EFFICIENCY OF FOXTAIL PALM FRUIT ACTIVATED CARBON IN MALACHITE GREEN DYE REMOVAL

by

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THESIS DECLARATION

I declare that this thesis entitled "Efficiency Of Foxtail Palm Fruit Activated Carbon In Malachite Green Dye Removal" 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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Date : ____________________________

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LIST OF ABBREVIATIONS

AC	Activated Carbon
BC	Before Century
BOD	Biochemical Oxygen Demand
CO_2	Carbon Dioxide
$C_{23}H_{25}N_2Cl$	Malachite Green
GAC	Granular Activated Carbon
HNO_3	Nitric Acid
H_2O	Dihydrogen Oxide (steam)
H_2SO_4	Sulfuric Acid
H_3PO_4	Phosphoric Acid
MG	Malachite Green
N_2	Nitrogen
NaOH	Sodium Hydroxide
PAC	Powdered Activated Carbon
TiO_2	Titanium Dioxide
UV	Ultraviolet
WAS	Wood Apple Shell
$ZnCl_2$	Zinc Chloride

LIST OF SYMBOLS

%	Percentage
^oC	Degree celcius
µm	Micrometer
g	Gram
g/mol	Grams Per Mol
h	Hours
mL	Milliliters
mg/L	Milligram per liter
min	Minutes
nm	Nanometer
ppm	Parts per million
rpm	Revolutions per minute
C_o	Initial Concentration
C_e	Equilibrium Concentration

EFFICIENCY OF FOXTAIL PALM FRUIT ACTIVATED CARBON IN MALACHITE GREEN DYE REMOVAL

ABSTRACT

The release of dye into the environment have adverse effect on human life, plants and animals. There were various technologies used to effectively remove the dye from water to reduce pollution such as adsorption. Utilization of agriculture biomass such as foxtail fruit had been found as interesting alternative based on its potential in activated carbon adsorption. In this study, activated carbon was prepared from the carbonization (300ºC, 2 hours) of foxtail fruit (*wodyetia bifurcate*) impregnated with HNO_3. Batch adsorption experiment was conducted by using incubator shaker to investigate the effect of contact time, adsorbent dosage and dye concentration for the adsorption of MG dye from aqueous solution. The absorbance of the MG dye (treated solution) had been analyzed by UV-Vis spectrophotometer to find the optimal condition for the efficiency of foxtail fruit activated carbon to treat MG dye in aqueous solution. Resulting from the parameter with the highest percentage removal was chosen for subsequent studies. This method can be considered as time and cost effective as foxtail fruit was easily access. Apart from the results, the optimization of the maximum removal of MG by foxtail fruit activated carbon was determined. The optimal adsorption at highest percentage removal, 97.83%, is obtained when using 1g of activated carbon, 60 minutes of contact time and 10 mg/L of dye concentration of malachite green.

KECEKAPAN KARBON TERAKTIF BUAH FOXTAIL DALAM PENYINGKIRAN PEWARNA MALAKIT HIJAU

ABSTRAK

Pelepasan pewarna kepada alam sekitar mempunyai kesan yang buruk terhadap kehidupan manusia, tumbuh-tumbuhan dan haiwan. Terdapat banyak teknologi yang digunakan untuk menyingkirkan pewarna daripada air secara berkesan untuk mengurangkan pencemaran sebagai contoh, penjerapan. Penggunaan biojisim pertanian seperti buah foxtail telah dijumpai sebagai alternatif yang menarik berdasarkan potensinya dalam penjerapan karbon teraktif. Dalam kajian ini, karbon teraktif telah disediakan dari karbonisasi (300ºC, 2 jam) buah foxtail (*wodyetia bifurkata*) yang dilembabkan dengan HNO_3. Eksperimen penjerapan berkumpulan telah dijalankan dengan menggunakan 'shaker' inkubator untuk mengkaji kesan masa, dos penjerap dan kepekatan pewarna untuk penjerapan malakit hijau daripada larutan akueus. Penyerapan pewarna daripada malakit hijau telah dianalisa dengan menggunakan Spektrofotometer UV-Vis untuk mencari keadaan optimum bagi kecekapan karbon teraktif daripada buah foxtail untuk merawat pewarna malakit hijau. Hasil keadaan dengan peratusan penyingkiran yang tertinggi dipilih untuk kajian seterusnya. Kaedah ini boleh dianggap menjimatkan masa dan kos efektif kerana buah foxtail mudah didapati. Secara tidak langsung, pengoptimuman penyingkiran maksimum malakit hijau telah ditentukan. Penjerapan optimum pada peratusan tertinggi, 97.83%, diperoleh apabila menggunakan 1 g karbon teraktif, 60 minit masa dan 10 mg/L kepekatan malakit hijau.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The increasing population in Malaysia which was reached 31,923,623 in March 2018 (Worldometers, 2018), caused many pollution including to the water system. Water pollution is becoming a serious problem in Malaysia and has negative impact on the water resources and it also affects living plants and organisms, the economy and population health (Rafia & Ataur, 2017).

Since the dyeing technique was discovered, the color effluent have been widely generated. Dye manufacturing, textile and other fabric finishing releases massive amounts of dye into the wastewater (Ratna & Padhi, 2012). The dyes from textile wastewater are highly resistant to light, pH and microbial attack that makes them to stay in the environment for a longer time (Wong, Senan & Atiqah, 2013). The wastewater will be harmful to the environment if it has not been treated before release to the water bodies. Therefore, several methods such as adsorption by activated carbon, chemical coagulation, ion exchange, electrolysis and chemical treatment have been established for removal of dye from effluent prior to discharge into the environment as stated by Geçgel, Özcan & Gürpınar (2013).

Textile industry is the greatest sources that contribute to water pollution after the agriculture (Fabon, Legaspi, Leyesa & Macawile, 2013). One of the chemical industries that involved in water pollution where the degree of pollution which characterized by its high water consumption and chemical usage is textile industry (Fabon et al., 2013). Dyeing process requires some amount of water. Wastewater that containing residues of reactive dyes and chemicals is often rich in colors which come from printing and dyeing units (Adinew, 2012).

Industrial chemicals with the possibility of solvent, dyes, cleaning materials and fuels, which are entering waterways through urban storm water runoff. The consequence is the drop in the amount of Biochemical Oxygen Demand (BOD) and dissolved oxygen. Consumer must prevent the water pollution by using environmentally household products such as cleaning agent and not overused the pesticides and fertilizers. More than 10,000 dyes generated a large volume of effluents anually that may caused from a usage in textile, paper, farming, rubber, plastics, leather, cosmetic, pharmaceutical, and food industries (Mondal, 2008).

There are many processes for water treatment such as water purification, electro-dialysis, distillation, ion exchange and reverse osmosis. There are also physical processes that included flocculation, sedimentation, adsorption, filtration and disinfection. The main reasons of treating the water are to get rid of contaminants that make the water look, taste and smell bad which may threaten health. Nowadays, there were many industries used the activated carbon as the adsorbent agent to treat dye from wastewater.

Activated carbon (AC) is a porous adsorbent material widely used for pollution removal in applications such as mercury removal in flue gas and water purification (Spahis, Addoun, Mahmoudi & Ghaffour, 2008; De M, Azargohar, Dalai & Shewchuk, 2013; Sumathi, Bhatia, Lee & Mohamed, 2010). The demand for AC increases as the concern over pollution increases. In addition, AC can be physically and chemically prepared from different raw materials like coal, biomass and nutshell (Zhou, Hao, Gao & Zhang, 2014; Horikawa, Takeda, Muroyama & Ani, 2002).

