REMOVAL OF METHYLENE BLUE USING ACTIVATED CARBON FROM FOXTAIL PALM FRUITS

by

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DECLARATION

I declare that this thesis entitled "Removal of Methylene Blue by using Activated Carbon from Foxtail Palm Fruits" is the result of my own research except as cited in the references. This thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature:

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Date : 10th January 2019

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REMOVAL OF METHYLENE BLUE USING ACTIVATED CARBON FROM FOXTAIL PALM FRUITS

ABSTRACT

Many industries are commonly known for using dyes. The disposed dyes can lead to serious harm to the water users and life in the aquatic because of the dye properties. Industry of textile is the major dye wastewater source which lead to serious pollution in the environment. Hence, the dye adsorption by activated carbon prepared from foxtail fruit palm was studied. The objective of this study were to prepare activated carbon from foxtail fruit palm and to study the effect of contact time, adsorbent dosage and initial concentration of dye usage toward the efficiency of the prepared activated carbon. Nitric acid was used as activating agent in this experiment, with impregnation time of overnight and 500 ˚C of 2.5 hours carbonization. The adsorption capability of foxtail fruit palm activated carbon was determined with the use of a dye called methylene blue. The methylene blue adsorption was identified based on a range of parameters including the contact time, adsorbent dose and initial dye concentration in order to investigate their effects in adsorption potential of foxtail fruit palm powder. This study indicates that activated carbon from foxtail palm fruits could be utilised as a low cost adsorbent to remove basic dyes by using commercialized activated carbon especially to treat wastewater. The results showed the methylene blue removal rate were at 150 mins (85.96%), 5g and 2mg/L (97.13%).The results were obtained.

PENYINGKIRAN BIRU METILINA MENGGUNAKAN KARBON AKTIF DARI BUAH PINANG

ABSTRAK

Kebanyakkan industri lebih dikenali dengan penggunaan pewarna. Pewarna yang dibuang boleh memudaratkan pengguna air dan kehidupan akuatik disebabkan oleh ciri-ciri pewarna. Industri tekstil adalah sumber utama air sisa pewarna yang menyebabkan pencemaran alam sekitar yang serius. Maka, penjerapan warna daripada karbon aktif disediakan daripada buah pinang dan dikaji. Objektif kajian ini adalah untuk menyediakan karbon aktif daripada buah pinang dan untuk mengkaji kesan tempoh masa, dos adsorbent dan kepekatan awal pewarna terhadap kecekapan karbon aktif yang telah disediakan. Asid nitric telah digunakan sebagai ejen pengaktifan dalam eksperimen ini, dengan masa impregnasi selama semalaman dan 500 ˚C selama 2.5 jam dikarbonkan. Kemampuan penjerapan buah pinang karbon aktif ditentukan dengan menyediakan pewarna biru metilina. Penjerapan biru metilina dilaksanakan perubahan pelbagai parameter operasi seperti minit masa, dos penjerapan dan kepekatan pewarna permulaan untuk menyiasat dan menentukan kesan dalam keupayaan penjerapan serbuk buah pinang. Keputusan menetapkan bahawa karbon aktif daripada buah pinang boleh digunakan sebagai berkos rendah dan sebagai teknik alternatif untuk menyingkirkan pewarna dengan menggunakan aktif karbon yang dikomesialkan terutama untuk merawat air sisa. Maka, keputusan diperoleh daripada karbon aktif daripada buah pinang yang menunjukkan parameter untuk penyingkiran biru metilina adalah pada 150 minit (85.96%), 5g dan 2 mg/L (97.13%). Keputusan telah diperolehi.

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LIST OF ABBREVIATIONS

BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
GDP	Gross Domestic Product
AC	Activated Carbon
MB	Methylene Blue
GAC	Granular Activated Carbon
PAC	Powdered Activated Carbon
BET	Brunauer–Emmett–Teller
rpm	Revolutions per minute

LIST OF SYMBOLS

%	Percentage
˚C	Temperature (degree Celsius)
g	Gram
mL	millilitre
mg/L	milligram per litre
nm	nanometre
µm	micrometre

CHAPTER 1

INTRODUCTION

1.1 Background of study

Dyes are synthetic or natural chemicals. Dyes are compounds that organic that can provide a long lasting and bright colour to another substances (Chincholi, Sagwekar, Nagaria, Kulkarni, & Dhokpande, 2014). Natural dyes are extracted from the natural sources including trees, plants and lichens. The first commercial synthetic dye was mauve, that found by British chemist called William H. Perkin, who identified and immediately exploited the commercial synthetic dye. Mauve had a temporary lifetime of commercial that lasts for approximately seven years, but Mauve was a success catalyzed activities that rapidly led to the finding of better dyes (Stothers & Abrahart, 2018). Dyes also can be catogorized as cationic (basic dyes), anionic (direct, acid, and reactive dyes) or non-ionic (disperse dyes).

Many industries involve the use of dyes including, leather, paper textile, plastics, rubber, pharmaceuticals, cosmetics, and food industries. The dyes were firstly applied in industry of textile (Chincholi et al., 2014). Many techniques have been used in dyeing such as vat dyeing, disperse dyeing, reactive dyeing, direct dyeing, and azo dyeing technique. For azo dye, they are made from an azoic diazo component and a coupling element (Stothers & Abrahart, 2018).

The discharge of the dye wastewater comprising a high level of Biological Oxygen Demand (BOD), high level of Chemical Oxygen Demand (COD), increase number of dissolved solids, and visible pollutants. Due to pigmented colour from effluents discharge of dyeing and are toxic to the aquatic life.

Some dyes are teratogenic, carcinogenic and mutagenic. Hence, it is necessary to treat the effluents dye before emitting to the environment (Chincholi et al., 2014).

Methylene Blue (MB) has a molecular formula of $C_{16}H_{18}CIN_3S$ is a cationic dye that has been applied in biology, medical science, chemistry, and dyeing industries (Pathania, Sharma, & Singh, 2013). Methylene Blue can be applied in the copying papers, ink productions, silk, plastics, leather and paper wool (Akl, Mostafa MM, & Mohammed SA Bashanaini, 2016). Methylene Blue wastewater that have greater concentrations, colour depth and discharge massively has turned into a major source of pollution. Thus, wastewater treatment became into a tough problem. Remove the organic dyes that come from the aqueous solution by using adsorption is an efficient technique (Bao & Zhang, 2012). Despite of low toxicity of MB, it can lead to human health effects including vomit, anemia , nausea, and hypertension after being exposed for a long term (Pathania et al., 2013).

