# REMOVAL OF METAMIFOP USING FOXTAIL PALM FRUITS AS POTENTIAL ACTIVATED CARBON

by

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

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2020

# DECLARATION

I hereby declare that the work embodies in this report entitled "Removal of Metamifop using Foxtail Palm Fruits as Potential Activated Carbon" is the result of original research except as cited in the references and is not concurrently submitted in candidature of any other degree.

Signature : ______________________________

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Date : 5/12/19

# ACKNOWLEDGEMENT

First and foremost, all praises to Allah for strengths and His blessings in completing this thesis. I would like to express my deepest gratitude to my supervisor, Dr. Nik Raihan binti Nik Yusoff because of her immense knowledge, continuous support and motivation that were given to me throughout the journey of completing this thesis.

I would like to thank to the Faculty of Earth Science (FSB) of Universiti Malaysia Kelantan for providing the laboratory materials, apparatus and instruments. I would also like to thank every laboratory assistants, who has helped me while conducting the research in the laboratory.

My greatest gratitude also goes to my beloved family especially my parents, Mr. Mohd Layli and Mrs. Masdalina for nourishing me with their endless blessings, financial support and motivation. Besides that, I would like to thank my friends especially my laboratory mates, Hanie 'Aqilah and Najiehah for lending a helping hand while completing this research.

Last but not least, I would like to thank everyone who has directly and indirectly involved in this research. Thank you for spending your valuable time, sharing new knowledges, giving suggestions and encouragement for me to be a good researcher.

**Removal of Metamifop using Foxtail Palm Fruits as Potential Activated Carbon**

## ABSTRACT

The rising demand on rice as staple food by the increasing human population urges the farmers to extensively protect their crops from infestation by using agrochemicals. Excessive utilization of agrochemical herbicides has caused a major issue of water pollution. A newly developed post-emergence formulation herbicide that has been studied is known as Nominee-M which consists of an active ingredient known as metamifop. Metamifop is widely used in herbicides to protect crops from weed infestation. This study was conducted to investigate the potential and efficiency of foxtail palm fruits as a potential activated carbon for the removal of metamifop. The activated carbon was produced from foxtail palm fruits through the chemical activation process by using nitric acid ($HNO_3$). The effect of adsorbent dose, contact time, and initial metamifop concentration toward the efficiency of the prepared activated carbon in removing metamifop was studied in this research. Adsorbent dose of 3 g recorded the highest percentage of metamifop removal which was 85.71% while adsorbent dose of 1 g recorded the lowest percentage of metamifop removal which was 77.99%. The effective adsorbent dose of 3 g was selected and used for the experiment on the effect of contact time. For the effect of contact, 60 minutes has recorded the highest percentage of metamifop removal which was 86.65% while 150 minutes has recorded the lowest percentage of metamifop removal which was 62.76%. The effective adsorbent dose and contact time of 3 g and 60 minutes respectively were selected and used for the experiment on the effect of initial metamifop concentration. For the effect of initial metamifop concentration, 10 ppm has recorded the highest percentage of metamifop removal which was 86.65% while 18 ppm has recorded the lowest percentage of metamifop removal which was 46.43%. 10 ppm was chosen as the optimum initial concentration of metamifop that is efficient for the removal of metamifop by activated carbon made from foxtail palm fruits. The highest percentage of removal obtained at optimized value of 3 g, 60 minutes and 10 ppm was 86.65%. The study has proven that through adsorption of metamifop by activated carbon made from foxtail palm fruits have the potential to reduce metamifop in water resources that has been contaminated.

**Penyingkiran Metamifop menggunakan Buah Pinang sebagai Karbon Aktif yang Berpotensi**



## ABSTRAK

Permintaan yang semakin meningkat terhadap beras sebagai makanan ruji yang berlaku disebabkan oleh peningkatan populasi manusia telah menggesa para petani untuk melindungi tanaman mereka dari ancaman dengan menggunakan racun rumpai. Penggunaan racun rumpai secara berlebihan telah mengakibatkan berlakunya isu utama iaitu pencemaran air. Kemunculan sebuah formulasi racun rumpai baru iaitu Nominee-M yang mengandungi metamifop sebagai bahan aktif telah dikaji. Metamifop telah digunakan secara meluas di dalam racun rumpai untuk melindungi tanaman daripada serangan rumpai. Kajian ini telah dikendalikan untuk menyelidik potensi dan kecekapan buah pinang sebagai karbon aktif untuk menyingkirkan metamifop. Karbon aktif telah dihasilkan daripada buah pinang melalui proses aktivasi kimia dengan menggunakan asid nitrik ($HNO_3$). Kesan dos penjerap, masa sentuhan dan kepekatan awal metamifop terhadap kecekapan karbon aktif yang telah disediakan untuk menyingkirkan metamifop telah dikaji dalam penyelidikan ini. Dos penjerap sebanyak 3 g telah merekodkan peratusan penyingkiran metamifop yang paling tinggi iaitu 85.71% manakala dos penjerap sebanyak 1 g telah merekodkan peratusan penyingkiran metamifop yang paling rendah iaitu 77.99%. Dos penjerap yang efektif sebanyak 3 g telah dipilih dan digunakan untuk eksperimen kesan terhadap masa sentuhan. Untuk kesan terhadap masa sentuhan, 60 minit telah merekodkan peratusan penyingkiran metamifop yang paling tinggi iaitu sebanyak 86.65% manakala 150 minit telah merekodkan peratusan penyingkiran metamifop yang paling rendah iaitu sebanyak 62.76%. Dos penjerap dan sentuhan masa yang efektif iaitu 3 g dan 60 minit telah dipilih dan digunakan untuk eksperimen kesan terhadap kepekatan awal metamifop. Untuk kesan kepekatan awal metamifop, 10 ppm telah merekodkan peratusan penyingkiran metamifop yang paling tinggi iaitu 86.65% manakala 18 ppm telah merekodkan peratusan penyingkiran metamifop yang paling rendah iaitu 46.43%. 10 ppm telah dipilih sebagai kepekatan awal metamifop optimum yang efisien untuk menyingkirkan metamifop oleh karbon aktif yang diperbuat daripada buah pinang. Peratusan penyingkiran metamifop paling tinggi telah diperolehi pada nilai optimum 3 g, 60 minit dan 10 ppm sebanyak 85.65%. Kajian ini telah membuktikan melalui penjerapan karbon aktif yang diperbuat daripada buah pinang mempunyai potensi untuk mengurangkan metamifop di dalam sumber air yang telah tercemar.