This study is conducted to prepare activated carbon from foxtail fruit (*wodyetia bifurcate*), to find out the efficiency of the prepared foxtail activated carbon to treat malachite green dyes in aqueous solution and to optimize the removal of malachite green by foxtail fruit activated carbon.

1.2 Problem Statement

Nowadays, water pollution is being the major concern in this demanding world. Sources of water pollution generally come from the livestock industry, manufacturing industry, agro-based industry and sewage treatment plants. This water pollution that hugely concern usually created from the abundant amount of chemical that mainly dyes which create visible contaminant to the water.

Dyes are extensively used in industries in their product development such as foods, clothes, plastics, printing, leather and cosmetics (Bharathi & Ramesh, 2013). As consequence, a significant amount of colored wastewater had been generated (Bharathi

& Ramesh, 2013). There are 10,000 commercially dyes produced annually with over 7×10^5 tonnes of dye stuff as stated by Bharathi and Ramesh (2013).

The growth of bacteria can be distrupt by dyes particle and it inhibit photosynthesis in aquatic plants because it absorb and reflect sunlight that penetrate into the water (Bharathi & Ramesh, 2013). Due to the fact that the presence of aromatic complex structure of dye they will refrain with the existence of source of light, microbacteria, and even oxidizing agent and the degradation of the dye color will be difficult as stated by Pearce, Lloyd and Guthrie (2003).

Synthetic dyes generally contain in wastewater and may cause a hazard to the environment. Different techniques have been implemented in order to remove dyes from aqueous solution due to the environmental and health concerns related with the wastewater effluents. The dye removal techniques can be categorized as physical, biological and chemical methods. Hence, adsorption by the activated carbon had been discovered as the efficient ways to remove dyes from aqueous solution. In this study, the activated carbon from foxtail palm fruit had been discovered as the alternative of the potential adsorbent in the removal of dyes.

1.3 Objectives

i. To prepare activated carbon from foxtail fruit (*wodyetia bifurcate*).

ii. To determine the efficiency of the prepared foxtail fruit activated carbon to treat malachite green dyes in aqueous solution.

iii. To optimize the removal of malachite green by foxtail fruit activated carbon by using three variables (dye concentration, contact time and adsorbent dosage).

1.4 Significance of Study

Nowadays, agriculture and industries are growing rapidly as well as the economic growth. But, as the development increase, the pollution also increases. Water pollution could lead to a serious health and environmental problem. The significance of this research is the exploration of physical process of water treatment that is convenience around certain area. This study also exposes about the importance of water purification for long living and shows how the water undergoes purification to serve safe drinking water.

The optimum condition of combination of the three conditions which are initial dye concentration, contact time and adsorbent dosage also will be discovered. Activated carbon from foxtail palm fruit can be used in water filter systems, as a complementary or a standalone filter. This research helps the industrial agencies to find alternative way which may be cheaper and effective to mitigate or reduce the water pollution associated with the emission of heavy metals to the water stream.

CHAPTER 2

LITERATURE REVIEW

2.1 Malachite Green Dye

Commercially, there are more than 100 000 types of dyes including acid, reactive, disperse, and sulphur dyes in which their production exceeds 150 metric tons annually (Wong, Senan, & Atiqah, 2013). The major group of synthetic dyes among them are azo dyes which makes up 70% of all commercial dyes (Hadi, Samarghandi & McKay, 2010).

Raval, Prapti and Nisha (2016) stated malachite green (MG) is belongs to triphenylmethane group and a water soluble cationic dye that available in green crystalline powder. The basic MG has been extensively used as a antifungal and antiseptic to control fish parasites and disease in the aquaculture industry (Zhang, Li, Zhang & Jing, 2008). However, used of malachite green in high concentration may kill the living organism such as fish due to the light resistance, inhibit photosynthesis and hence dissolved oxygen is low. Malachite green is hard to adsorb from aqueous solutions because it has complex structures and properties that make it inconvenient and toxic to major microorganisms (Sartape, Mandhare, Jadhav, Raut, Anuse & Kolekar, 2013). The chemical structure of malachite green shown in Figure 2.1.

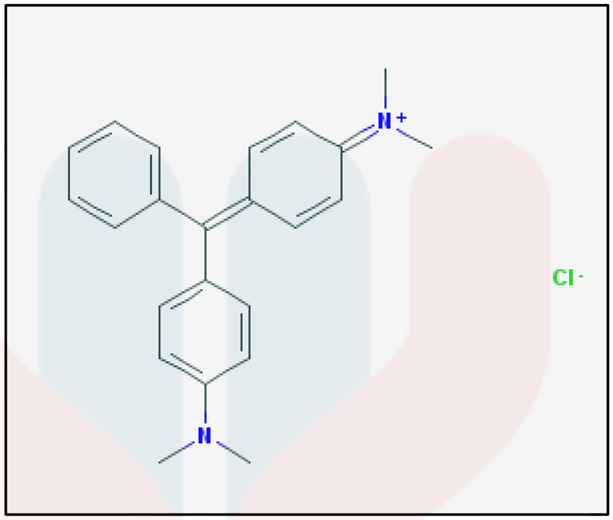

Figure 2.1: Chemical structure of malachite green (Source: https://pubchem.ncbi.nlm.nih.gov/image/imagefly.cgi?cid=11294&width=300&height=300)

MG is highly cytotoxic to mammalian cells and acutely toxic to a wide range of aquatic and terrestrial animals (Sartape et al., 2013). It is relatively fatal in both acute and chronic exposures to freshwater fish because it is multi-organ toxin that been revealed by both clinical and experimental observations (Sartape et al., 2013). It poses a potential environmental problem and can causes serious public health hazards (Sartape et al., 2013). Sartape et al. (2013) stated that it also reduces food uptake, growth and fertility rates of microorganisms and causes failure to the liver, spleen, kidney and heart, inflicts lesions on the skin, eyes, lungs and bones and produces significant teratogenic effects. Hence, a proper efficient treatment of wastewater that containing this toxic dye is necessary and vital.

2.2 Dye Removal

Dyes are non biodegradable (Sartape et al., 2013). Chemical oxidation and coagulation, froth flotation, adsorbate adsorption, electro-dialysis and cloud point extraction considered as the alternative methods for dye removal from textile wastewater (Elhami, 2010). There were many treatment technology that have been implemented for the adsorption of dye from the effluent such as photocatalytic (Neelavannan, Revathi & Ahmed Basha, 2007), biodegradation (Daneshvar, Khatae, Rasoulifard & P.M., 2007), and adsorption process (Hameed, Din & Ahmad, 2007b; Fan, Zhou , Yang, Chen & Yang, 2008; Hameed & El-Khaiary, 2008b), chemical coagulation and flocculation, ozonation, cloud point extraction, oxidation, nano-filtration, chemical precipitation, ion-exchange, reverse osmosis and ultra-filtration (Malik & Sanyal, 2003; Malik & Sanyal, 2004; Lorenc-Grawbowsk & Gryglewic, 2007).