The production of the textile is one of the oldest and have the most technologically of whole industries complex. The increasing demand towards the products of textile, mills of textile and their wastewater have been escalating proportionally. At the same time, it will cause a huge pollution problem towards the world include health and environmental problems (Sana Khan & Abdul Malik, 2013). Dyes also can be considered as major pollutants due to many chemicals in the wastewater of textile (Sana Khan & Abdul Malik, 2013).

Contamination of dyes in waste water lead to troubles in few ways due to the existence of dyes in water. Dyes are undesirable and capable of being seen even though in very little amount. The dyes interact with sunlight penetration into the water, inhibit the aquatic biota growth, slow down the process of photosynthesis and disturb the solubility of gas in the water bodies (Garg et al., 2014). Dyes are the complex organic compounds. At the same time, they resist towards the washing, light and microbial invasions. Thus, dyes cannot be decomposed easily (Wang et al., 2008).

All the procedures of dying textile need a very high usage of water in order to get rid of dye fiber hydrolyzate and unfixed dyes (Prico, Scarlat, Moga, & Jianu, 2015). Besides the problem of high usage of water, dyeing contamination of waste water is the major issue of the faces of textile industries (Prico et al., 2015).

This may cause toxic carcinogenic breakdown products formation into municipal environment due to direct emit of dyes that contain effluents. The highest toxicity rates were detected amongst basic and diazo direct dyes. Therefore, it is a must to minimize the dye concentration in the wastewater (Lata et al., 2007)

Meanwhile, adsorption has been proven to be an efficient way on taking out organic matter from aqueous solutions. At the same time, in terms of low the initial cost, easy on operation, simplicity of design and insensitivity to toxic substances (Lata et al., 2007).

Adsorption occurs when the molecules in liquid or gas state cause zero reaction but highlight on connecting surface and it is the most discharge method to remove the dyes of industrial wastewater. It is required small cost, efficiency, easy operation and so on. Huge potential on activated carbon as adsorbent for the treatment (Fazlur Rahman, 2016).

Adsorbents have been widely used to remove the organic contaminants that resistant biologically by using activated carbon. Adsorption by activated carbon can be costly treatment and this lead to the encouragement of research to prepare the economical activated carbon, in terms of chemical or physical activation (Gamal O. El-Sayed, Mohamed M. Yehia, & Amany A. Asaad, 2014). The practise of the use of the by-products of agricultural as raw materials may reduce the cost manufacturing (Gamal et al. 2014).

Abundance of biomass from foxtail fruit palms in Malaysia lead to investigation of the removal of dye based on the foxtail fruit palm as activated carbon. These trees have crown shafted, thin trunked, medium height of pinnate palm that is very fascinating in impression. Plus, they also a species of monoecious of palm tree which means that a single tree which has both male and female flowers. Therefore, a single tree can produce viable seeds. Leaves are plumose (fluffy) and this species wants full sun in most areas and tolerates heat. Cold tolerance is, at best, into the low 20˚C and growth rate is medium. Small plants are slow to get started. It tolerates heat well. Mature height averages 25 feet. Enthusiasts like this species because it is not overly large and can fit into a small planting area (Bergman, 2017).

Figure 1.1: Foxtail Palm Tree

Figure 1.2: Foxtail fruit

1.2 Problem Statement

Dyes act as an aesthetic colour addition and belong to main class of chemicals in most of the industrial processes, particularly in the industrial textile.

However, contaminations of the soil and natural water bodies occur due to the inefficiency of the dyeing processes, insufficient waste water treatment and poor handling of spent effluent. The wastewater that produces from textile industries may cause a threat towards the environment (Sarayu & Sandhya, 2012). Thus, dyes need to be treated where the best method to treat dye is using activated carbon. Removal of commercial activated carbon is quite costly. Hence, foxtail fruit palms as the agricultural-by-product will be used as raw material for activated carbon production the removal of dyes. Through this, the fruit will be fully utilize and reducing the agricultural waste to the environment.

1.3 Objectives

The aim of this study is to examine the potential of foxtail palm fruits as a low cost dye adsorbent. The objectives of this study are:

i. To prepare activated carbon from foxtail fruit palm

ii. To study the effect of contact time, adsorbent dosage and initial concentration of dye usage toward the efficiency of the prepared activated carbon.

1.4 Scope of Study

This study focus on using the agricultural waste which was foxtail palm fruits as activated carbon to remove the dyes from methylene blue. The foxtail fruit palm is collected from the tree that has been planted around SMK Jeli, Jeli, Kelantan

(N05˚42’06.2” E101˚50’40.1”). In this study the whole foxtail fruit palms were used as adsorbent. The study consists of various experimental parameters including contact time, adsorbent dose and initial dye concentration to show the optimize conditions of dye removal.

1.5 Significance of Study

The results of this research is useful especially in textile industries due to following reasons:

i. This study gives the value of foxtail palm fruits as a waste product.

ii. This study helps on minimizing the total textile dye from being discharged into river stream.

CHAPTER 2

LITERATURE REVIEW

2.1 Textile industry

The industry of textile is the world's oldest branch of consumer goods manufacturing. It is various and heterogeneous sector that involves the whole production chain of transforming chemical and natural fibres including wool, cotton, and oil into end-user goods for household goods, garments and industrial textiles. Textiles are relatively intertwined with governance, social and environmental (EU, 2013)

Man-made textile fibre is a very famous industry in Malaysia especially among the East Coast of Peninsular Malaysia. The hand-made batik is a traditional inherited industry especially for the Malays community. Today, this industry has contributed to the growth of economy in Kelantan and Terengganu states. In 2008, Malaysia has produced approximately 400 000 tons of man-made fibers including staple, nylon, and polyester filament that contributed to about 1.03% of the world's production (Pang & Ahmad Zuhairi Abdullah, 2012). Malaysia was the fifteenth largest producer of textile fiber and ninth largest in Asian region in 2008 (Pang & Ahmad Zuhairi Abdullah, 2012).

This industry has the greatest forecast on the annual export growth that presents 7.80% per annum (Lee, Zulkifli Mohamed Udin, & Mohamad Ghozali Hassan, 2014). Furthermore, the Department of Statics Malaysia has announced the textile and apparel grew the Gross Domestic Product (GDP) at 1.70% on the sector of manufacturing in 2012 (Lee et al., 2014).