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| ACCase | Acetyl-coenzyme A carboxylase |
| PRB | Permeable Reactive Barrier |
| ZVI | Zero Valent Iron |
| SE | Suspo-emulsion |
| SEM | Scanning Electron Microscopy |
| PAC | Powdered Activated Carbon |
| GAC | Granular Activated Carbon |
| BET | Brunauer-Emmett-Teller |
| $CaCl_2$ | Calcium chloride |
| $HNO_3$ | Nitric acid |
| NaCl | Sodium chloride |
| UV-Vis | UV-Visible Spectrophotometer |
| g | Gram |
| ppm | Parts per million |

# LIST OF SYMBOLS

| | |
|---|---|
| % | Percentage |
| ˚C | Temperature (degree Celsius) |
| ε | Molar extinction coefficient ($dm^3$ $mol^{-3}$ $cm^{-3}$) |

# CHAPTER 1

# INTRODUCTION

## 1.1 Background of Study

The rising demand on rice as staple food by the increasing human population urges the farmers to extensively protect their crops from infestation by using agrochemicals. Agrochemicals are medium used for the management of agricultural ecosystem to protect crops from any diseases, pests and weeds which includes fertilizers, herbicides and pesticides. Apart from crops protection, the uses of these chemical has contributed to the efficiency of farmers while maintaining the supply of agricultural products to meet the global food supply.

In Malaysia, minimum prices, input and output subsidies of agrochemical for paddy rice has established since decades ago in ensuring food security while enhancing the income of paddy farmers. Due to this supportive measures, it has stimulated the extensive use of agrochemicals by the farmers. In between 2009 to 2011, it was reported that the use of agrochemicals by the paddy rice farmers has substantially increased from 170 to 188 thousand tonnes (Knoema, 2013). A research on the use of pesticides by Malaysian farmers has reported that these farmers used pesticides for their crops in a higher amount and doses than which has been recommended (Mohamed et al., 2016).

To protect crops production from weed infestation, farmers took an alternative to use herbicides. An herbicide is defined as a chemical substance that is extensively used in agricultural activities for the manipulation and control of undesirable growth of vegetation to maximize the crops production. Herbicides are categorized into selective and non-selective (Sally & Alex, 2018). Selective herbicides destroy specific unwanted plants without harming desirable vegetation while non-selective herbicides destroy most of the species of plants (Sally & Alex, 2018). Herbicides can be directly applied to the plant, soil or onto the foliage before, during or after planting of crop. Herbicides such as Nominee-M has been widely used by the farmers in agricultural field. Nominee-M contains almost 9.5% of metamifop as an active ingredient. Metamifop is known as lipid synthesis inhibitor which disrupts the growth of weeds by inhibiting the activity of acetyl-coenzyme A carboxylase (ACCase) which is very important for the biosynthesis of plants (Xia, et al., 2016).

Despite the contribution of agrochemicals as a medium for protection of crops which also increase the work efficiency of the farmers, excessive use of the chemicals can cause diffuse water pollution. Diffuse water pollution is described as any activities which does not have any specific point of discharge (Hannah, 2017). Contamination of water caused by agrochemicals will affect human and aquatic species. Contaminated water is not suitable for human consumption. Besides that, runoff of agrochemicals into larger water bodies can causes eutrophication, a phenomenon when a body of water is enriched with nutrients such as nitrogen and phosphorus which initiate the growth of algae (Chislock et al., 2013).

Water pollution can be encountered through environmental remediation by removing the pollution or contaminants from soil, sediment, surface water or groundwater. There are various remediation technologies which can be categorized into in-situ and ex-situ remediation. In-situ remediation is referred to treatment of the contamination without removing the groundwater or soils while ex-situ remediation require excavation of contaminated soils or extraction of contaminated water. Remediation technologies includes bioremediation, phytoremediation and permeable reactive barriers (PRB).

PRBs is widely used for the remediation of groundwater. PRBs is the placing of reactive materials in the subsurface which is intended to impede a contaminated plume by providing a pathway through the reactive materials (Thiruvenkatachari et al., 2007). To achieve a remediation concentration goals down-gradient of the barrier, it involved an alteration of the contaminants into a form that can be tolerated by the environment (Thiruvenkatachari et al., 2007). The examples of reactive materials are zero valent iron (ZVI), lime, microbial remediation and activated carbon.

In this study, activated carbon from foxtail palm fruits was chosen as the reactive material for the removal of metamifop. Activated carbons can be applied for both in-situ and ex-situ groundwater remediation because they are chemically stable and suitable to be use as adsorbent (Thiruvenkatachari et al., 2007). High surface area and presence of different types of functional groups of the activated carbon enable it to possess a high adsorption capacity for contaminants either organic or inorganic (Thiruvenkatachari et al., 2007). From this study, the potential and efficiency of foxtail palm fruits as an activated carbon for the removal of metamifop was evaluated through the effect of adsorbent dose, contact time and initial metamifop concentration.

## 1.2 Problem Statement

The formulated herbicide that has been studied was Nominee-M which consists of an active ingredient known as metamifop. Metamifop is widely used in herbicides to protect crops from weed infestation. Besides its contribution towards protecting crops and increasing work efficiency, the excessive use of the herbicides can cause diffuse water pollution. This pollution will affect both human and aquatic species. Contaminated water is not suitable to be consumed by human. Besides that, runoff of agrochemicals into larger water bodies can causes eutrophication, a phenomenon when a body of water is enriched with nutrients such as nitrogen and phosphorus which initiate the growth of algae. Hence, this study was conducted to investigate the potential and efficiency of foxtail palm fruits as a potential activated carbon for the removal of metamifop from the environment.