According to Gecgel, Ozcan and Gurpmar (2013), activated carbon sorption is the effective method to remove dyes and pigments. Activated carbon sorption is considered as a better option for adsorption due to its large surface area and high pore volume. Coal based activated carbon has been widely used but the cost and generation acts as a limitation. Conventional biological treatment processes revealed as low efficiency in dye removal (El Ashtoukhy, 2009). Therefore, non-conventional and inexpensive adsorbents which is from bottom ash and fly ash, coir pith, cassava peel, cotton, orange peel, bagasse fly ash, cellulose-based wastes, kaolinite, zeolite, wheat straw, rice husk, sawdust, char fines and oil mill waste have been used (Reddy & Kotaiah, 2008).

Adsorption defined as the accumulation process of substances on a suitable interface in a solution. Adsorbate defined as the substance that being removed from the liquid phase at the interface. While adsorbent is the solid, liquid or gas phase where the adsorbate accumulates. Ponkarthikeyan and Sutha Sree (2017) stated that generally the adsorption process is classified as either *physisorption* (Physical Adsorption) or *chemisorption* (Chemical Adsorption). Adsorption that involved intermolecular forces (Van der waals force), hydrogen bonding and ion exchange process named as physisorption while adsorption that involved valence forces / chemical bonds called as chemisorptions (Ponkarthikeyan & Sutha Sree, 2017).

In the past study, wood apple shell (WAS) considered as having a good adsorption capacity of MG as an adsorbent in a very short period of agitation (Sartape et al., 2013). In India, they used Limonia acidissima (wood apple) medicinally in sweet making (Sartape et al., 2013). Increase in the pH values consequently increase the adsorption of MG to adsorbent (Pan & Zhang, 2009; Baek, Ijagbemi, Jin & Kim, 2010).

From the previous study, the feasibility of using agro-waste Areca Husk as activated carbon for the adsorption of MG from aqueous solution had been explored (Basker, Syed Shabudeen, Daniel & Kumar, 2014). Basker et al. (2014) stated that good potentiality for the carbons particles to be used as a sorbent for the removal of MG from wastewater had been established from the research.

2.3 Activated Carbon

Activated carbons are disordered, microporous forms of carbon, with a very high porosity and surface area (Abdul Rahim, Zaiton, R Dewi & Inderan, 2008). They can be prepared from a large number of raw materials, especially agro-industrial by-products such as walnut shells and coconut shells. The useful properties of activated carbon is well known since ancient times (Leimkuehler, 2010). Egyptians used charcoal as an adsorbent for medicinal purposes and a purifying agent when traces back to 1500 BC (Leimkuehler, 2010). Ancient Hindu societies once used charcoal to purified their water by filtration (Leimkuehler, 2010). Nowadays, activated carbons are used in pharmaceutical and food industry to get rid of color, for chemical purification, and act as electrodes in the batteries (Leimkuehler, 2010).

Activated carbon is available in different forms depends on its usage or application. Commonly, activated carbon consists of three types which are extruded carbon, granular activated carbon (GAC) and powdered activated carbon (PAC). Carbonization is one of the processes in making activated carbon continued by an activation of carbonaceous material from vegetable origin (Leimkuehler, 2010). The importance of carbonization is boost the enrichment of the carbon content and creation of an initial porosity while activation helps in pore enlargement (Jena, 2012).

The high surface area of activated carbon makes it appropriate for adsorbing chemical substances form wasted water or air, depending on its structure (Silgado, Marrugo & Puello, 2014). Activated carbon is a material with high porosity that consist of hydrophobic graphene layer as well as hydrophilic surface functional groups that make them beneficial for sorption and catalytic applications (Viswanathan, Neel & Varadarajan, 2009).

The adsorbent that most utilized for dye removal from aqueous solution is activated carbon (Tan, Ahmad & Hameed, 2008). However, the expansive use of activated carbon to treat dye from industrial wastewater is costly (Pavan, Lima, Dias & Mazzocato, 2008b) and consequently limit its large application for wastewater treatment. Therefore, there is increasing interest in obtaining low-cost adsorbents that are able to remove dyes from liquid effluents (Wang, Boyjoo, Choueib & Zhu, 2005; Wang & Zhu, 2006; Wang & Li, 2007; Wang, Ang. & Tade, 2008).

Taking into account to deal with the increasing world demand, the huge amount of activated carbon was required and biomass derivatives catch the attention because they are abundant and low-cost material (generally agricultural residues) and accessed from the renewable sources (Prauchner & Rodriquez-Reinoso, 2012).

Activated carbons that produce from coconut shells is commonly used for treatments where high rate of adsorption is needed because of the characteristic of high volumes of micropores (Leimkuehler, 2010). Sawdust and other woody scrap materials also effective for adsorption from the gas phase because they contain strongly developed microporous structures (Leimkuehler, 2010).

2.4 Activation Process

An oxidation, referred to as activation, is carried out in order to create micropores after the initial porous structure that has been generated by carbonization (Beguin & Frackowiak, 2010). Activation can be carried out either by chemical or physical methods (Jena, 2012). In physical activation, the precursor is first carbonized in an inert atmosphere before activated by using oxidizing agents such as steam or carbon dioxide (Sharifirad, Koohyar, Rahmanpour & Vahidifar, 2012). Physical activation consist of two steps, which are carbonization followed by activation process. The carbonaceous precursor will be carbonized in an inert atmosphere and subsequent activation of the resulting char happened in the presence of carbon gasification reactants (gaseous) such as carbon dioxide, steam or air or a suitable combination of the above mentioned gaseous activating agents (Viswanathan, Neel & Varadarajan, 2009). Physical activation is considered to be environmental-friendly technology as gaseous activation agents is being used as well as it does not produce wastewater (Viswanathan, Indra Neel & Varadarajan, 2009). Viswanathan, Neel and Varadarajan (2009) also stated that the inherent drawback of this method is to obtain well developed pore structure, its require large amount of internal carbon mass.

In chemical activation, to extinguish the majority of hydrogen and oxygen content from the carbon structure, the carbon is reacted at high temperatures with a dehydrating agent (Beguin & Frackowiak, 2010). Chemical activation consist of single step process which is the carbonization of precursor with chemical agents (Viswanathan, Neel & Varadarajan, 2009). Viswanathan, Neel and Varadarajan (2009) also stated chemical activation involved the used of some acids and solid activating agent such as alkali and substance that contained alkaline earth metal like H_3PO_4. The activating agents influence the decomposition of pyrolytic that inhibit the development of tar and hence elevate carbon production because it act as dehydrating agents as stated by Viswanathan, Neel and Varadarajan (2009). As a result, the chemical activation method generate a better porous structure comparatively (Viswanathan, Neel & Varadarajan, 2009). However, in spite of the good aspect, the chemical method has its own deficiency which is a proper washing of the activated char is needed to remove the inorganic residue material that may lead to serious pollution problem (Viswanathan, Neel & Varadarajan, 2009).

The production of AC by chemical activation, the most important variables in the process are: ratio of mixture, carbonization temperature and time (Gratuito, Panyathanmaporn, Chumnanklang, Sirinuntawittaya & Dutta, 2008). A loss of substantial amount of carbon mass during the activation process correlates to an increase in porosity (Beguin & Frackowiak, 2010). Activating agent reacted with the carbon and hence developed the porous structure during the activation. Those activating agents may include bases, synthetic acids, and other substances that are in a stream of activating gases such as steam (H_2O), nitrogen (N_2) or carbon dioxide (CO_2).

