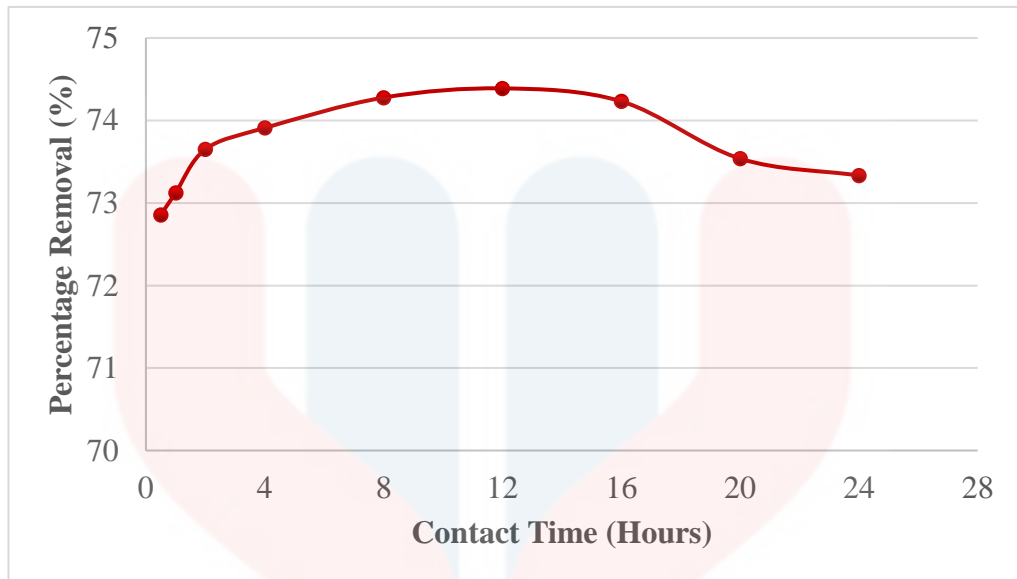


Figure 4.8 : Effect of initial dye concentration on the removal of MY dye using cassava peel

#### 4.7 Effect of pH

Figure 4.9 shows the effect of pH on adsorption of MY dye onto the cassava peel. The pH remarkably affected the adsorption capacity of the MY dye onto cassava peel. According to theory, the percentage of dye removal should be higher in acidic solution than those in neutral and alkaline solutions. This is because the MY dye is an anionic dye (acid dye).

Yoshida et al. (1993), studied effect of pH on adsorption of acid dye by using chitosan molecules. He declared that at lower pH more protons will be available and change the amino groups of chitosan molecules to form  $-NH^{3+}$  groups. So that, the electrostatic attraction between negatively charged dye anions and positively charged adsorbents will increase and make the dye adsorption increase. At the same time, when pH increase above 7, the surface of the adsorbent will be occupied by negatively

charged ions and the repulsive force will be produced with anionic dye. This situation cause the adsorption of anionic dye decrease.

However, in this study, the higher percentage of dye removal was obtained at pH 8. This result was vice versa from the theory. This maybe because of the presents of N-H compound, lignin, glucose and starch in adsorbent. At low pH values, the presence of excess hydrogen ion in the solution competes with the cationic groups of the adsorbent surface. At higher pH values, the hydrogen ions decreases and the positive charge of adsorbent surface enhancing attraction of more amount of the anions of the MY dye. This situation give hint that the effect of pH not only depend on electrostatic mechanism but it also depend on chemical reaction between the adsorbent and dye molecules (Al-Degs et al., 2007). Data for effect of pH can be obtained in Appendix A.6.