## 1.3 Objectives

1. To produce activated carbon using foxtail palm fruits through the chemical activation process for the removal of metamifop.
2. To study the effect of adsorbent dose, contact time, and initial metamifop concentration influence toward the efficiency of the prepared activated carbon in removing metamifop.

## 1.4 Scope of Study

This study focused on the preparation of foxtail palm fruits as activated carbon for the removal of active ingredient in herbicides which is metamifop. The foxtail palm fruits were collected from Jeli, Kelantan. In this study, the foxtail palm fruits were carbonized. The carbonized foxtail palm fruits were prepared using nitric acid as chemical activation agent. Stock solution was prepared by dissolving Nominee-M formulation with deionized water. A series of standard solution of metamifop were prepared from the stock solution. To investigate the efficiency of foxtail palm fruits as activated carbon in removing metamifop in the prepared solution, the study covered several parameters which includes the effect of adsorbent dose, contact time and initial concentration of metamifop.

## 1.5 Significance of Study

In this study, the potential and efficiency of foxtail palm fruits as an activated carbon for the removal of metamifop was evaluated through the effect of adsorbent dose, contact time, and initial metamifop concentration. Through this study, foxtail palm fruits can be commercialized as an effective agricultural materials for activated carbon. The production of activated carbon using foxtail palm fruit can be applicable for the remediation of herbicide residue accumulated in soil and water.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Diffuse Water Pollution from Agriculture

Diffuse water pollution is described as any activities which does not have any specific point of discharge which contributed to a significant impact on water quality. Agricultural activities are one of the major contributor of diffuse water pollution due to washing off agrochemicals such as fertilizer, pesticides and herbicides into surface water which seeping into the groundwater (Hannah, 2017). Diffuse water pollution from agricultural activities is influenced by several key factors.

Agrochemicals are originally used to enhance the productivity and safety of crops. However, the excessive use of these agrochemicals has adversely affected the environment through the degradation of the water quality. Increased use of fertilizer has affected the quality of water by percolation through the soil and runoff of nutrients to the freshwater system which causes eutrophication of groundwater, lakes and rivers. Eutrophication has become one of the most pressing environmental concern. It is defined as an increased in the availability of growth factor limitations required for photosynthesis such as sunlight, carbon dioxide and nutrient which initiate the excessive growth of plant and algal (Chislock et al., 2016). Eutrophication has caused biodiversity loss, hypoxia and death of fishes.

A study has shown a comparison on the consumption of fertilizer in China, Republic of Korea, United Kingdom and United States. It was reported that China has the largest consumption of fertilizer which increased fourfold from 1978 to 2012 compared to the other three countries which has shown a great reduce on the consumption of fertilizer (Smith & Siciliano, 2014). Diffuse water pollution has contributed an environmental impacts to China which includes acidification of soil, eutrophication of lakes and increased nutrients concentration in groundwater (Cui et al., 2014). Besides that, it was reported that China has shortage of safe drinking water to support 300 million of rural residents (Liu & Yang, 2012).

## 2.2 Classification of Pesticides

Pesticides is defined as a substance or mixture that are utilized to destroy and for the prevention from pest which includes insects, weeds or pathogens (Kaur et al., 2017). Pesticides has a diverge properties in terms of physical, chemical and identical.

Pesticides are classified based on their function and type of pests it can destroy (Kaur et al., 2017). It includes insecticides, fungicides and herbicides which are commonly used in agricultural sector. The function of insecticides are to kill insects and fungicides are used to kill fungi. As for herbicides, it is utilized to kill weeds and any other unwanted plants.

Next, pesticides can be classified based on their chemical composition into four main groups of organic compounds. The groups are synthetic pyrethroids, carbamates, organophosphorus and organochlorines (Kaur et al., 2017). Synthetic pyrethroid pesticides have a longer residual effects compared to natural pyrethroid pesticides because it is chemically produced through the structural duplication of the natural pyrethrins (Kaur et al., 2017). Carbamates and organophosphates have a similar structure of compounds. However, the origin of carbamates are carbamic acid while organophosphates are phosphoric acid (Kaur et al., 2017). As for organochlorines pesticides, it consists of five or more chlorine atoms. In the environment, organochlorines pesticides have a longer residual effect (Kaur et al., 2017).

## 2.3 Metamifop as an Active Ingredient in Herbicide

Staple food can be defined as food that is that is consumed by a community in their routine. It contributes to a significant proportion of the calorie required as a standard diet of the community (Fathima et al., 2017). Rice is one of the example of major staple food known for its nutritional value (Saha et al., 2016). In the global production of rice, 19.3% has been contributed by India as they are the main producer of rice (Saha et al., 2016). In India, the farmers took an initiative to cultivate their rice using direct-seeded method due to monsoon failure and water shortage. The method has inhibited early hand or mechanical weeding. It was reported that about 33% yield of rice production in India is lost due to weed infestation (Saha et al., 2016). To overcome the production loss due to the attack of weed, the Indian farmers has applied herbicide in their agricultural field. Despite of its advantage, the use of herbicide has contaminated the environment through the residue of the herbicide which is detrimental to animal and human health (Nagami, 2004).

A newly developed post-emergence formulation herbicide known as Nominee-M was chosen for this study. Nominee-M is an off-white viscous liquid with a mixture formulation of bispyribac sodium+metamifop 14% suspo-emulsion (SE) as shown in the Table 1.1. SE is a solid and liquid formulation of active ingredients which dispersed in an aqueous phase. One of the active ingredients is in the form of suspension and the other is in the form of emulsion. SE is very accessible to be handled and measured due to being non-flammable and good miscibility in water.