At the same time, the massive number of textile fibers produced by textile industry which involve dyes during its production in Malaysia also post significant effects to the environmental quality, especially with respect to the liquid effluent (Pang & Ahmad Zuhairi Abdullah, 2012).

2.1.1 Usage of Textile Industry

Textiles are very beneficial where they are being used in almost each possible context. Textiles usually are being used as materials in producing bags, kites, sails, clothing, parachute, flags, furnishing, and tents.

2.1.2 Problems Caused by Textile Industry

The textile industry uses a lot of toxic chemicals that can lead to the health and environmental problems. Dyes are major pollutants among those chemicals in the wastewater of textile. The environmental problems related with textile industry in the world are usually connected with pollution of water. This is due to the discharge of untreated effluent and the usage of toxic chemicals in processing of textiles (Sana Khan & Abdul Malik, 2014). Therefore, workers of the textile industry can be exposed to toxic chemicals in the sectors of dyeing, printing and finishing of the textiles. The workers in the textile industries also work with fixatives and solvents, agents of crease-resistance that will emit formaldehyde, flame retardants with toxic compounds and antimicrobial agents. Exposure towards the formaldehyde can lead to many type of cancer such as nasal, esophageal, cancers of stomach and thyroid. Plus, the chemical also can lead to cause dermatitis and eczema (Skyle, 2018).

Textile waste is a reason of the significance environmental degradation and illnesses of human. The functioning cells that normal is disturbed because of the chemical pollution which can cause the alteration especially in the biochemical and physiology of animal mechanisms.

This is causing the impairment in the main functions which involve the osmoregulation, reproduction, respiration, and mortality (Sana Khan & Abdul Malik, 2014).

Furthermore, industry of textile also produces atmospheric emissions during their various processes. Emission of gases have been recognized as the second contributor to the pollution issues while the waste water from industry of textile is the first contributor (Skyle, 2018). Emissions in the air such as dust, acid vapours, mists, bad odours and boiler exhausts. The combustion of diesel causes air emission that have many main sources such as ovens, point source boilers, storage tanks, warehouses, diffusive source solvent based, wastewater treatment and spills (Gupta, Biswas, & Agrawal, 2017). Workers that work with cotton are exposed to the significant amount of cotton dust including pesticides and soil particles. The exposure can cause mount respiratory disorder and fatal byssinosis disease called brown lung that may cause chest tightening, wheezing, shortness of breath and coughing (Skyle, 2018).

High noise level also will increase. Due to the exposure towards high noise level is usual in textile factories, especially those who live in the developing countries where the machines are old are not well maintain. This causes a range of health problems to the workers including to the loss of hearing, sleep disorders, anxiety, changes in blood pressure and other ailments (Skyle, 2018).

2.2 Activated Carbon

Residues of agriculture are good source materials to produce the carbonaceous adsorbents. Activated carbons have variety of physical and chemical properties based on the types of agricultural residue including pistachio shell, rice husk, biotreated barley husk, and raw barley husk. This approach could increase the value for the agricultural residues, reduce the waste water treatment cost, and give a potentially method for cost-effective towards the existing commercial activated carbons (Hsing-Cheng, Horng, Pan, & Shin-Ku., 2011).

Activated carbon is known as a versatile adsorbent because of its distinguished properties like large surface area and pore volume, extensive adsorption capacity, diverse structure of pores, and high degree of surface reactivity.

Applications that related to the usage of activated carbon including the removal the colour, odour, and taste from water and wastewater; In addition, activated carbon also good on the natural gas recovery, purification of air in inhabited spaces like chemical industries, as catalysts and also catalyst supports (Hsing-Cheng et al., 2011). AC has better capacity of adsorbing a wide spectrum of dyes and other pollutants from the wastewater (Chen, Liu, Yang, & Tan, 2015).

Adsorbent is commonly used as activated carbon due to its high capacity to adsorb diverse organic compound including dyes, pharmaceutical, heavy metal, and surfactants (Saeedeh Hashemian, Khatereh Salari, & Zahra Atashi Yazdi, 2014). Furthermore, the adsorbents in the activated carbon that carbonaceous have huge surface are and structure that porous which make it very efficient (Anjum & Murugesan, 2016).

However, the cost for activated carbon is relatively expensive. Another alternative ways are being made to have effective use and low cost at the same time, able to sorb another substance naturally to get rid of trace contaminants of the wastewater (Saeedeh Hashemian et al., 2014) .The surface of activated carbon is non-polar which gives result in the affinity of non-polar adsorbates like organics.

The major activated carbon's application during adsorption is where the huge quantity of activated carbons are being consumed. The purification of industrial waste water and domestic become increase due to the consumption.

Various methods are available including oxidation, aeration, coagulation, and adsorption of activated carbon that have the greatest wide spectrum technology exist and available at the present moment (Goyal & Bhagat, 2012). The more essential parameters that determine and effect the inorganics adsorption from the aqueous solution are the acidic carbon-oxygen surface groups that exist on the surface of carbon and the pH solutions. Both of the parameters will determine the ionic concentration, the nature and also molecular species inside the solutions (Goyal & Bhagat, 2012). Activated carbon also functions as the removal for the strong odour of dissolved organic compounds in the industrial waste water (Athimoolam & Velayutham, 2014).

There are two methods on the usage of activated carbons where the dissimilar properties and use it in different ways. First, granular activated carbon (GAC) is usually used to remove trace elements including the organic trace elements, which may exist in the water and normally resistant biological treatment. In spite of their low concentration, these elements will cause worst smell, taste or colour. Second, powdered activated carbon (PAC) is usually use in biological processes as the water that have organic elements can be toxic. Water is treated by adding PAC, and after certain amount of contact time pass and agitation, the particles will be sediment for their pre-separation.

The economic viability of this process depends on the existence of an efficient, which means the solid regeneration once its capacity for adsorption is done. The GAC regenerates easily through oxidation of the organic matter and subsequent surface elimination of solid in an oven. The properties of the activated carbon declines, which it must to reload part of it in each cycle with virgin carbon. Meanwhile, PAC is more hard to regenerate, but much easier to produce (Condorchem, 2013) .