Activating agents that belong to the class of alkaline earth metal salts, and mineral acids, such as, H_3PO_4, H_2SO_4, and HNO_3, have been widely utilized in the process of chemical activation of the carbon materials (Viswanathan, Neel & Varadarajan, 2009). Viswanathan, Neel and Varadarajan (2009) also stated that there are two benefits when activate the char with HNO_3. First, easily remove of traces of activating agent and its degraded the char and other is the production of oxygen rich surface functional groups (Viswanathan, Indra Neel & Varadarajan, 2009). Chemical activation using H_2SO_4 at moderate temperatures produces a high surface area and high degree of micro-porosity (Santhi, Manonmani, Vasantha & Chang, 2016).

The benefits of the chemical activation over physical activation are lower carbonization temperature and its require shorter time of activation compare to physical activation (Sahira, Mandira, Prasad & Ram, 2013). Moreover, the activated carbon that obtained by chemical activation is mesoporous with a larger surface area (Viboon, Chiravoot, Duangdao & Duangduen, 2008).

2.5 Foxtail Palm Fruit

According to Perez, Kobayashi & Sako (2009), foxtail palm, *wodyetia bifurcata* is a member of the Arecaceae, or known as palm family. The genus is named in conjunction with "Wodyeti," an Australian aborigine who was the last man of his tribe to have knowledge of the flora and fauna of its region (Perez, Kobayashi & Sako, 2009). When they reach around 12 years of age, foxtail reach maturity and able to bloom (Perez, Kobayashi & Sako 2009). Perez, Kobayashi and Sako (2009) also stated that this plant classified as monoecious because both male and female flowers are borne the capable of self-fertilization.

Fertilized female flowers produce large, oval-shaped, green fruits that turn orange-red and approximately $1\frac{1}{4}$ inches wide and $2\frac{1}{4}$ inches long with a single seed within each fruit when it reached maturity (Perez, Kobayashi & Sako 2009). According to Mary, Michael , Melissa, and Heather (2010), the relatively fast growth of foxtail fruit and its bushy fronds make it look quite different from many other palms on the market hence people like it. Mary et al. (2010) stated that it considered as a desirable landscape specimen because it resemble to royal palm and other similar aesthetic value.

Moreover, if it was given a proper and well-drained crop soil with a slightly lower pH, good source of light, and space, this palm can significantly grow well indoors as a potted plant (Mary et al., 2010). This palm is drought-resistant, but it exhibits the best growth when enough water is applied at its base (Mary et al., 2010).

2.6 Activated Carbon from Different Raw Materials

Activated carbon can be an incredibly versatile product as it can be produced from an abundance of different raw materials in many different locations depending on what raw material is available (Leimkuehler, 2010). Generally, some of the raw materials include plants shells, the stones of fruits, metal carbides, carbon blacks, woody materials, asphalt, polymer scraps and scrap waste deposits from the sewage (Leimkuehler, 2010).

Raw material that contain highly developed microporous structure such as sawdust and other woody scrap materials make them good for adsorption from the gas phase (Leimkuehler, 2010). Highly homogenous adsorbents with significant hardness, resistance to abrasion and high micropore volume of activated carbon can be produced from olive, plum, apricot and peach stones (Leimkuehler, 2010). An agricultural solid waste, groundnut shell, has been used as an activated carbon for the removal of MG from aqueous solution by Malik, Ramteke and Wate (2007).

Agriculture waste are attractive because they are abundant and their great implementation in removing dyes from aqueous solutions as well as they are having low amount of sediment to be disposed to the environment (Hameed & El-Khaiary, 2008b). An agriculture waste that are widely accessible which is leaf biomass was discovered as an adsorbent for different pollutants such as dyes by various researchers (Han, Zou, Yu, Cheng, Wang & Shi, 2007; Immich & de Souza, 2009; Ponnusami, Vikiram & Srivastava, 2008; Weng, Lin & Tzeng, 2009).

It is vital to choose the correct precursor for the right application because variation of precursor materials contain varied carbons pore structure (Leimkuehler, 2010). The amount of macropores that contained in the precursor can determine their reactivity (Leimkuehler, 2010). The importance of macropores is to give more routes for adsorbate molecules to get through to the micropores during adsorption of adsorbate (Beguin & Frackowiak, 2010). Precursors that contain a greater amount of volatile substances correlates to high reactivity of the activated substance (Leimkuehler, 2010). The degree of activation can be lowered if the reactivity is too high (Leimkuehler, 2010).

CHAPTER 3

MATERIALS AND METHODS

3.1 Chemicals and Reagents

Table 3.1 below showed the list of chemicals that had been used in the making of the activated carbon and dye solution. Other than that, distilled water also had been used in all sample preparations and experiments.

Table 3.1: List of chemicals

Chemicals	Brand	Concentration/Purity
Malachite Green	Bendosen	100 ppm
Nitric Acid (HNO_3)	R & M	65%

3.2 Instruments

Table 3.2 below showed the instrument that had been used in this study.

Table 3.2: List of instruments used

Instrument	Brand	Model
UV-Visible Spectrophotometer	HACH	DR5000
Incubator Shaker	IKA	
Furnace	Wise Therm	

3.3 Methodology

3.3.1 Sampling of Raw Material

Raw material that had been used in this research to produce activated carbon was from foxtail palm fruits (*wodyetia bifurcate*). They were collected around Jeli, Kelantan, Malaysia. Figure 3.1 shows the foxtail palm fruit and its tree. Figure B1 in Appendix B showed the raw foxtail fruit.

Figure 3.1: Foxtail palm tree

3.3.2 Preparation of Activated Carbon

The fruits were rinsed with distilled water to remove dust or any impurities in order to prepare char from foxtail fruit (*wodyetia bifurcate*) before drying process in oven for 100ºC overnight. Appendix B (Figure B2 and B3) showed the clean foxtail fruit and dry foxtail fruit respectively. The dry foxtail left cool at room temperature.

Next, the dried raw material was carbonized in the furnace at 300ºC for 2 hours to eliminate the moisture and any volatile impurities from the fruit as can seen in Appendix B (Figure B4). The purpose of carbonization process is to enrich the carbon content and to create an initial porosity in the char (Abdul Rahim et al., 2008). After carbonization process, the char left cool before taken out from the furnace. Then it had been let cool in the dessicator for about 24 hours. Next, the char was crushed into small pieces using mortar and pestle and sieved through 250 µm mesh-size. The sieved sample was then weighed and the actual weight was recorded. Then it was kept in the polyethylene bag and kept dry in the desiccator for further use.

Next stage was the chemical activation. Firstly, 40 g of oven dried foxtail fruit was soaked and impregnated in the 250 mL beaker with 80 mL of concentrated HNO_3. The solution then mixed vigorously for 30 minutes until it became paste. Next, paste were left impregnated overnight in the fume hood. Fume hood can decrease or eliminate the exposure of the char to volatile liquids, dusts and mists (Environmental Health & Safety, 2018). Then the slurry was weighed and placed in the crucibles. Next, the weighed slurry was carbonized in the furnace at 500ºC for two hours and 30 minutes. The distilled water and Buchner funnel is used to wash the activated carbon after the chemical activation until it reached pH 7. After that, the drying of activated carbon run in the oven at 150ºC for 3 hours and kept in tight polyethylene bag and stored in dessicator.

3.3.3 Preparation of Dye Solutions

The MG dye that was supplied by Bendosen (Malaysia) has a molecular formula $C_{23}H_{25}N_2Cl$ with molecular weight of 329.50 g/mol. The preparation of 100 mg/L of MG stock solution is carried out with distilled water. The solutions for batch adsorption obtained by diluting the stock solutions in accurate proportions regarding to the required initial dye concentrations.