**Table 1.1:** Active ingredients of Nominee-M

| Active ingredients | Percentage (%) |
|---|---|
| Metamifop | 9.5 |

Metamifop is a synthetic herbicide that belongs to the pyrimidinyl carboxy group and aryloxyphenoxy propionic acid group respectively which were used to control weeds in cereal crops such as rice. Metamifop is known as a lipid synthesis inhibitor (Xia, et al., 2016). Metamifop disrupts the growth of weeds by inhibiting the activity of acetyl-coenzyme A carboxylase (ACCase) which is very important for the biosynthesis of plants. Metamifop is translocated from the uptake point to the growing meristem of the plants (Xia, et al., 2016).

## 2.4 Residue of Metamifop in the Environment

Metamifop have a half-life of 70 days with the range of 18-120 days (Janaki & Chinnusamy, 2012). Under aerobic conditions, metamifop is relatively persistent in soil. Metamifop has a lower solubility in water and it can decomposes before melting point is reached. Photodegradation is the main mechanism of metamifop degradation in the environment. There are several factors that influenced the degradation rate of herbicides in soil which includes temperature, moisture and texture of the soil (Janaki & Chinnusamy, 2012). Besides that, tropical climatic conditions also influenced the degradation rate of herbicides due to uneven distribution and intensity of rain.

A study on the determination of the presence of metamifop residue in soil and bioaccumulation in paddy grains and straw was conducted in India. Metamifop was applied with different dosage of 0, 75, 100 and 125 g per hectare to the weeds of 2-3 days and 5-6 leaf stages (Janaki & Chinnusamy, 2012). It was reported that the soil sample which was applied with 125 g per hectare of metamifop has the highest concentration of metamifop residue at both 2-3 leaf and 5-6 leaf stage compared to the rice grain and straw. The study has concluded that increase in the dose of metamifop application has increased the concentration of metamifop residue in the soil (Janaki & Chinnusamy, 2012).

Another study was conducted in India on the new mixture formulation of bispyribac-sodium and metamifop in rice. The study focused on the dissipation kinetics of the herbicides. Bispyribac-sodium and metamifop was applied in the rice field with different dosage of 70 and 140 g per hectare. Through the study, it was reported that no metamifop residue was recorded in the harvested straw, grain, and husk. The study has concluded that the application of the new mixture of herbicide to rice cultivation does not contribute to any negative effects to the rice and is safe to be consumed by human (Saha et al., 2016). However, it was reported that the concentration of metamifop residue and its dissipation rate in soil is higher.

The rate of herbicides dissipation is influenced by the type of soil, pH, content of organic matter, type of interaction between active ingredient with soil and condition of the environment (Long et al., 2014). Excessive amount of herbicides which continuously applied on the plants will be accumulated in the soil as residues. The residue will contaminate the groundwater due to leaching and runoff of the residue. A study on the management of paddy field weeds has proved that the effective amount of metamifop that can be utilized is 100 g ai/hectare (Ravi et al., 2013). It may persist in the irrigation water if more than 100 g ai/hectare of metamifop is used without a proper treatment. The persistence of metamifop may cause bioaccumulation which can become pollutants (Sondhia, 2008).

## 2.5 Activated Carbon

Activated carbon is defined as a form of carbon that went through a series of process to produce a porous carbon material. The pore network enable the removal of impurities by activated carbon through the mechanism of adsorption (Haycarb, 2019). Porosity will influence the rate of adsorption and chemical reactions of the activated carbon. Adsorption is referred to the adhesion or attachment of adsorbates (atoms, ions and molecules) onto the surface of adsorbent (activated carbon). Adsorbates are trapped and enclosed in between the internal pore structure of the carbon. There are two types of adsorption which are physical adsorption and chemisorption (Haycarb, 2019). Physical adsorption involves the attachment of adsorbates by weak forces of attraction which are van der Waals or London dispersion forces while chemisorption involves the strong forces of chemical bond attraction between adsorbates and the chemical compounds on the pore wall of the activated carbon (Haycarb, 2019). The utilization of activated carbon produced from agricultural waste such as rice husk has been commercialized as a replacement for the current expensive treatment of removing contaminants from the environment. Activated carbon can be applied for purification of gas or water, extraction of metal, recover of gold, treatment of sewage and medicine.

### 2.5.1 Physical and Chemical Activation

The physical activation of activated carbon involved utilization of oxidizing gases such as air, $CO_2$ and $H_20$ steam which is conducted in the thermal processes under temperature below 700˚C (Khadija et al., 2015). This process is aimed to produce a porous structure which can increase the capacity of activated carbon for the adsorption (Khadija et al., 2015). The carbon materials are converted by oxidant and produce opening pores of CO and $CO_2$ in the materials of the activated carbon.

As for chemical activation, two processes are involved which includes the process of heating and chemical treatment. Heating process only require less heat compared to physical activation (Khadija et al., 2015). Chemical agents such as potassium hydroxide, sodium hydroxide and nitric acid are used during the chemical treatment.

These chemicals are added to improve the surface area and porous structure size of the activated carbon materials (Khadija et al., 2015).

### 2.5.2 Classification of Activated Carbon

Based on the physical properties, activated carbon can be grouped into powdered activated carbon (PAC) and granular activated carbon (GAC). The main characteristic that differs PAC and GAC is the size of particle. The diameter of PAC is between 0.15 to 0.25 mm while GAC is between 1.2 to 1.6 mm (Haycarb, 2019). PAC have a lower cost of processing and high flexibility compared with GAC. However, GAC is harder, recyclable, easy to handle, can last longer and able to purify large volume of gas and liquid compared to PAC (Haycarb, 2019). PAC is mainly utilized for adsorption involving liquid phase while GAC is applied for adsorption involving both liquid and gas phases (Haycarb, 2019).

### 2.5.3 Factors Influencing the Efficiency of Activated Carbon

Efficiency of activated carbon for adsorption is influenced by several factors which includes dose concentration, adsorbent dose, contact time and pH. Several study were conducted to investigate these factors that influenced the efficiency of activated carbon.