Farah Amni Daud et al., (2016) studied on activated carbon produced from the foxtail fruit palm (empty fruit bunch) to treat methylene blue. The study showed on the effect of dye concentration and contact time that the highest percentage removal can be achieved during longer contact time as well as higher concentration of dye. This is because, the molecules have need to cross the boundary layer film onto adsorbent surface before the methylene blue molecules diffuses into the structure of porous of the adsorbent in the dye adsorption process (Tan & Hameed, 2001).

A study conducted by Wu et al., (2014) on the effect of dye concentration and adsorbent dose proposed that an increase in the adsorbent dose lead to the increase of dye removal. This is because of greater adsorbent dose have huge excess in adsorption sites So do the same study on the effect of contact time and adsorbent dose where the percentage removal become lowest with minimum adsorbent dose and contact time (Wu et al., 2014).

Introduction for adsorption of more binding sites has increased the removal of MB. The result showed that 99.9% of methylene blue has been removed under the optimized conditions. This proves that activated carbon from foxtail fruit palm have the potential as an adsorbing agent (Alqaragully, 2014).

2.3 Chemical Activation

Chemical activation forms from carbonization and activation procedure. These procedures will form the surface of internal area and edge sites by generating the structure of porous. The sites of edge are included in the surface functional groups formation mostly on functional groups that contain oxygen.

Chemical activation can be made by using variety of difference acids such as HNO_3, KOH, $ZnCl_2$, H_2SO_4, $FeCl_2$, H_3PO_4 as typical activating agent (Anjum & Murugesan, 2016). The presence of activating agent and the carbonisation conditions can affect the pore structures development (Okibe, Gimba, Ajibola, & Ndukwe, 2013)

During the chemical activation, a precursor of activated carbon is impregnated with an chemical agent and then carbonised in an inert atmosphere. The chemical activation compared to the physical activation comprising shorter activation time and lower carbonisation temperature. Furthermore, the activated carbon based on the chemical activation is mesoporous with a greater surface area (Sahira, Mandira, Prasad, & Ram, 2013).

2.3.1 Nitric Acid (HNO_3)

Nitric Acid is a powerful oxidising compound and a strong acid that has been used in the making of a range of major chemicals including intermediates of organic chemical, fertilizers, dyes, pharmaceuticals, polyurethanes, insecticides, explosives, fungicides and synthetic fibers (Clarke & Mazzafro, 2005).

Nitric acid is a colourless, poisonous liquid and highly corrosive that results in choking red or yellow fumes in the moist air. It is compatible with the water in every proportion. Nitric acid also ionizes readily in the solution as a conductor of electricity. Nitric acid is known as *aqua fortis (Encyclopedia, 2018).*Nitric acid is chemically activated the various raw material in producing activated carbon include foxtail fruit palm.

Before the adsorption, activated carbon is washed by acid including HCl or HNO3. The acid can get rid of the accumulated impurities on the activated carbon's surface including Nitrogen (N), Phosphorus (P), Calcium (Ca), Potassium (K), Aluminium (Al), Silicon (Si) and Iron (Fe). The acid wash also can enhance the existence of surface chemistry by introducing the hydrophilic functional group such as acid or based group. Lastly, they also enhance the surface area by opening the mouth of pores (Allwar Allwar, Retno Hartati, & Is Fatimah, 2017).

Better surface areas will be obtained by treating the Brunauer–Emmett–Teller (BET) and also Langmuir surface area with nitric acid. Activated carbons that have been introduced with the nitric acid was potentially increase the properties in physical's term. Activated carbons are involving the surface area, pore size distribution and volume of pores. The result of impregnating nitric acid with activated carbon also as evidence that nitric acid has detached some contaminants attached on the surface activated carbon, for instance, Fe, Si, K and Al with success. This is because the pores on the surface areas of activated carbon was seen clearly with full of cavities (Allwar Allwar et al., 2017).

2.4 Agriculture Waste

Agricultural wastes are the residues that come from the growing and processing of raw agricultural products, for example fruits, meats, poultry, vegetables, dairy products and crop.

All of these are non-product outputs from production and processing the products of agricultural that may consist material that able to give advantages to human being. However, the economic values are low than the collection, processing and transportation cost for the beneficial use (Obi, Ugwuishiwu, & Nwakaire, 2016).

Megaton of wastes from agriculture, for instance corncobs, hulls, straws, and cornstalks are produced each year. Those are segregated very well, ready to collect and have a lot of purposes as raw material (Arnold, 1931). In the recent years, agricultural wastes turn into the sources of major pollutions. Environmental pollution will occur due to the improper way of agricultural wastes disposition. Many valuable resources of biomass are wasted (Wang et al., 2016).

The conversion of agricultural waste can increase the economic value by turning the waste into something useful (Harshwardhan & Upadhyay, 2017).

2.4.1 Uses of Agricultural waste

Waste products from agricultural and forestry are coming from resources that no longer used and they are broadly available. Plus, they are environmentally friendly also. Hence, the agricultural wastes have better potential to act as adsorbents (Saeedeh Hashemian et al., 2014).

The dyes removal from wastewater using process of adsorption by agricultural waste provides an alternative path. Adsorbents are usually chosen because of its availability in nature, environment friendly behaviour and low cost effective (Fahim Bin Abdur Rahman, Maimuna Akter, & M. Zainal Abedin, 2013).

The adsorption approach are being used widely and activated carbons have been often used as adsorbent (Hala Ahmed Hegazi, 2013).

2.4.2 Foxtail Fruit Palm as Agriculture Waste

Foxtail palm, Wodyetia bifurcate *I.K Irvine* is a member of the Arecaceae, or palm, family. Foxtail palms has extraordinary beauty, adaptability and rapid growth in partial shade to sunny. Foxtail palm can grow in a range of soil pH from 5.6 until 7.8 as long as the medium is not drain. They can tolerate with the sand and wind. These trees are elf-cleaning and naturally drop their old leaves (Perez, Kobayashi, & Sako, 2009).

In Malaysia, foxtail fruit palm is a commercial plant that usually be planted along the streets and farms. The foxtail fruits have a bright red colour once it has ripen and will fall off to the ground.

2.5 Activated Carbon from Agriculture Waste

Waste materials from agriculture and industries have been used as activated carbons (Saeedeh Hashemian et al., 2014). Activated carbon (AC) is a carbonaceous material that can be made from low cost materials that contain low inorganic content and high carbon content by using pyrolysis method. The by-products of agricultural like bamboo, coconut husks, coconut shells, sugar beet bagasse, rice straw, oil palm fiber, rattan sawdust etc. These products have the potential as a great adsorbents of assorted pollutants (Zeid Abdullah ALOthman, Mohamed Abdelaty Habila, & Rahmat Ali, 2011). Agricultural waste becomes the choice for activated carbon because it is a renewable source.