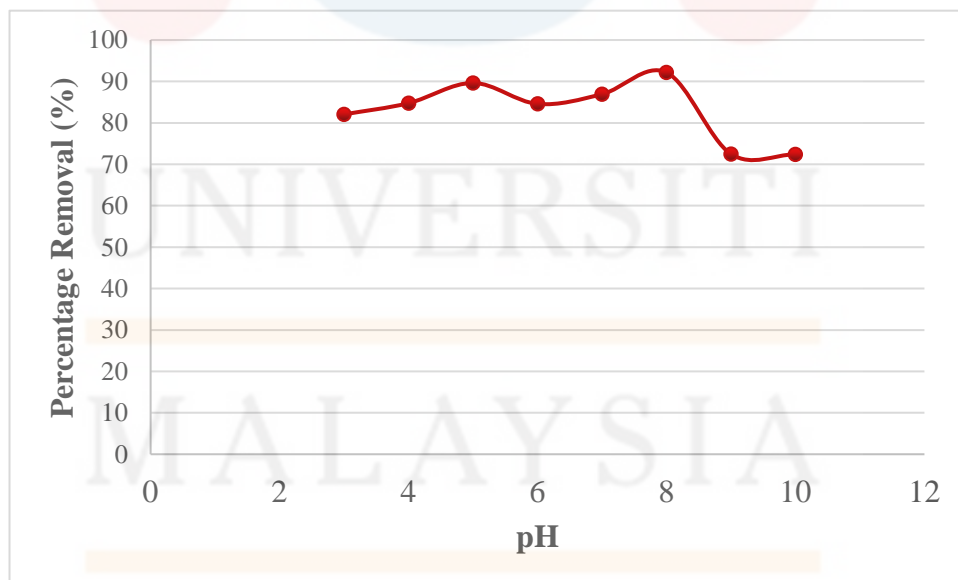


Figure 4.9 : Effect of pH on the removal of MY dye using cassava peel

## 4.8 Adsorption Isotherm

Adsorption isotherm studies is very important because it helps to discover the distribution of adsorbent molecules between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. It is the equilibrium relationship between the amount of adsorbate removed and the amount remaining (Ola et al., 2005). Adsorption isotherm study also help to identify whether the adsorption process occur on homogeneous sites or heterogeneous surfaces of the adsorbent. In this study, Langmuir isotherm and Freundlich isotherm were used to carry out the adsorption isotherm study.

The adsorption values for the adsorption of MY on cassava peel is tabulated in Table 4.2. Figure 4.10 shows the Langmuir adsorption isotherm plot for contact time (a) and pH (b). Figure 4.11 shows the Freundlich adsorption isotherm plot for contact time (a) and pH (b). Data for Langmuir and Freundlich adsorption isotherm can be obtained in Appendix B.1 and B.2.

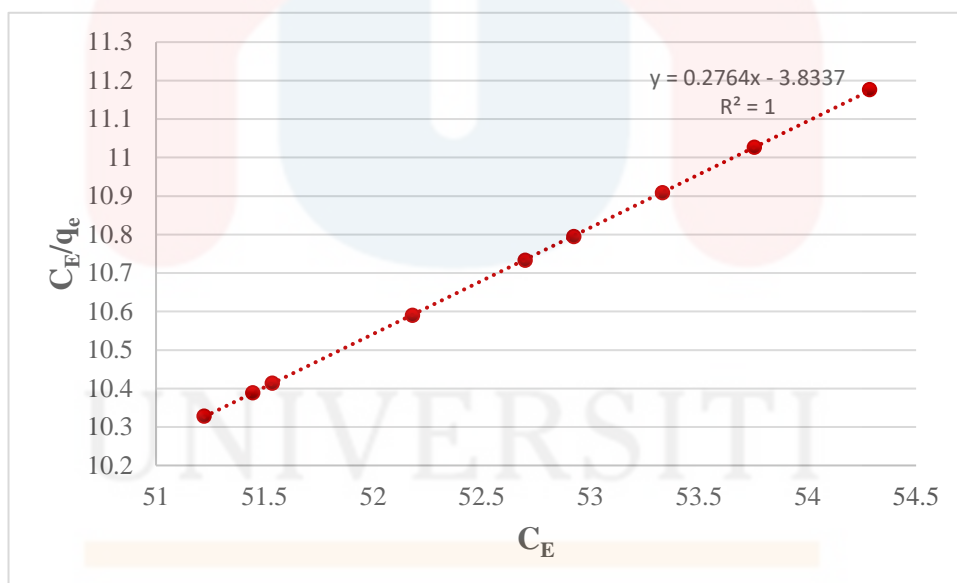
Table 4.2 : Langmuir and Freundlich adsorption isotherm parameters for contact time and pH

Adsorption parameters	Langmuir adsorption isotherm parameters			Freundlich adsorption isotherm parameters		
	$Q_{max}$ (mg/g)	$K_L$ (L/mg)	$R^2$	$K_F$	$n$	$R^2$
Contact time	3.618	-0.072	1	20.202	-2.798	0.9999
pH	4.352	-0.1631	0.9955	11.005	-4.983	0.9477