Firstly, removal of contaminants influenced by the concentration of the contaminants. The higher the concentration of contaminant, the higher the capacity of removal by activated carbon. This was supported by a study of Congo red removal by adsorption of activated carbon produced from coir pith that was conducted in India. To study the reaction of dose concentration on the efficiency of adsorption by activated carbon, different concentration of dye with 20, 40, 60 and 80 mg/L was used (Namasivayam & Kavitha, 2002). Based on the results, as the concentration of dye increased from 20 to 80 mg/ L of dye, the percentage of dye removed from the solution was decreased from 66.5 to 30.5 (Namasivayam & Kavitha, 2002). This can be concluded that the capacity of adsorption by activated carbon has increased with the increased in the concentration of dye (Namasivayam & Kavitha, 2002).

Besides contaminant concentration, the study also investigate the effect of adsorbent dose on the rate of adsorption by activated carbon. Different adsorbent dose from 100-900 mg/50 ml was used (Namasivayam & Kavitha, 2002). Based on the results, it has shown the increased in adsorbent dose has increased the percentage of dye removal (Namasivayam & Kavitha, 2002). This is caused by the larger surface area of adsorbent. In the same study, the effect of contact time on the rate of adsorption by activated carbon was studied. The experiment has shown that the longer the contact time of dye with activated carbon, the higher the percentage of the dye removed by the activated carbon (Namasivayam & Kavitha, 2002).

The efficiency of activated carbon in removing contaminant is also influenced by pH. Thus, a comparative study on the adsorption of methylene blue and Congo red by activated carbon was conducted using different pH of 4, 6 and 8 (Amni et al., 2016). Based on the investigation, the results has shown that methylene blue has the highest percentage of removal compared to Congo red with 93.89%, 94.64% and 92.32% with pH of 4, 6 and 8 respectively (Amni et al., 2016). It shows that there was no significant difference in the percentage of methylene blue removal. This can be concluded that effect of pH is insignificant for methylene blue. In contrast, Congo red shows a significant difference at pH 4 with 53.25% of Congo red removal (Amni et al., 2016). At pH 6 and 8, Congo red does not show any significant difference in the percentage of removal (Amni et al., 2016). This has shown that the effect of pH influenced the removal of Congo red.

### 2.5.4 Removal of Pesticides using Activated Carbon from Agricultural Waste

A low-cost activated carbon can be commercially produced from agricultural wastes such as wood, sugarcane husks, coconut shells, rice husks and corn cobs. It is economically viable in removing contaminants from the environment because these wastes are abundance and locally available (Kadirvelu et al., 2003).

Due to the high surface area and porosity of activated carbon produced from agricultural wastes, it is widely used for the removal of herbicides in water. The capacity of activated carbon to adsorb contaminants are based on the types of raw materials, the preparation process and the condition of the treatment (Ahmad et al., 2010). A study was conducted at Bluefields, Nicaragua to produce an activated charcoal using coconut shells for the removal of pesticide contaminants in water.

Activated charcoal were produced with two different chemical activation and a blank activated charcoal was also prepared (Cobb et al., 2018). Chemical activation involved in the production of activated charcoal by impregnating the charcoal with calcium chloride ($CaCl_2$) and sodium chloride (NaCl). It was carbonized at higher temperature at range of 500 to 800˚C. Based on the results, activated charcoal from coconut shells has a great adsorption potential of contaminants. The results has shown that activated charcoal that was impregnated with NaCl has a greater efficiency compared to $CaCl_2$ while the blank activated carbon did not show any changes (Cobb et al., 2018).

Another study was conducted to study the efficiency of coals and coconut shells as activated carbon from agricultural waste. It was reported that both activated carbon can be utilized as an adsorbent in removing pheonoxyacetic acid pesticides in aqueous forms (Ignatowicz, 2009). However, the physico-chemical properties of the adsorbent and adsorbate influenced the efficiency to remove the contaminants. The adsorbent properties include the Brunauer–Emmett–Teller (BET) surface area and total volume of pore while the adsorbate properties include the character of the acid and active carbon mass (Ignatowicz, 2009). From the study, it was reported that activated carbon with NP-5 carbon produced from coconut shells has a great efficiency in removing the pheonoxyacetic acid pesticides (Ignatowicz, 2009).

Besides the utilization of coals and coconut shells as activated carbon, wood is another agricultural waste that can be used as adsorbent for the removal of pesticides. A study was conducted to investigate the efficiency of wood as an adsorbent. Based on the report, the efficiency of the activated carbon to remove the contaminants become greater with increasing initial concentration and decreasing of the adsorbent size (Mishra & Patel, 2008). The potential of wood as an adsorbent can be improved through the chemical activation with hydrochloric acid and nitric acid (Mishra & Patel, 2008).

## 2.6 UV-Visible Spectrophotometer

UV-visible spectrophotometer is used to measure the absorbance value of ultra violet (UV) or visible light at a single wavelength or over a range in the spectrum (Royal Society of Chemistry, 2009). The region of UV light ranging from 190 to 400 nm while visible light ranging from 400 to 800 nm. It can be used for both qualitative and quantitative analysis. A cell or cuvette is a container which is optically flat and transparent used to hold liquid sample. Blank refers to a reference cell or cuvette that consists solvent in which the sample is dissolved (Royal Society of Chemistry, 2009).

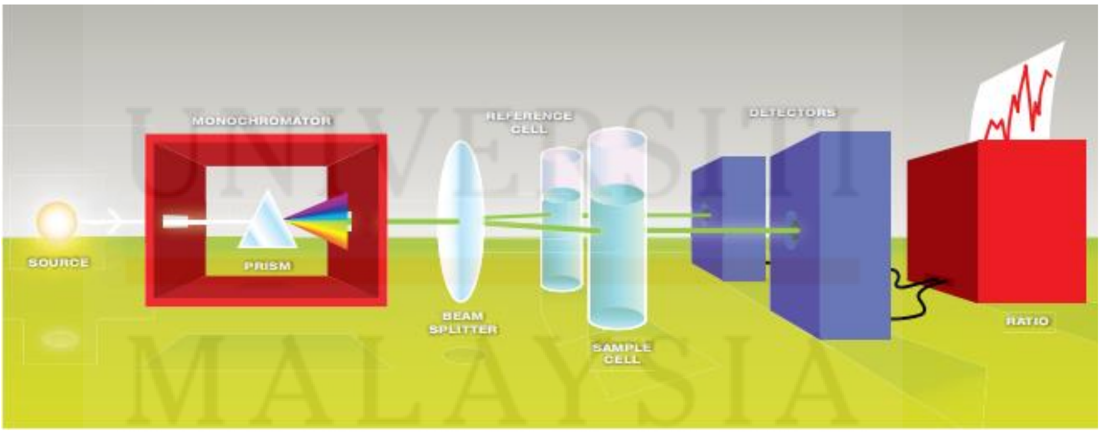


**Figure 2.1**: A schematic of UV-Visible spectrophotometer (Royal Society of Chemistry, 2009)

The radiation of UV and visible light that covers from 200-800 nm is provided by a combination of tungsten or halogen and deuterium lamps as the source of light.