In order to get specific volumes of MG dye solution according to the concentration, $M_1V_1 = M_2V_2$ equation will be calculated to get the volume before dilution (V_1). After getting specific volumes of MG by using the equation, the dilution process will be carried out where diluted MG stock solution (100 mg/L) has been transferred into five different conical flask of 25 mL (V_1) according to the parameters respectively.

$$M_1V_1 = M_2V_2 \tag{3.1}$$

where:

M_1 = Molarity before dilution

M_2 = Molarity after dilution

V_1 = Volume before dilution

V_2 = Volume after dilution

3.3.4 Optimization of Activated Carbon Preparation from Foxtail Palm Fruit

Effect of Contact Time

Dilution of 2 mg/L of MG solution (25 mL) treated with 1g of activated carbon. The mixture placed in shaker and stirred for 30 minutes at 150 rpm. Then, the supernatant liquid (treated dye) was filtered using 0.45µm filter paper (Chin. & S., 2013). Then the residual dye concentrations from the treated solution were analyzed by UV-Vis spectrophotometer at maximum wavelength 617 nm (Mohammad, Amir Hossein, Bayram, Abolfazl, Ghasem & Mehdi Vosoughi, 2013). The steps repeated for 60, 90, 120 and 150 minutes time respectively to find the optimum time for the adsorption. The time required to attain this state of equilibrium is termed as 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 (Bello, Adelaide, Hammed & Popoola, 2010).

Effect of Adsorbent Dosage

Dilution of 2 mg/L from MG stock solution (25 mL) treated with 1 g of activated carbon. The mixture placed in shaker and stirred for optimum time that was found in the contact time adsorption, at 150 rpm. Then, the supernatant liquid (treated dye) was filtered using 0.45 µm filter paper (Chin. & S., 2013). Then the residual dye concentrations from the treated solution were analyzed by UV-visible spectrophotometer at maximum adsorption wavelength 617 nm (Mohammad et al., 2013). The steps repeated for 2, 3, 4, and 5 g of adsorbent dosage respectively to find the optimum adsorbent dosage for the adsorption.

Effect of Dye Concentration

Dilution of 2 mg/L of MG solution (25 mL) treated with optimum dosage of activated carbon that found on the above adsorption experiment. The mixture placed in shaker and stirred for optimum time that had been found for the adsorption, at 150 rpm. Then, the supernatant liquid (treated dye) was filtered using 0.45 µm filter paper (Chin. & S., 2013). Then the residual dye concentrations from the treated solution were analyzed by UV-visible spectrophotometer at maximum adsorption wavelength 617 nm (Mohammad et al., 2013). The steps repeated for 4, 6, 8 and 10 mg/L of MG concentration.

3.3.5 Percentage Removal

The efficiency of adsorption by foxtail fruit activated carbon in adsorption of MG dye was calculated by using the formula:

$$\% \text{ Removal} = (C_o - C_e) \times 100 / C_o \quad (3.2)$$

where C_o and C_e are the initial and the equilibrium concentrations of the dye respectively.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter discussed the interpretation of graphs that represent the percentage removal of MG. The purposed of this study were achieved by recognizing the removal percentage of MG dye by activated carbon from optimum condition in three different parameters. The results is shown in Appendix A (Table A1, A2 and A3). To analyze those results, different contact time, different dosage of adsorbent and different initial concentration of MG dye was given to treat the aqueous solution. The solution that has been treated shown in Appendix C (Table C1). Figure 4.1 show the stock solution of MG. The final absorbance of MG dye solution was analyzed by using UV-Vis Spectrophotometer at 617nm and the removal percentage was calculated and the optimum condition for the removal was determined.

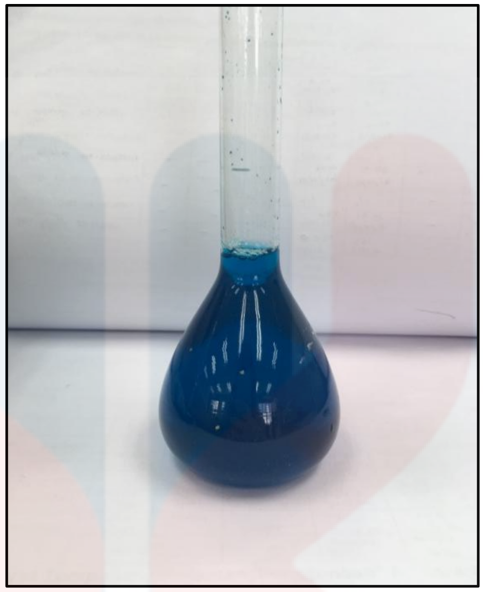

Figure 4.1: 100 mg/L of stock solution of malachite green dye

4.2 Optimization of Parameters Using Batch Adsorption

4.2.1 Effect of Contact Time

The contact time of the adsorption to occur is one of the most vital parameters that significantly affect the performance of removal of dye. This parameter was carried out by five different contact time, 30, 60, 90, 120 and 150 minutes, respectively. The effect of contact time on the percentage removal of MG dye was carried out at fixed initial dye concentration (2 mg/L), 25 mL of dye solution and adsorbent dosage (1 g) with pH 7 at room temperature 27ºC. The absorbance also had been test with UV-Vis spectrophotometer at wavelength of 617 nm.

The graph of percentage removal against contact time is plotted with the data collected from the experiment. The graph represents the relationship between Contact Time (min) (x) and percentage removal (%) (y) for the treated solution. From Figure 4.2, it is found that the uptake of the MG dye by activated carbon was increase and slightly decreased after it reached 60 minutes of contact time or till saturation is allowed. The adsorption percentage is slightly decreased after the optimum time which may be due to the weak physical adsorption of adsorbent (Ngadi, Chiek & Aida, 2013).

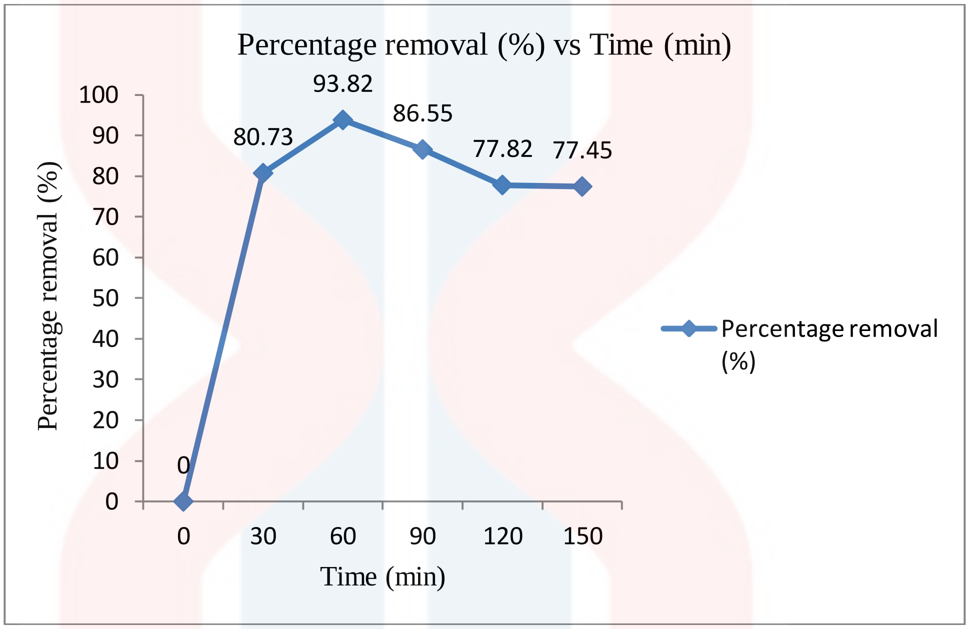

Figure 4.2: Percentage removal of malachite green by contact time

This shows that the equilibrium can be assumed to be achieved after 60 minutes of contact time. Within 60 minutes, the maximum amount of MG was sequestered from the aqueous solution. Contact time of 150 minutes recorded the lowest percentage removal with 77.45% whereas at 60 minutes the removal was as high as 93.82%. There was a rapid increase of adsorption rate at 60 minutes of contact time, then decreased and slowly to be constant after that till 150 minutes which it may be due to the availability of complete active bare surface as stated by Sartape et al. (2017).