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CHAPTER 3

METHODOLOGY

3.1 Sampling of raw materials

In this research, the raw materials was *Wodyetia Bifurcate I.K Irvine* fruits that used to make the activated carbon. The fruits were sampled at SMK Jeli, Jeli, Kelantan, Malaysia.

3.2 Carbonization of Foxtail Palm Fruits

First, the foxtail palm fruit was collected. Next, the fruits were cleaned and washed thoroughly by using distilled water to get rid of any dirt and surface impurities. Then, the fruits were dried at 100˚C overnight in the oven and cooled down in room temperature afterwards. The dried fruit was kept in tight polyethylene bag and put in desiccators for the further usage. The dried foxtail fruit was carbonized at 300˚C for exactly 2 hours in furnace. Then, the fruit was cooled down in room temperature. The fruit was crushed into small pieces by using pestle and mortar and sieved through 250 µm, weight and recorded. The sieved fruit was stored in tight polyethylene bag and kept dry in desiccators.

3.3 Preparation of Activated Carbon Using Nitric Acid as Chemical Activation Agent

The foxtail fruit AC was prepared with the chemical activation process. About 40 g of oven dried foxtail fruit was soaked and impregnated in beaker that contained 80 mL of concentrated HNO_3. The mixture was mixed vigorously for 30 minutes until became paste with constant stirring. The paste was left impregnated for overnight in fume hood for the chemicals to fully react. After that, the slurry was weight and placed in dry crucibles and carbonized at 500˚C for 2.5 hours in a furnace. The AC was washed by using the distilled water and adjusted the pH to about 7. The AC was dried at 150˚C for 3 hours in the oven. The dried AC was kept in tight polyethylene bag and stored in desiccators for further use.

3.4 Adsorption Test

3.4.1 Effect of contact time

The adsorption study on the effect of contact time on efficient removal of colour from Methylene Blue dye. The MB was selected in this study due to its powerful adsorption onto solids (Shahryari, Goharrizi, & Mehdi Azadi, 2010). This adsorption test was performed by mixing 25 mL of methylene blue dye with 2 mg/L concentration with 1 g of foxtail fruit activated carbon in Erlenmeyer flasks set (250 mL) with contact time at 30 minutes. The mixture was left for 2 hours at 150 rpm in an isothermal shake to accomplish the equilibrium state (Chin, 2014). Then, the MB dye was filtered by using 0.45 μm Whatman filter paper. The UV-VIS spectrophotometer was used to identify the optical density of adsorbed dye by the activated carbon at the maximum absorbance of 668 nm wavelength (Wong, Senan, & Atiqah, 2013). Same steps were repeated for 60, 90, 120 and 150 minutes.

3.4.2 Effect of Adsorbent Dose

The adsorption study on the effect of adsorbent dose on efficient colour removal from MB dye. This adsorption test was performed by mixing 25mL of methylene blue dye with 2 mg/L concentration with 1 g of foxtail fruit activated carbon in 250 mL Erlenmeyer flasks set with optimised contact time. The mixture was placed and kept for optimum contact time and at 150 rpm in an isothermal shake to accomplish the equilibrium state (Chin, 2014). Then, the MB dye was filtered using 0.45 μm Whatman filter paper. The usage of UV-VIS Spectrophotometer was to identify the optical density of adsorbed dye by the activated carbon at the maximum absorbance of 668 nm wavelength. (Wong et al., 2013). Same steps were repeated for 2 g, 3 g, 4 g, and 5 g.

3.4.3 Effect of Initial Dye Concentration

The adsorption study on the effect of initial dye from MB dye. Initial concentration of methylene blue dye solution at 2 mg/L with 25mL of methylene blue in a set of Erlenmeyer flasks (250 mL). The MB was treated with optimum weight from previous parameter of adsorbent dose of foxtail fruit activated carbon with contact time at 15 minutes. The mixture was placed and kept for optimum contact time and at 150 rpm in an isothermal shake to accomplish the equilibrium state (Chin, 2014). Then, the MB dye was filtered by using 0.45 μm Whatman filter paper. The UV-VIS Spectrophotometer was used to identify the optical density of adsorbed dye by the activated carbon at the maximum absorbance of 668 nm wavelength (Wong et al., 2013) .Same steps were repeated for 4, 6, 8 and 10 mg/L.