The output produced from the light source is directed to the diffraction grating. It will efficiently separates the light into its component colours of different wavelength.

The light intensity that passes through a reference cell (**$I_0$**) and the sample cell (**I**) can be measured for each wavelength. The light is absorbed by the sample when I is less than **$I_0$**. The relationship between absorbance (A), **$I_0$** and **I** shows in the equation below (Royal Society of Chemistry, 2009):

$$A = \log_{10} \frac{I_0}{I} \quad (2.1)$$

UV-visible spectroscopy can be used to measure the sample concentration. Based on Beer-Lambert Law, absorbance is directly proportional to the concentration of sample and can be expressed in the equation below (Royal Society of Chemistry, 2009):

$$A = \varepsilon c l \quad (2.2)$$

Where

A = absorbance

l = optical path length

c = concentration of solution (mol $dm^{-3}$)

ε = molar extinction coefficient ($dm^3$ $mol^{-3}$ $cm^{-3}$)

Beer-Lambert Law is obeyed when the calibration graph is plotted with absorbance against the concentration of solution and is in the form of linear. From calibration graph, the concentration of unknown solution of sample can be determine through the absorbance value.

# CHAPTER 3

# MATERIALS AND METHODS

## 3.1 Materials and Instrument

In this study, Nominee-M with active ingredient of metamifop was used. Preparation of metamifop solution was done by dissolving the Nominee-M solution using deionized water. Foxtail palm fruits were used as the raw materials. Nitric acid ($HNO_3$) was used to impregnate the raw materials as activating agent. In this study, a HACH DR6000 UV-Vis spectrophotometer was used to measure the absorbance value of the metamifop solution before and after being treated with activated carbon.

## 3.2 Collection of Raw Materials

Foxtail palm fruits (*Wodyetia bifurcata*) were collected as raw materials for the production of activated carbon at Jeli, Kelantan, Malaysia.

## 3.3 Carbonization of Foxtail Palm Fruits

Firstly, collected foxtail palm fruits were cleaned and washed thoroughly using distilled water to remove any impurities. Next, the fruits were dried 100˚C overnight in the oven and left to cool down in room temperature. The dried fruits were kept in tight polyethylene bag and was placed in the desiccator before carbonization process.

The dried foxtail palm fruits were carbonized at 300˚C for 2 hours in furnace and left to cool down in room temperature. The carbonized carbon were crushed using pestle and mortar into small pieces and sieved through 250 µm. The weighed was recorded. The sieved carbonized carbon were transferred in tight polyethylene bag and was placed in the desiccator.

## 3.4 Preparation of Activated Carbon using Nitric Acid as Chemical Activation Agent

Preparation of foxtail palm fruits as activated carbon involved the process of chemical activation. Firstly, about 40 g of carbonized carbon was completely soaked and impregnated with 80 ml of concentrated $HNO_3$ in a beaker. The mixture was mixed vigorously with constant rate of stirring about 30 minutes until it became a paste. The mixture was left impregnated in fume hood for overnight to ensure the chemical has been fully reacted which produced slurry. The slurry was weighed and placed in dry crucibles for carbonization process. It was carbonized in a furnace for 2.5 hours at

500˚C. Next, to achieve pH 7, the activated carbon was washed with distilled water and placed in the oven for 3 hours at a 150˚C. Lastly, the dried activated carbon was kept in tight polyethylene bag and placed in desiccators.

### 3.5 Preparation of Metamifop Solution

1000 ppm of metamifop stock solution was prepared by dissolving 10.5 g of Nominee-M formulation into 1 L of deionized water. The stock solution was filled into a 1000 mL of volumetric flask covered with aluminium foil to prevent interference of light. The stock solution was stored in refrigerator at 4˚C.

### 3.6 UV-Visible Spectrophotometer (UV-Vis)

A HACH DR 6000 UV-Vis spectrophotometer involved in this study to determine the absorbance spectra of the metamifop. The UV-Vis spectrum was recorded at 500nm. Calibration curve was constructed to determine the final concentration of the metamifop solution. Table 3.1 shows the operation method of the UV-Vis. The spectra obtained was used to analyse the significant deviation in the parent peak of the compound.

**Table 3.1**: Operation method of UV-Visible spectrophotometer

| Parameter | Condition |
|---|---|
| Light source | Gas-filled deuterium (UV) and tungsten (visible) |
| Wavelength | 500 nm |

### 3.7 Removal of Metamifop by Adsorption Process

#### 3.7.1 Effect of Adsorbent Dose

The adsorption test was performed by mixing 50 ml of 10 ppm metamifop solution with 1 g of activated carbon in Erlenmeyer flasks set (250 mL) for about 30 minutes in an incubator shaker at 200 rpm. Next, the metamifop solution was filtered using 0.45 μm Whatman filter paper. The absorbance of metamifop solution after treated with activated carbon was determined using UV-Visible spectrophotometer. The steps were repeated with different adsorbent dose of activated carbon at 2 g, 3 g, 4 g and 5 g. The effective adsorbent dose of 3 g was selected and used for the next subsequent experiment.