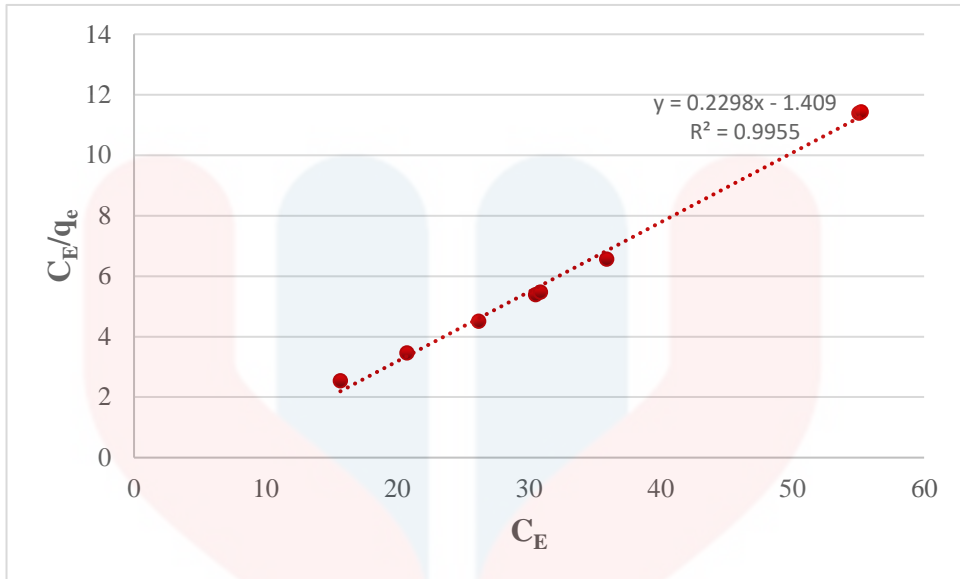
From Table 4.2, it can be clearly seen that the correlation coefficient ( $R^2$ ) values of Langmuir are very close to 1 and it indicated that the adsorption follows the

Langmuir adsorption isotherm. On the other hand, the values of Freundlich constant ( $n$ ) are less than 1. According to theory, the Freundlich constant ( $n$ ) should have values lying in the range of 1 to 10 for classification as favorable adsorption. However, in this study, the negative  $n$  values indicated that the process is classified as not favourable adsorption.

From the data, it can be concluded that the maximum adsorption capacity is based on the Langmuir isotherm. It was proved that the monolayer adsorption of MY dye takes place on the homogeneous surfaces of the cassava peel. The maximum adsorption capacity obtained from this study was 3.618 mg/g.

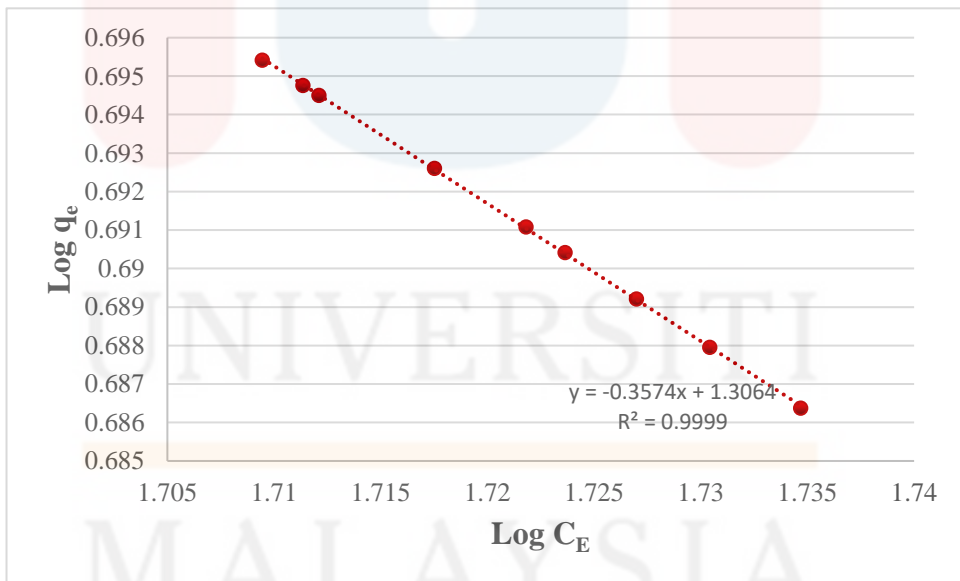


(a)