Generally, the increase in contact time in certain extent caused a rise in the rate of removal of dye (Mahanti & Laxmi, 2014). This is due to the availability of time for the dye and adsorbent to collide and efficiently bind to each other. However, in this case, further increase of contact time between adsorbate and adsorbent, does not relatively step-up the rate of adsorption because of the accumulation of dyes on the active site of the adsorbent (Ansari & Mosayebzadeh, 2010). At this point, the desorption of dye from the adsorbent is in a state of dynamic equilibrium with the adsorption of dye onto the adsorbent (Mahanti & Laxmi, 2014).

The rate of removal was constant during the adsorption when equilibrium is achieved is because due to the saturation of the active sites do not allow further adsorption to occur (Leechart, Nakbanpote & Thiravetyan, 2009). Saturation means the particles of MG dye are fully bind to all the active sites of the adsorbent. A similar trend is observed in a previous study conducted by Sharma in 2013. Hence, the contact time of 60 minutes was chosen for subsequent experiment for next parameter.

4.2.2 Effect of Adsorbent Dosage

The effect of dose of adsorbent was observed based on varying the dosage of adsorbent of pH 7 from 1, 2, 3, 4 and 5 g, respectively. The effect of adsorbent dosage on the MG dye uptake by activated carbon was investigated at fixed initial dye concentration (2 mg/L), 25 mL of dye solution and contact time (60 minutes) at room temperature 27ºC . The absorbance also had been test with UV-Vis spectrophotometer at wavelength of 617 nm. The graph of percentage removal against adsorbent dosage is plotted with the data collected from the experiment.

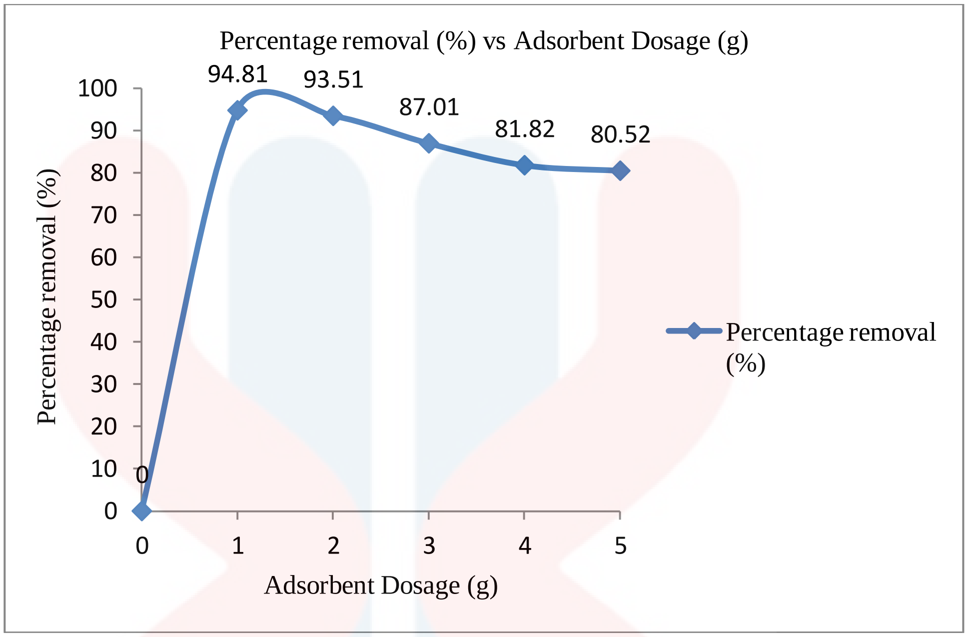

Figure 4.3: Percentage removal of malachite green by adsorbent dosage

The graph represents the relationship between Adsorbent Dosage (g) (x) and percentage removal (%) (y) for the treated solution. From the Figure 4.3, the adsorption of MG dye decreased approximately with the increased in adsorbent dosage. The figure shows that the optimum amount of dose of adsorbent is 1 g at which maximum amount of dyes were removed. There were no significant increase after that.

Generally, increasing adsorbent dosage may leads to increase in surface area of adsorbent and hence more adsorption sites are available to adsorb MG dye from aqueous solution (Low et al., 2012). However, the aggregation of adsorbent particles at higher dosage will lead to the decrease in the surface area and an increase in the diffusion path length (Belay & Hayelom, 2014).

From the previous study, it was found that the rate of adsorption decreased after the configuration of equilibrium (Sartape et al., 2017). This may be attributed to overlapping or aggregation of adsorption sites resulting in a decrease in total adsorbent surface area available to MG and as an increase in diffusion path length (Garg, Kumar & Gupta, 2004). This is because the adsorption capacity of adsorbent available was not fully utilized at a higher adsorbent dosage compare to lower adsorbent dosage. Thus, it might be possible that the increases of adsorbent dosage may decreases adsorption capacity. The solution may contain excessive adsorption site. The adsorption rate decrease with increase in adsorbent dosage.

From previous study, the increasing rate of the percentage removal of dye has been found to be rapid and then declined as the dose increased (Mahanti & Laxmi, 2014). Bharati and Ramesh (2013) report that the phenomenon is based on the fact that the adsorbate (dye) is more easily access with the decrease in adsorbent dose, hence the removal per unit weight of the activated carbon is higher.

There is less commensurate increase in adsorption with rise in adsorbent dosage, resulting from many sites remaining unsaturated during the adsorption (Jain, Gupta, Bhatnagar, Jain & Suhas, 2003). After a certain dosage the increase in removal efficiency is insignificant with respect to increase in dose (Bharati & Ramesh, 2013). This is due to the fact that, at higher adsorbent concentration there is a very fast superficial adsorption onto the adsorbent surface that produces a lower solute concentration in the solution than when adsorbent dose is lower (Bharati & Ramesh, 2013). Thus, the amount of absorbed dye per unit mass of absorbent is reduced with increasing adsorbent dose.

As consequence, while dose of absorbent increases from 1, 2, 3, 4 to 5 g, the dye removal percent decreases from 94.81%, 93.51%, 87.01%, 81.82% and 80.52% at constant time respectively. 1 g of adsorbent dosage seems to be sufficient enough to treat 25 mL of dye solution with 2 mg/L concentration. Thus, the optimum percentage removal can be seen achieved with 1 g of adsorbent dosage and almost less vary, hence the adsorbent dosage of 1 g was chosen for the subsequent experiment for different initial dye concentration.