### 3.7.2 Effect of Contact Time

The adsorption test was performed by mixing 50 ml of 10 ppm metamifop solution with the effective adsorbent dose of 3 g of activated carbon from previous experiment in Erlenmeyer flasks set (250 ml) with contact time at 30 minutes with 200 rpm in an incubator shaker. Next, the metamifop solution was filtered using 0.45 μm Whatman filter paper. The absorbance of metamifop solution after treated with activated carbon was determined using UV-Visible spectrophotometer. The steps were repeated with different contact time at 60, 90. 120 and 150 minutes. The effective adsorbent dose of 3 g and contact time of 60 minutes were selected and used for the next subsequent experiment.

### 3.7.3 Effect of Initial Metamifop Concentration

The adsorption test was performed by mixing 50 ml of 10 ppm metamifop solution with the effective adsorbent dose of activated carbon and contact time which were 3 g and 60 minutes respectively from the previous experiment in Erlenmeyer flasks set (250 mL) at 200 rpm in an incubator shaker. Next, the metamifop solution was filtered using 0.45 μm Whatman filter paper. The absorbance of metamifop solution after treated with activated carbon was determined using UV-Visible spectrophotometer. The steps were repeated for 12 ppm, 14 ppm, 16 ppm and 18 ppm of metamifop solution.

### 3.8 Percentage Removal of Metamifop

The percentage of metamifop removal was calculated using the following equation:-

$$\frac{Ci - Cf}{Ci} \times 100 \qquad (3.1)$$

Where:-

C$i$ = Initial concentration of metamifop solution

C$f$ = Final concentration of metamifop solution

## 3.9 Method flowchart

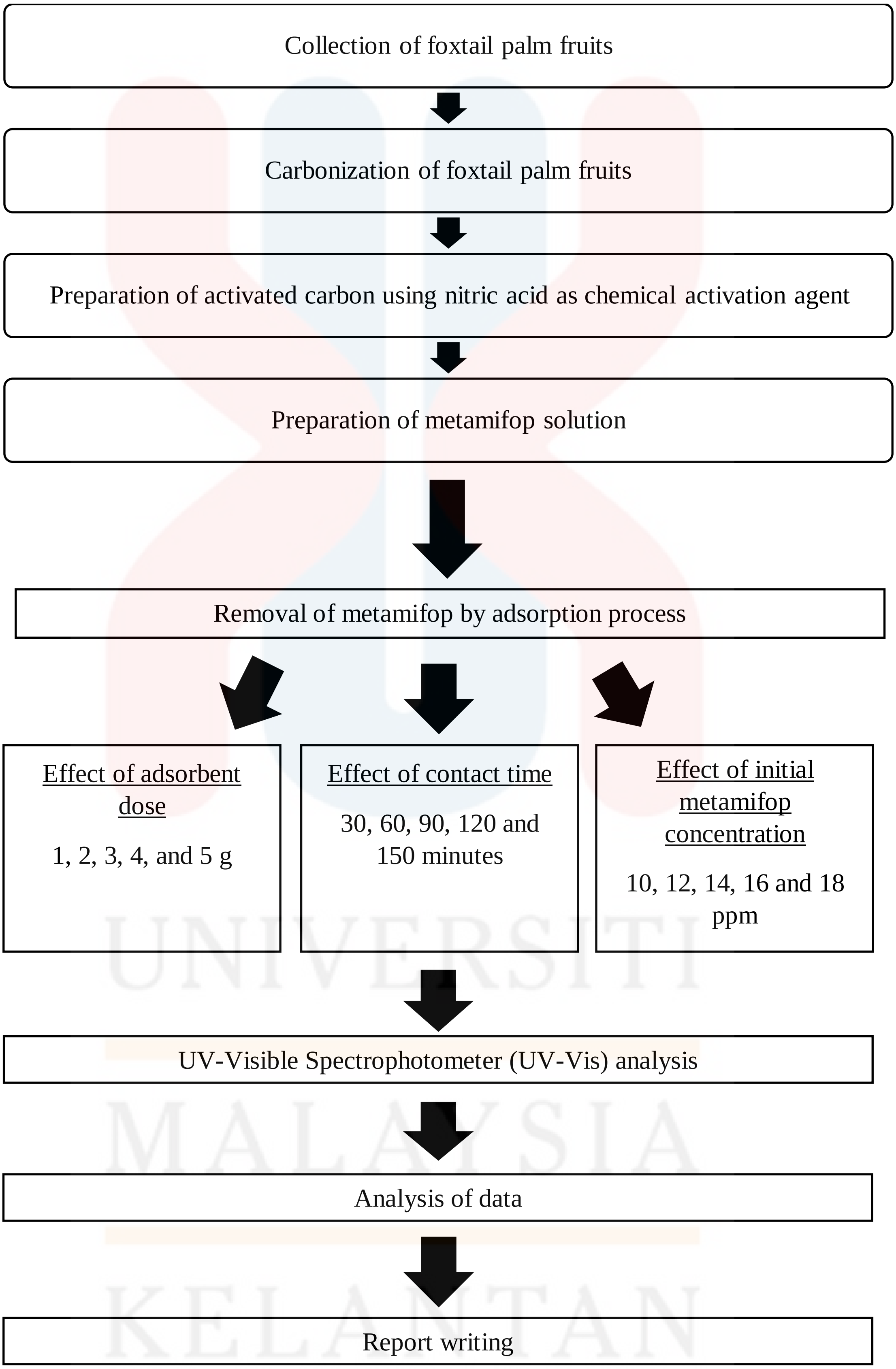


**Figure 3.1:** Method flow chart

# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.1 Calibration Curve of Metamifop

1000 ppm of metamifop stock solution was prepared and diluted to prepare standard solutions with known concentration of 2 ppm, 4 ppm, 6 ppm, 8 ppm, 10 ppm and 12 ppm. The standard solutions were measured using UV-Visible spectrophotometer at wavelength of 500 nm. Using Excel 2013, a calibration curve of absorbance at 500 nm against the concentration of standard solutions was generated. A liner trendline (red dashed line) on the graph has shown the best-fit straight line that indicates the general pattern and to compare the linearity of the data. All values of the data have a strong direct relationship with the coefficient of determination, $R^2$ = 0.9989.This indicates that 99.89% of the absorbance value is due to the concentration of metamifop.