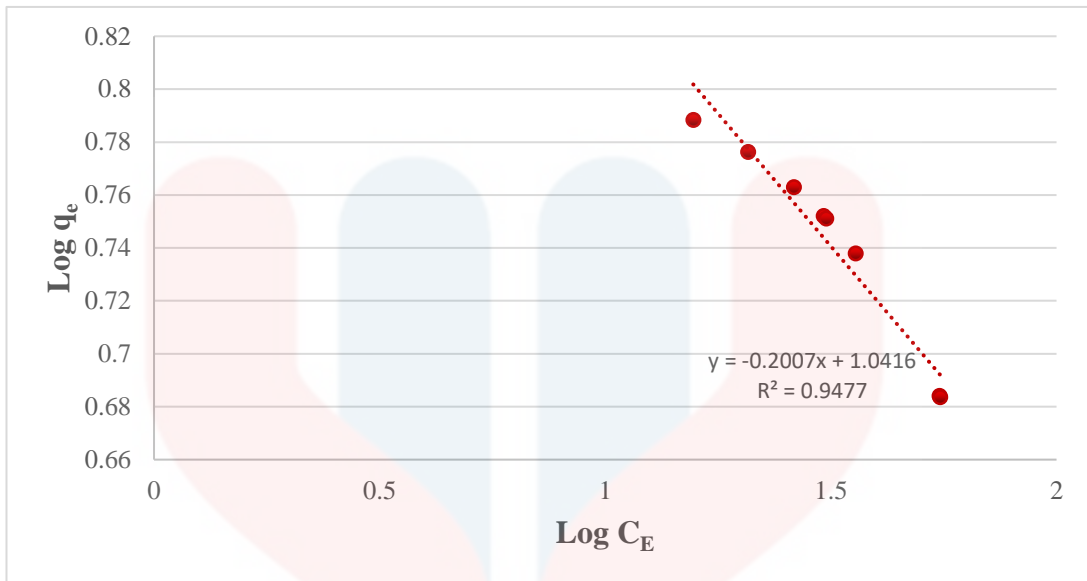


(b)

Figure 4.10 : Langmuir adsorption isotherm plot for contact time (a) and pH (b)



(a)



(b)

Figure 4.11 : Freundlich adsorption isotherm plot for contact time (a) and pH (b)

## CHAPTER 5

### CONCLUSION AND RECOMMENDATION

#### 5.1 Conclusion

This study proved that the cassava peel as a low cost adsorbent has potential to remove MY dye from aqueous solution. The functional groups and porous structure of the cassava peel was identified by conducting characterisation using FT-IR and SEM. The cassava peel efficiently suitable to remove 77 % of MY dye from aqueous solution under optimum condition.

First of all, the percentage of dye removal decreased with the increased in adsorbent size. It found that  $< 0.125$  mm size of adsorbent was optimum for the adsorption of MY dye. Then, for the effect of adsorbent dosage, 3 g was the optimum dosage for the adsorption of MY dye. It showed that the higher the adsorbent dosage, the higher the percentage of dye removal until it reaches equilibrium.

Moreover, this study revealed that the percentage of dye removal increased with the increased in initial dye concentration. In this study, 150 mg/L was the optimum concentration to adsorb 3 g of adsorbent. At the same time, the percentage of dye removal increased with contact time until it reaches equilibrium. Based on data, at 8, 12,

16 hours the percentage of dye removal almost constant and after 16 hours it decreased. This situation indicated the optimum adsorption was done at 8 hours.

Finally, pH 8 (alkaline) were chosen as optimum pH for the removal of MY dye from aqueous solution using cassava peel. The percentage of dye removal does not show any steady increase or decrease with increased of pH value. This is maybe because of the chemical reaction between the adsorbent and dye molecules.

The Langmuir and Freundlich adsorption isotherm models were used for the description of the adsorption of MY on cassava peel. The data were in good agreement with the Langmuir isotherm rather than the Freundlich isotherm. The maximum adsorption capacity was 3.618 mg/L with  $R^2$  value nearest 1.