4.2.3 Dye Concentration

The effect of initial dye concentration on the rate of adsorption of MG dye by foxtail palm fruit AC was investigated at fixed absorbent dosage (1 g), 25 mL of MG dye solution with different initial concentration and 60 minutes of contact time with pH 7 at stabily maintained temperature at 27ºC.

By increasing MG concentration from 2, 4, 6, 8 and 10 mg/L, respectively, the removal percentage of dye increased from 88.20% to 97.83%. Refer Appendix C (Table C2) for before and after treatment solution. From Figure 4.4, it is evident that with the increase in the initial dye concentration the amount of MG adsorbed by the activated carbon also increasing. The graph represents the relationship between Dye Concentration (mg/L) (x) and percentage removal (%) (y) for the treated solution.

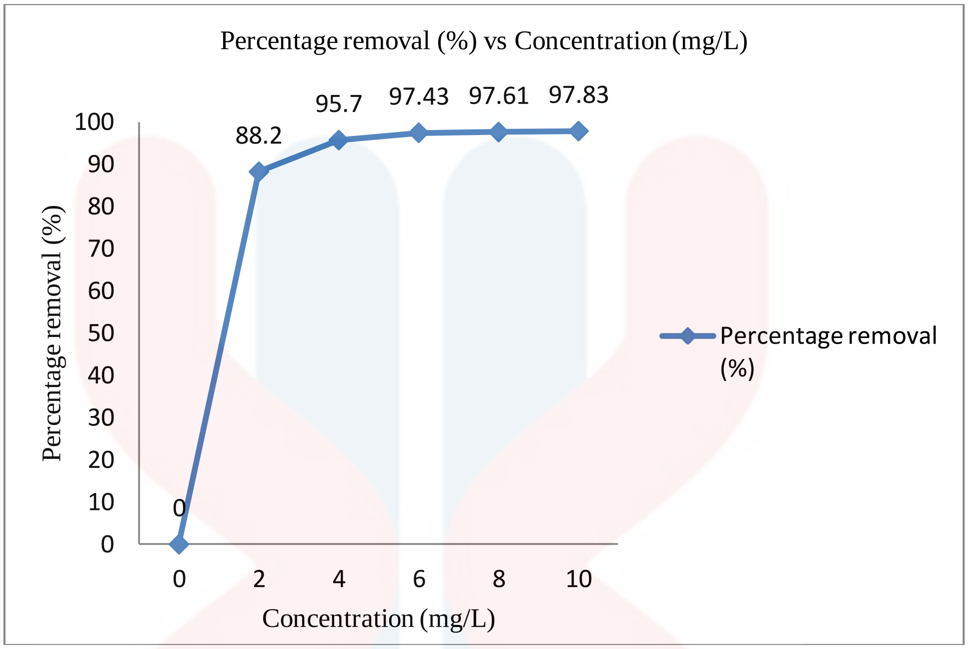

Figure 4.4: Percentage removal of malachite green by dye concentration

The figure shows that the removal is slightly increase in the increase of dye concentration. The percentage removal was found to be the lowest at the concentration of 2 mg/L with 88.20%, whereas at 10 mg/L the removal was as high as 97.83%. It show that the highest percentage removal can be achieve with higher concentration. Sartape et al. (2017) stated that increase in dye concentration will improve the fundamental interaction between the activated carbon and dye and overcome the resistances to mass transfer of adsorbate by providing necessary driving force. Therefore, rate of dye removal increased with an increase in dye concentration.

Normally the dye removal will decrease along with the increase in initial dye concentration (Mahanti & Laxmi, 2014). This is because, Bharati and Ramesh (2013) stated that for a given mass of absorbent, the amount of dye it can absorbed is fixed. But in this case, the actual amount of dye adsorbed increased with increase in dye concentration. This is happening because of the high driving force for mass transfer at a high initial dye concentration (Bulut & Aydin, 2006). The initial dye concentration provides the essential driving force to get over resistances to the mass transfer of MB between the aqueous and the solid phases (Low, Teng, Morad & Azahari, 2012).

The adsorption percentage of biochar at equilibrium increases with the increase in initial dye concentration (Mohamad, Wei, Mohammad & Wei, 2017). Bazrafshan, Zarei, Nadi & Zazouli (2014) also stated that this trend could be attributed to the fact that for a high concentration of dye, there is a high driving force for mass transfer between aqueous and solid phases. A similar trend of study was explained by Rajeshkannan, Rajasimman and Rajamohan (2011).

Besides, increasing the initial dye concentration indeed increases the number of dye particle, and this would increase the number of collisions between dye ions and the surface area of the adsorbents which enhances the adsorption process (Krika & Benlahbib, 2015).When the active sites of adsorbent are surrounded by higher number of dye molecules, it definitely leads to a more efficient adsorption (Mohamad et al., 2017).

Hence, higher initial concentration enhances the interaction between the absorbates and absorbents. The removal of MG achieves 97.83% at initial dye concentration of 10 mg/L. Thus, this point was the optimum condition for the initial dye concentration as it contributed to highest percentage removal of MG. Therefore, 10 mg/L of initial dye concentration has a higher adsorption uptake compared to 2, 4, 6, and 8 mg/L of initial dye concentration.

4.3 Suggested Optimum Condition

1 g of foxtail palm fruit activated carbon took 60 minutes to remove 97.83% of 10 mg/L dye concentration. Hence, the highest percentage removal from three variables was 97.83% at 10 mg/L dye concentration, 60 minutes contact time and 1 g of adsorbent dosage. Optimization adsorption process is necessary to obtain highest percentage removal (Farah Amni, Norhisyam & Rozidaini, 2016). Therefore, batch adsorption is used to seek the optimum point of the three variables which are contact time, adsorbent dosage and dye concentration.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Preparation of activated carbon from agriculture waste which is foxtail palm fruit, has been presented in this study. On the basis of the above, one could conclude that foxtail palm fruit is the effective adsorbent to treat MG dye in aqueous solution. This research also evaluated and discussed about the optimal condition of three effects (contact time, adsorbent dosage and initial dye concentration) on dye removal to achieve high adsorption capacity or percentage removal. Hence, the highest percentage of MG removal by foxtail fruit activated carbon was obtained under the optimum conditions with 97.83% removal with initial concentration 10 mg/L for 1 g absorbent dosage in 60 minutes by shaking at 150 rpm at 27 ^{o}C ±.

5.2 Recommendations

This treatment can be improved by activating the foxtail palm fruit (raw and carbonized) using base activation sodium hydroxide (NaOH) or acid activation, phosphoric acids (H_3PO_4) and zinc chloride ($ZnCl_2$). By doing this activation either base activation or acid activation, it enhances the production of highly developed porous structures. Hence, the surface area of the foxtail palm fruit activated carbon will be increase as well as improving the ability of MG removal from the aqueous solution.

The used of this low-cost absorbent in the technology of dye removal is considered since it is inexpensive, renewable, accessible and have a potential as an adsorbing agent. Finally, it is concluded that it is a good alternative to take the foxtail palm fruit activated carbon as MG dye adsorption to treat aqueous solution economically and effectively. Foxtail palm fruit have suitable adsorption capacity to treat MG dye. Further research should be conduct by concentrated to enhance dye removal by the performance of the adsorption process from industries wastewater such as printing and textile industry.