METHOD FLOW CHART

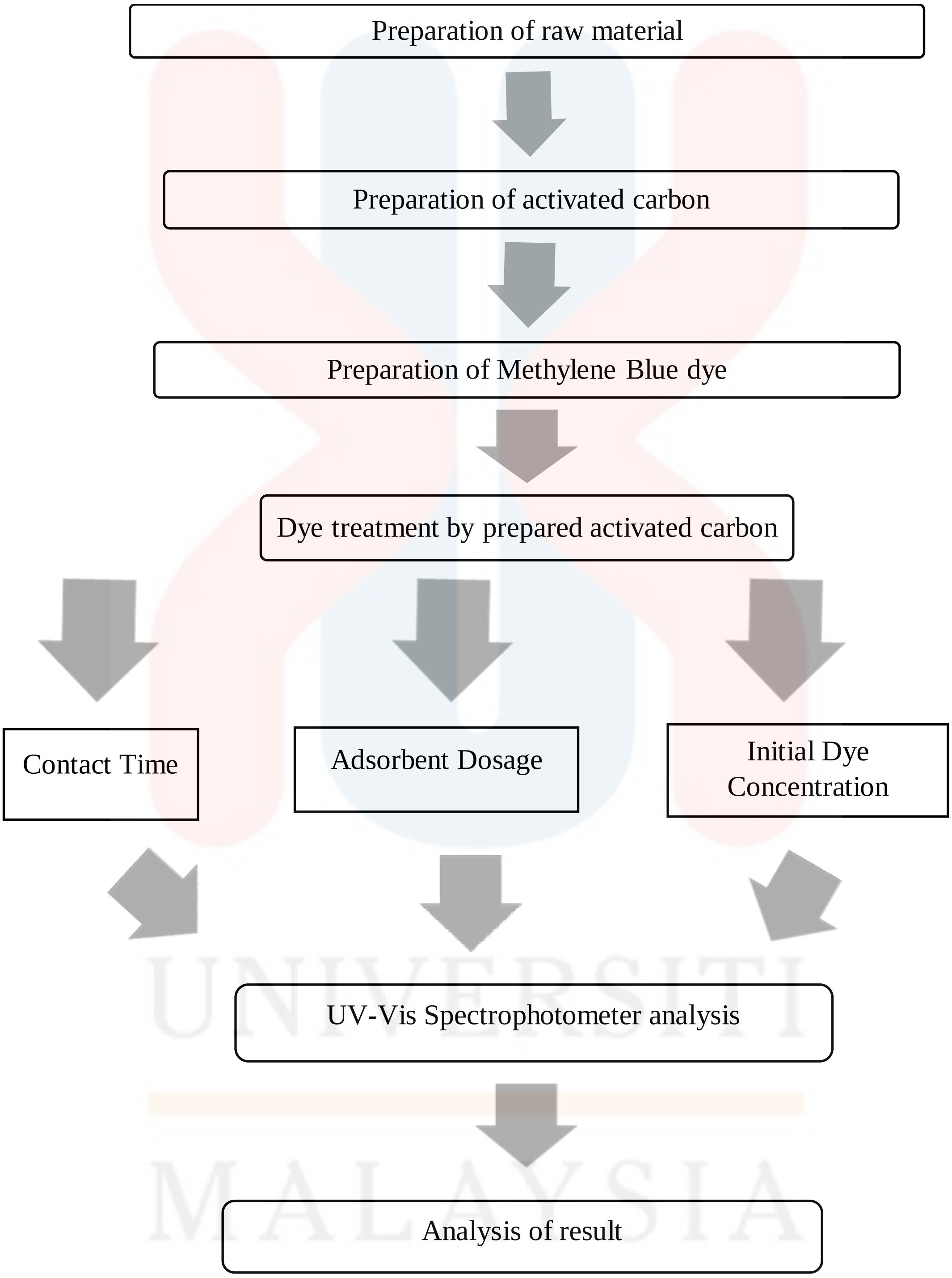

Figure 3.4.4: Method flow chart

3.5 Percentage removal

The dye removal's percentage is calculated by using the following equation:

The percentage of removal of dye= $\frac{Co-Ci}{Co} x\ 100\%$

Where:

Co = Initial dye concentration

Ci = Dye concentration after being treated with foxtail fruit palm

CHAPTER 4

RESULT AND DISCUSSION

4.1 Adsorption Experiment

4.1.1 Effect of Contact Time

In the first phase of optimization with foxtail fruit palm activated carbon, the contact time were adjusted for 30, 60, 90, 120 and 150 minutes. The MB concentration solution, adsorbent dose, and initial dye were fixed with 1g and 2mg/L of MB respectively. Figure 4.1.2 shows the effect of contact time on MB adsorption.

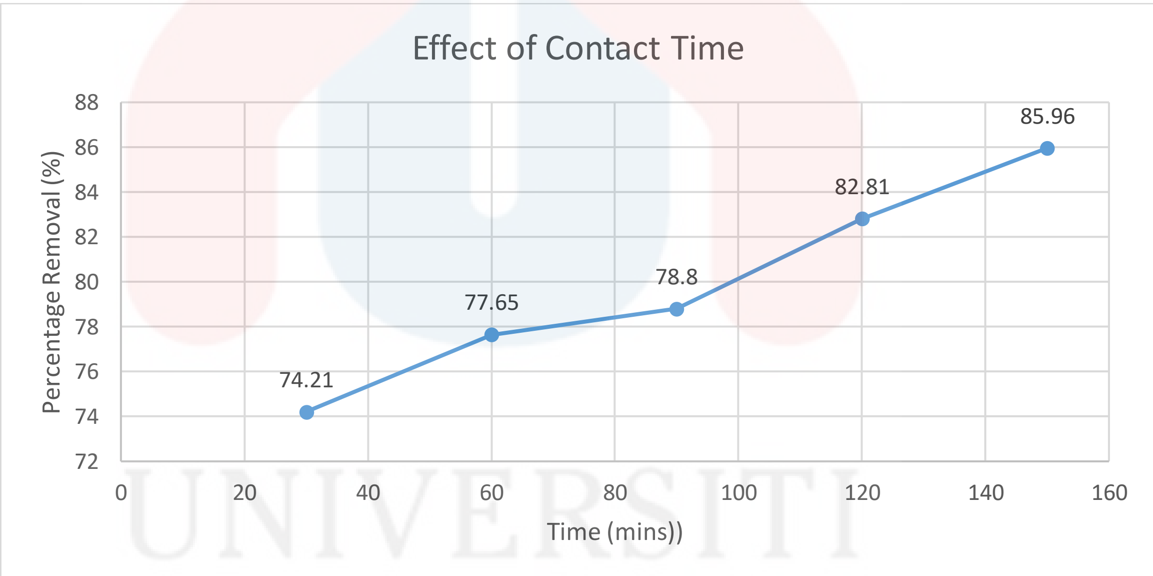

Figure 4.1.1: Effect of Contact Time

Figure 4.1.1 shows the pattern can be noticed from the result obtained were not slightly increasing. The results at 30 and 60 mins showed 74.21% and 77.65% of total removal respectively. As the time increases from 90 to 120 mins, the removal percentages increased from 78.80% to 82.81% each. Further increment to 85.96% was obtained for 150 mins of contact time removal.

The result indicates that the removal percentage was slightly increased with the contact time.

It was proved from the study that, as the contact time increases, the percentage removal also increases too. During the dye adsorption process, the MB molecules have to come across the boundary layer film first and go onto the surface of adsorbent before the methylene blue molecules diffuse into the porous structure of adsorbent (Tan & Hameed, 2001). This is because larger number of molecules will cause the MB solutions concentration to have longer time to be adsorbed. In this parameter, 150 mins has been selected for subsequent experiment.

4.1.2 Effect of Adsorbent Dose

The influence of adsorbent dose on the removal of methylene blue was investigated with weights of 1, 2, 3, 4 and 5g of foxtail palm fruits activated carbon. The range of adsorbent doses were tested while other parameters such as contact time from previous adsorbent experiment (150 mins), initial dyes concentration of methylene blue

(2 mg/L) and initial volume (25 mL) were kept constant.