## **5.2 Recommendations**

There are some recommendations to improve the study. Firstly, it suggested to further evaluate the adsorption performance of the cassava peel for removing MY dye from waste effluents from different industrial process. This will provide insight concerning the adsorption mechanism and performance of the adsorbent which may be interfered by other components present in the effluents.

Desorption studies by using different chemical and biological treatment methods need be perform to understand clearly about the mechanism of MY dye adsorption. Other than that, surface modifications of the adsorbents should be carried out and efficiency for dye removal need to be evaluated as reported by Senthil et al. (2013), who



performed adsorption by using raw Bangalora (Totapuri) mango seed kernel powder (RMS) and surface-modified Bangalora (Totapuri) mango seed kernel powder (SMMS) for the removal of methylene blue (MB) dye from aqueous solution.

Besides, biochar and activated carbon from cassava peel can be used as adsorbent. This is because biochar and activated carbon have more adsorption capacity compared to raw adsorbent (Ahiduzzaman and Sadrul, 2016). Moreover, there are lack of literature on the usage of cassava peel as biochar and activated carbon for the removal of dyes. Thus, it is encouraged to do modification of cassava peel into biochar and activated carbon for the removal of dyes.

In addition, the characterisation of cassava peel using Brunauer–Emmett–Teller (BET) and X-ray Fluorescence (XRF) should be carried out. By using BET, the surface area and pore sizes of the cassava peel can be studied and the XRF can be used to study the elements in the cassava peel.

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## APPENDIX A

**A.1** : Standard Curve data for Metanil Yellow dye

Concentration (mg/L)	Abs Reading 1	Abs Reading 2	Abs Reading 3	Average Reading	Std Dev
0.5	0.028	0.028	0.027	0.028	0.0005
1	0.064	0.061	0.061	0.062	0.0017
2	0.108	0.108	0.108	0.108	0
3	0.166	0.166	0.165	0.166	0.0006
4	0.222	0.222	0.222	0.222	0
5	0.275	0.277	0.276	0.276	0.001
10	0.528	0.529	0.529	0.529	0.0006
20	1.049	1.048	1.047	1.048	0.001

Abs Reading = Absorbance Reading

Std Dev = Standard Deviation

**A.2** : Adsorption of Metanil Yellow dye on different adsorbent size

Adsorbent Size (mm)	R1	R2	R3	Average Reading	Ce (mg/L)	Percentage Removal (%)
< 0.125	1.377	1.379	1.382	1.379	26.301	47.397
0.125<x<0.3	1.723	1.722	1.712	1.719	32.827	34.345
0.3<x<0.7	1.83	1.847	1.848	1.842	35.188	29.624

R = Absorbance Reading

Ce = Final dye concentration

**A.3 : Adsorption of Metanil Yellow dye on different adsorbent dosage**

Adsorbent Dosage (g)	R1	R2	R3	Average Reading	Ce	Percentage Removal (%)
0.5	2.173	2.172	2.172	2.172	41.522	16.956
1	1.953	1.93	1.944	1.942	37.107	25.785
2	1.33	1.33	1.333	1.331	25.380	49.240
3	0.873	0.895	0.898	0.889	16.890	66.220
4	0.894	0.887	0.892	0.891	16.935	66.131
5	0.895	0.889	0.888	0.891	16.928	66.143
6	0.877	0.874	0.871	0.874	16.608	66.783
7	0.848	0.852	0.853	0.851	16.167	67.666

R = Absorbance Reading

Ce = Final dye concentration

**A.4: Adsorption of Metanil Yellow dye on different initial dye concentration**

Initial Dye Concentration (mg/L)	R1	R2	R3	Average Reading	Ce	Percentage Removal (%)
30	0.652	0.66	0.659	0.657	12.443	58.522
50	1.03	1.033	1.033	1.032	19.641	60.718
100	2.063	2.089	2.076	2.076	39.679	60.321
150	2.599	2.636	2.55	2.595	49.641	66.906
200	2.571	2.575	2.572	2.573	49.212	75.394
250	2.741	2.738	2.753	2.744	52.501	79.000
300	2.738	2.701	2.713	2.717	51.989	82.670
400	2.703	2.773	2.71	2.729	52.207	86.948