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APPENDIX A

Percentage Removal of Malachite Green by Contact Time

Table A1: Percentage removal by Contact Time

Contact Time (minutes)	**Initial Reading (a.u.)**	**1st Reading (a.u.)**	**2nd Reading (a.u.)**	**3rd Reading (a.u.)**	**Average Reading (a.u.)**	**Percentage Removal (%)**
30	0.275	0.055	0.048	0.055	0.053	80.73
60	0.275	0.028	0.011	0.011	0.017	93.82
90	0.275	0.036	0.038	0.036	0.037	86.55
120	0.275	0.060	0.062	0.061	0.061	77.82
150	0.275	0.063	0.061	0.061	0.062	77.45

Percentage Removal of Malachite Green by Adsorbent Dosage

Table A2: Percentage removal by Adsorbent Dosage

Adsorbent dosage (g)	**Initial Reading (a.u.)**	**1st Reading (a.u.)**	**2nd Reading (a.u.)**	**3rd Reading (a.u.)**	**Average Reading (a.u.)**	**Percentage Removal (%)**
1	0.077	0.003	0.003	0.005	0.004	94.81
2	0.077	0.004	0.005	0.005	0.005	93.51
3	0.077	0.009	0.010	0.010	0.010	87.01
4	0.077	0.014	0.014	0.015	0.014	81.82
5	0.077	0.015	0.015	0.015	0.015	80.52

Percentage Removal of Malachite Green by Initial Dye Concentration

Table A3: Percentage removal by Dye Concentration

Dye concentration (mg/L)	**Initial Reading (a.u.)**	**1st Reading (a.u.)**	**2nd Reading (a.u.)**	**3rd Reading (a.u.)**	**Average Reading (a.u.)**	**Percentage Removal (%)**
2	0.161	0.019	0.019	0.019	0.019	88.20
4	0.300	0.013	0.013	0.012	0.013	95.70
6	0.467	0.012	0.012	0.011	0.012	97.43
8	0.628	0.015	0.015	0.016	0.015	97.61
10	0.783	0.016	0.017	0.017	0.017	97.83

APPENDIX B

Activated Carbon of Foxtail Fruit

Raw Foxtail Fruit

Figure B1: Raw foxtail fruit

Clean Raw Foxtail Fruit

Figure B2: Clean raw foxtail fruit

Oven Dry Foxtail Fruit

Figure B3: Oven dry foxtail fruit in the preparation of raw material

Carbonization of Foxtail Fruit

Figure B4: Carbonized foxtail fruit

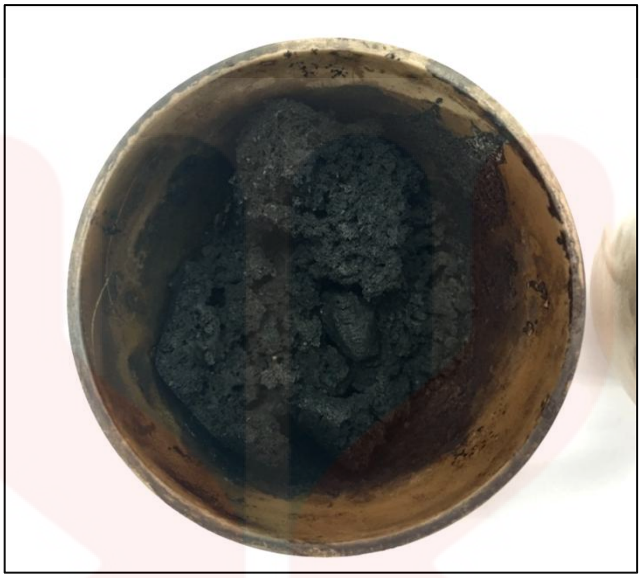


Figure B5: Foxtail fruit activated carbon (before grind)

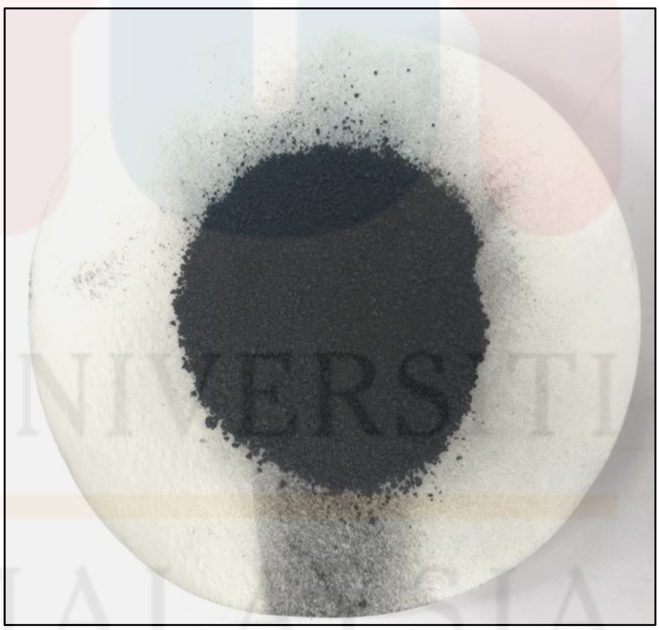


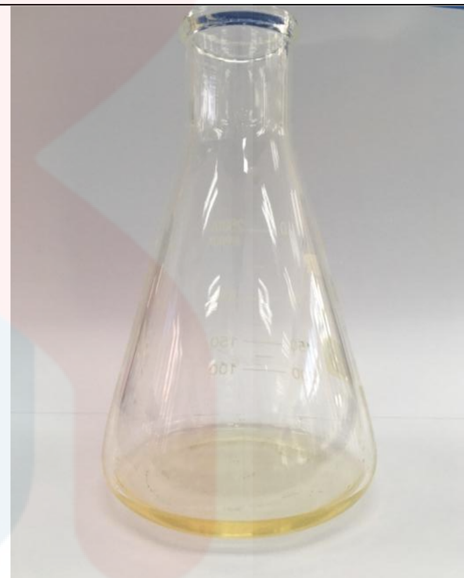
Figure B6: Foxtail fruit activated carbon (after grind)

APPENDIX C

Before and After Treated Solution for Contact Time, Adsorbent Dosage and Dye Concentration

Before and After Treated Solution for Contact Time and Adsorbent Dosage

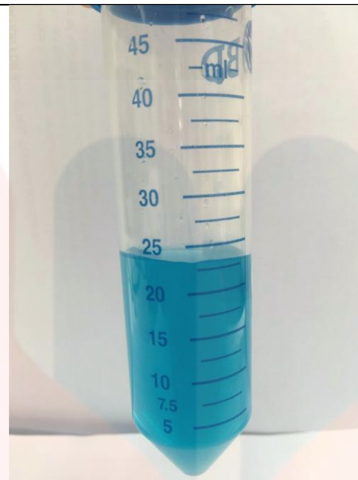
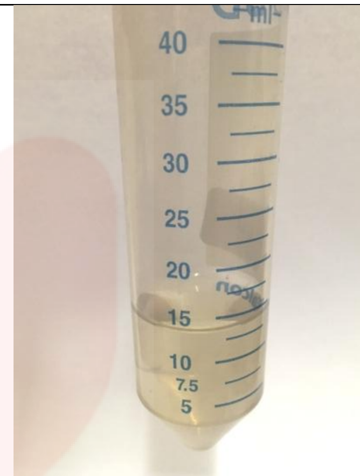
Table C1: Malachite green dye solution before and after treated

Before Treat	**After Treated**
	

Before and After Treated Solution for Dye Concentration

Table C2: Different dye concentration of malachite green dye solutions before and after treated

Concentration (mg/L)	Before Treated	After Treated
2		
4		
6		

8		
10