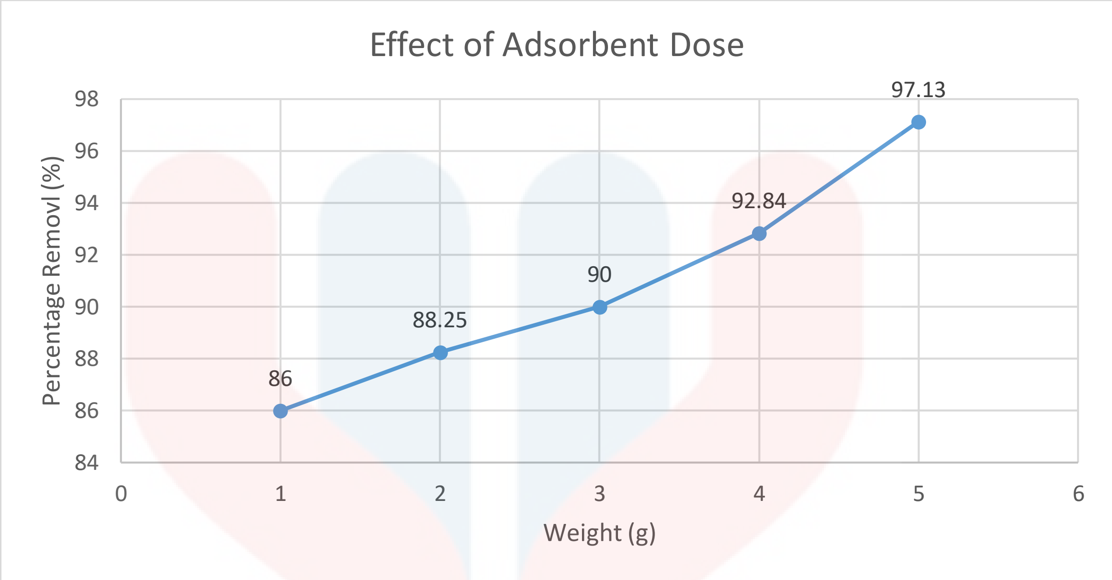

Figure 4.1.2: Effect of Adsorbent Dose

Figure 4.1.2 shows the removal efficiency gradually increased with the increasing dosages of activated carbon. The result shows that removal efficiencies were 86% and 88.25% of removal when the weight of activated carbons were 1 g and 2 g respectively. Next, that for 90% and 92.84% for 3 g and 4 g respectively. The removal efficiency was 97.13% for 5 g of activated carbon. The obtained results were due to large excess of adsorption sites which have been provided by the higher adsorbent dose (Wu et al., 2014). The introduction of many binding sites for adsorption with increasing adsorbent doses could increase in the removal of methylene blue (Alqaragully, 2014). Hence, as the contact time was increased with the adsorbent dose, the chances for the total removal of dye were decisive. Thus, the optimized dosage of 5 g was selected for the subsequent experiment.

4.1.3 Effect of Initial Dye Concentration

The total adsorption is largely dependent on the initial dye concentration for the dye removal. The initial dye concentration effect relies on immediate relation between the dye concentration and the available sites on the sites of adsorbent (Mohamad Amran

Mohd Salleh, Dalia Khalid Mahmoud, Wan Azlina Wan Abdul Karim, & Azni Idris, 2011).

For the assessment of the effect of initial concentration, 25 mL of different initial concentration was treated onto the adsorbent. In order to achieve optimum performance of the adsorption of MB dye in the last parameter, the initial dye concentration of MB dye were varied to 2, 4, 6, 8 and 10 mg/L. The other parameter such as contact time (150 mins) and adsorbent dose (5 g) were kept constant.

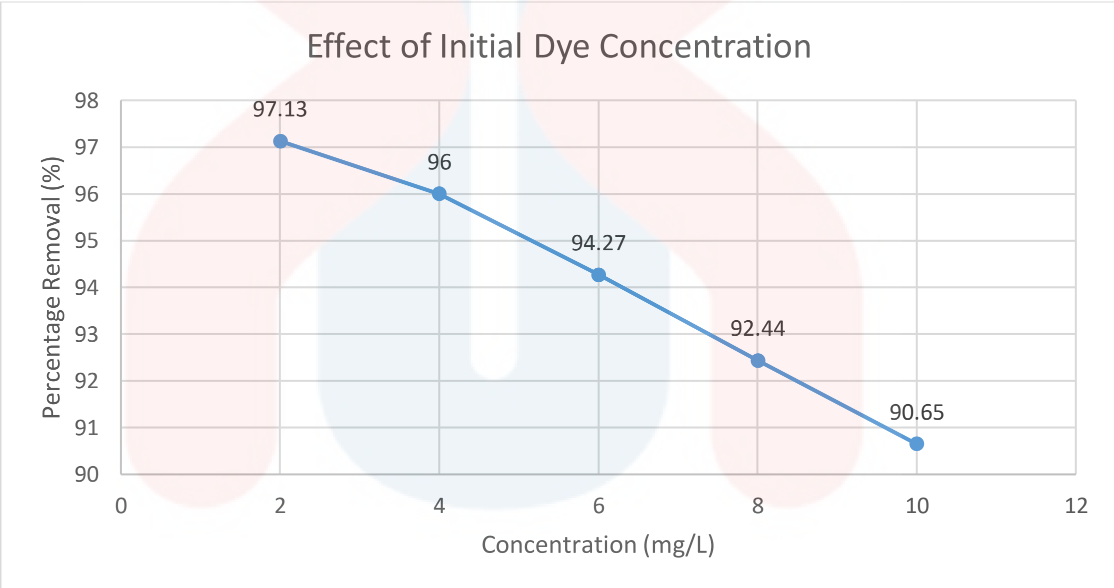

Figure 4.1.3: Effect of Initial Dye Concentration

The dye removal percentages of methylene blue with concentrations of 2 and 4 mg/L showed slight decrease from 97.13 % to 96%, respectively while concentration of 6 mg/L had 94.27% percentage removal.