R = Absorbance Reading

Ce = Final dye concentration

**A.5 : Adsorption of Metanil Yellow dye on different contact time**

Contact Time (Hours)	R1	R 2	R3	Average Reading	Ce	Percentage Removal (%)
0.5	2.847	2.833	2.831	2.837	54.286	72.857
1	2.804	2.811	2.813	2.809	53.755	73.123
2	2.756	2.748	2.759	2.754	52.699	73.650
4	2.723	2.717	2.742	2.727	52.181	73.909
8	2.636	2.696	2.735	2.689	51.445	74.277
12	2.657	2.714	2.661	2.677	51.221	74.389
16	2.721	2.666	2.694	2.694	51.535	74.233
20	2.678	2.887	2.733	2.766	52.923	73.538
24	2.768	2.723	2.871	2.787	53.333	73.334

R = Absorbance Reading

Ce = Final dye concentration

**A .6 : Adsorption of Metanil Yellow dye on different pH**

pH	R1	R2	R3	Average Reading	Ce	Percentage removal (%)
3	1.869	1.889	1.879	1.879	35.898	82.051
4	1.59	1.618	1.583	1.597	30.486	84.757
5	1.081	1.088	1.098	1.089	20.735	89.632
6	1.622	1.826	1.402	1.617	30.863	84.568
7	1.372	1.356	1.387	1.372	26.161	86.920
8	0.821	0.826	0.828	0.825	15.668	92.166
9	2.836	2.906	2.887	2.876	55.041	72.480
10	2.933	2.876	2.846	2.885	55.207	72.396

R = Absorbance Reading

Ce = Final dye concentration

## APPENDIX B

### DATA ANALYSIS

**B.1** : Equilibrium adsorption capacity for Metanil Yellow dye at different contact time

Contact Time (Hours)	$C_E$	$q_e$	$C_E/q_e$	$\log q_e$	$\log C_E$
0.5	54.286	4.857	11.177	0.686	1.735
1	53.755	4.875	11.027	0.688	1.730
2	52.699	4.910	10.733	0.691	1.722
4	52.181	4.927	10.590	0.693	1.718
8	51.445	4.952	10.389	0.695	1.711
12	51.221	4.959	10.328	0.695	1.709
16	51.535	4.949	10.414	0.695	1.712
20	52.923	4.903	10.795	0.690	1.724
24	53.333	4.889	10.909	0.689	1.727

**B.2** : Equilibrium adsorption capacity for Metanil Yellow dye at different pH

pH	$C_E$	$q_e$	$C_E/q_e$	$\log q_e$	$\log C_E$
3	35.898	5.470	6.563	0.738	1.555
4	30.486	5.650	5.395	0.752	1.484
5	20.735	5.975	3.470	0.776	1.317
6	30.863	5.638	5.474	0.751	1.489
7	26.161	5.795	4.515	0.763	1.418
8	15.668	6.144	2.550	0.788	1.195
9	55.041	4.832	11.391	0.684	1.741
10	55.207	4.826	11.439	0.684	1.742