The 8 and 10 mg/L also showed slight decreased from 92.44% to 90.65%. Coincidently, the removal percentage of MB dye was dropped from 97.13 % to 90.65% due to the increase of the initial dye concentration from 2 mg/L to 10 mg/L. The overall accumulation of methylene blue escalated with increasing initial concentration was probably because of more contact of adsorbent sites with methylene blue (Mohammad Arifur Rahman, S.M. Ruhul Amin, & Alam, 2012). The dye removal percentage decreases with increasing concentrations of initial dye. This is likely due to saturation of the adsorption sites on the adsorbent surface. There are unoccupied active sites on the adsorbent surface at low concentration (Kannan & Sundaram, 2001). As the concentration of initial dye increases, the active sites that are required for dye molecules adsorption will be increased too (Kannan & Sundaram, 2001). On the other hand, the increase of concentration of initial dye may increase adsorbent capacity due to the greater driving force for mass transfer at a greater concentration of initial dye (Bulut & Aydın, 2006).

Furthermore, the active sites of adsorbent might contact with the most sample solution of methylene blue at low concentration. However, the active sites are saturated at high dye concentrations which have been filled up and not available which cause the active surface cannot having contact with all methylene blue (Mohammad Arifur Rahman et al., 2012). From the study on the effect of initial dye concentration, it was shown that the lowest initial concentration, 2 mg/L have the highest percentage removal, 97.13%. Thus, this value has been selected as the optimum concentration parameter.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion.

Adsorption process on the liquid phase were constructed to study the capacity of adsorption and adsorbent ability to remove Methylene Blue dye from aqueous solution. Activated carbon from foxtail fruit palm was prepared by NHO_3 aqueous solution. Concentrated NHO_3 as activating agent that have gone through with 1:2 soaking ratio, overnight soaking period and also 500˚C with two and half hours of carbonization have generated more pore sites for adsorbent as more vacancies of specific adsorbent surfaces. Plus, the use of NHO_3 able to remove some contaminants attached on the surface activated carbon and hence gave a better performance in activated carbon (Allwar Allwar et al., 2017). The methylene blue dye removal in aqueous solution can be made by foxtail fruit palm which is a good raw substance that can be efficient adsorbent. Effect on the parameter such as contact time, adsorbent dose and initial dye concentration were investigated by using a low cost adsorbent. It was discovered that adsorption was high with 85.96% removal of contact time (150 mins), 97.13% removal of adsorbent dose and initial dyes (5g and 2 mg/L). Thus, from the results of this study, the activated carbon from the foxtail fruit palm materials that have been utilized may offer as prospective precursor to treat wastewater contaminated with methylene blue dyes effectively.

5.2 Recommendations for future research

The application of Wodyetia bifurcate *I.K Irvine* materials to remove the methylene blue dye was studied. The results indicate the foxtail fruit palm as an effective adsorbent material for dye wastewater treatment. Nevertheless, some recommendations need to be addressed for future research especially on increasing the surface area value of the activated carbon from foxtail fruit palm. The study can be done by experimenting other parameter such as pH value, temperature and particle size. These parameters also can optimize the efficiency of the activated carbon. Other than that, researchers also can investigate other dyes including malachite green, congo red or methyl red to study the effectiveness in removal.

Furthermore, other chemicals also can be used instead of HNO_3 in this study as an alternative chemical substance. This might be improvised if the foxtail fruit palm be treated with other chemicals that play role as catalyst to the adsorbent to elevate the adsorption capacity efficiency.

Besides, testing the water quality for the wastewater to investigate the water quality. This is to examine the capability of activated carbon as a potential adsorbent. Last but not least, activated carbon is advocated to be a part for the adsorbent as they are more effective. This is due to its huge surface area, better developed porosity and versatile surface chemistry.

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APPENDIX A

Percentage removal of Contact Time

Table A1: Co : 0.349

Time(mins)	First absorbance	Percentage Removal (%)
30	0.090	74.21
60	0.078	77.65
90	0.074	78.80
120	0.060	82.81
150	0.049	85.96

Percentage removal of Adsorbent Dose

Table A2: Co: 0.349

Weight (g)	First absorbance	Percentage Removal (%)
1	0.049	86.00
2	0.041	88.25
3	0.035	90.00
4	0.025	92.84
5	0.010	97.13

Percentage removal of Initial Dye Concentration

Table A3: Co: 0.349, 0.373, 0.524, 0.714, 0.888

Concentration (mg/L)	First absorbance	Percentage Removal (%)
2	0.010	97.13
4	0.015	96.00
6	0.030	94.27
8	0.054	92.44
10	0.083	90.65

APPENDIX B

Preparation of Foxtail Palm Fruit Activated Carbon

Figure B1: Foxtail Palm Fruit

Figure B2: Dried foxtail palm fruit

Figure B3: Sieved foxtail fruit palm

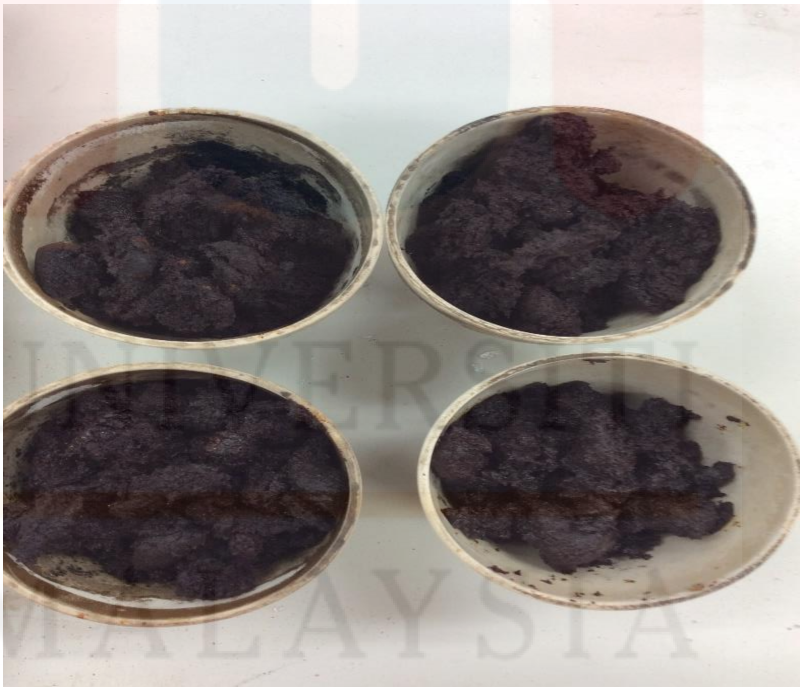

Figure B4: Soaked and impregnated foxtail with HNO_3

APPENDIX C

Methylene Blue

Figure C1: Methylene Blue powder

Figure C2: Freshly Prepared Methylene Blue dye