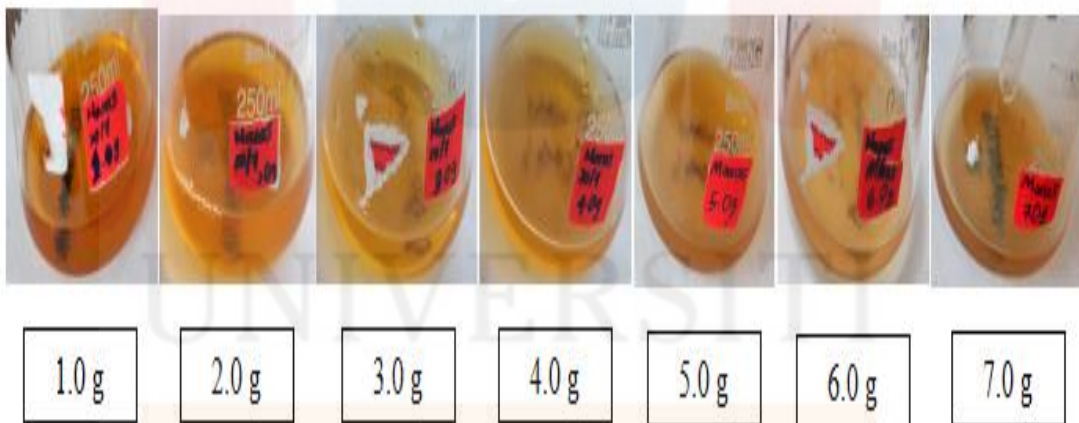


## APPENDIX C

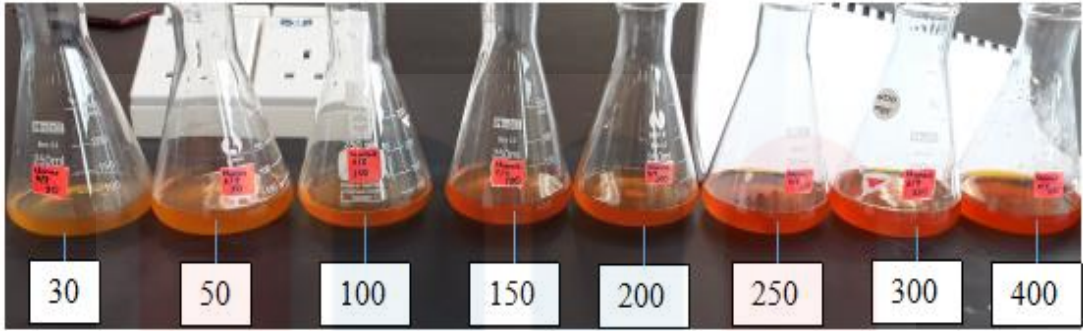
### PHOTO FROM EXPERIMENTAL STUDY



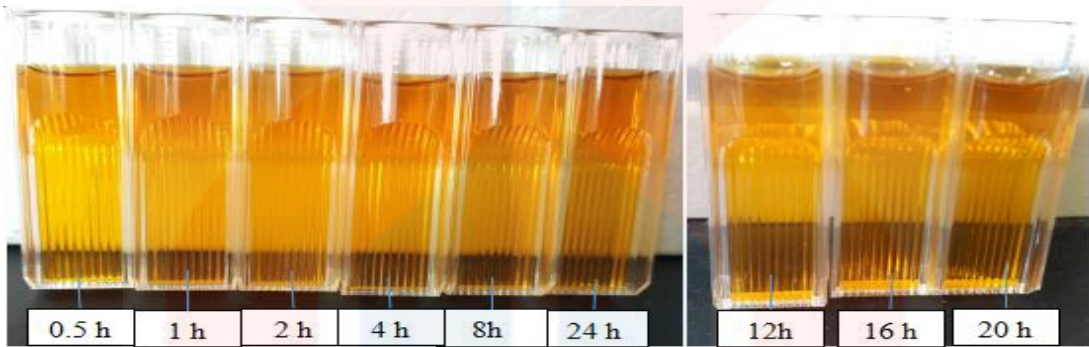
C.1 : Different size of cassava peel



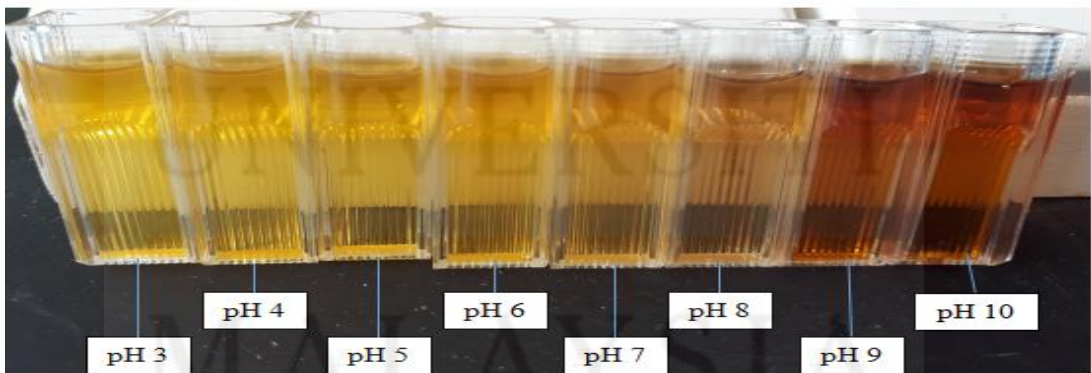
C.2 : Effect of different dosage after adsorption



C.3 : Initial dye concentration after adsorption



C.4 : Contact time after adsorption



C.5 : pH after adsorption

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