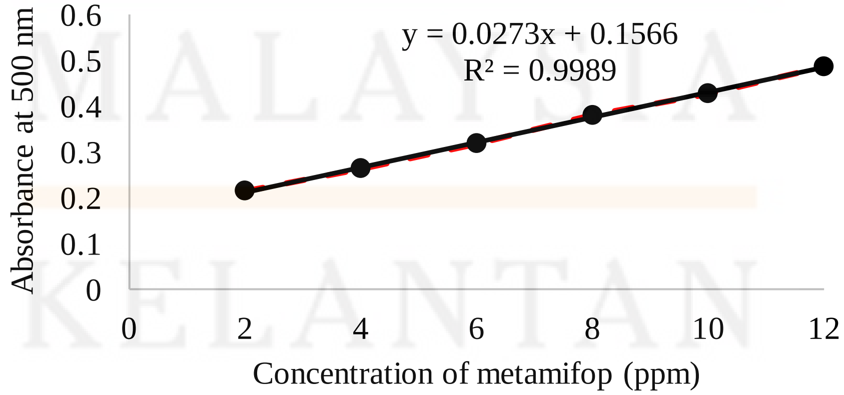


**Figure 4.1:** Calibration curve of metamifop

## 4.2 Removal of Metamifop by Adsorption Process

### 4.2.1 Effect of Adsorbent Dose

The effect of the adsorbent dose on the adsorption efficiency of activated carbon from foxtail palm fruits for the removal of metamifop was conducted. In the experiment, activated carbon was loaded into the metamifop solution with different dose of 1 g, 2 g, 3 g, 4g and 5 g. The initial concentration of metamifop solution and contact time were fixed at 10 ppm and 30 minutes respectively. Figure 4.2 shows the effect of adsorbent dose on the removal of metamifop solution.

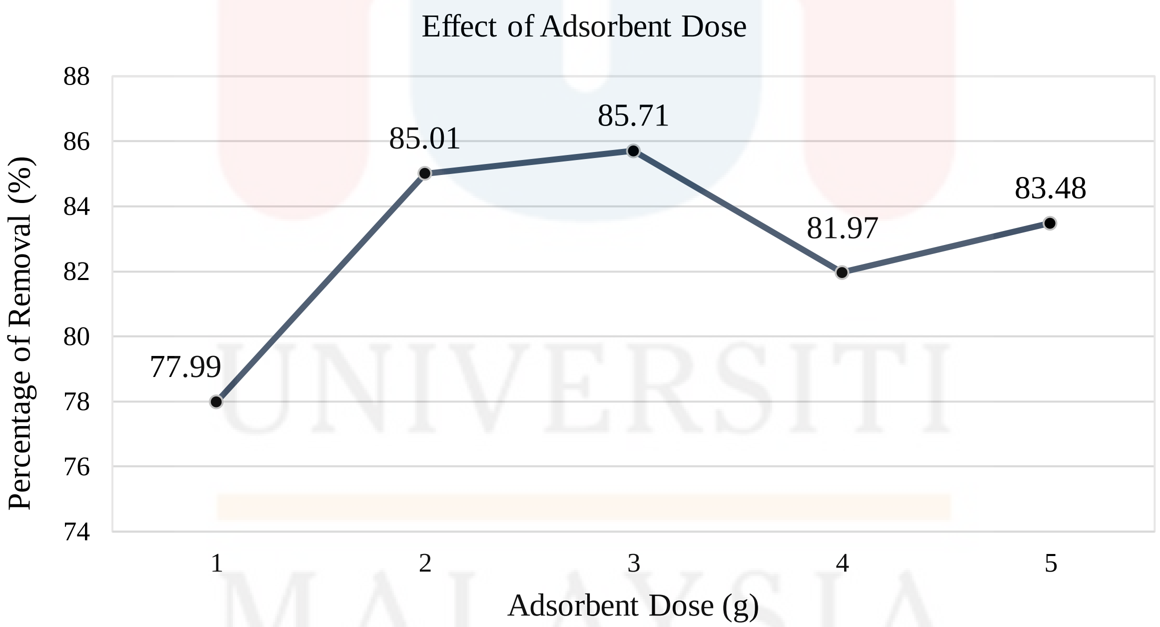


**Figure 4.2:** Effect of adsorbent dose for the removal of metamifop by activated carbon

The efficiency of the activated carbon for the adsorption of metamifop solution increases at the adsorbent dose of 1 g, 2 g and 3 g due to large surface area and has high availability of adsorption sites. However, the adsorption efficiency of the activated carbon were slightly decreases at the adsorbent dose of 4 g and 5 g. By increasing the adsorbent dose of activated carbon, the percentage removal of metamifop solution was found to decrease. This result indicates that the increased in the amount of adsorbent reduces the total surface area that is available for the adsorption of metamifop solution due to overlapping or aggregation on the sites of adsorbent (Julius & Joseph, 2013). At adsorbent dose of 4 g, the percentage removal of metamifop is slightly decreases compared to adsorbent dose of 5 g because the activated carbon was adhered at the wall of the conical flask which has reduced the efficiency of the activated carbon in removing the metamifop in the solution.

Adsorbent dose of 3 g recorded the highest percentage of metamifop removal which was 85.71% while adsorbent dose of 1 g recorded the lowest percentage of metamifop removal which was 77.99%. 3 g was chosen as the optimum adsorbent dose for the subsequent experiments.

**4.2.2 Effect of Contact Time**

The effect of the contact time on the adsorption efficiency of activated carbon from foxtail palm fruits for the removal of metamifop was conducted. In the experiment, activated carbon was loaded into the metamifop solution with different contact time of 30, 60, 90, 120 and 150 minutes. The initial adsorbent dose of activated carbon and the concentration of metamifop solution were fixed at 3 g and 10 ppm respectively. Figure 4.3 shows the effect of contact time on the removal of metamifop solution.

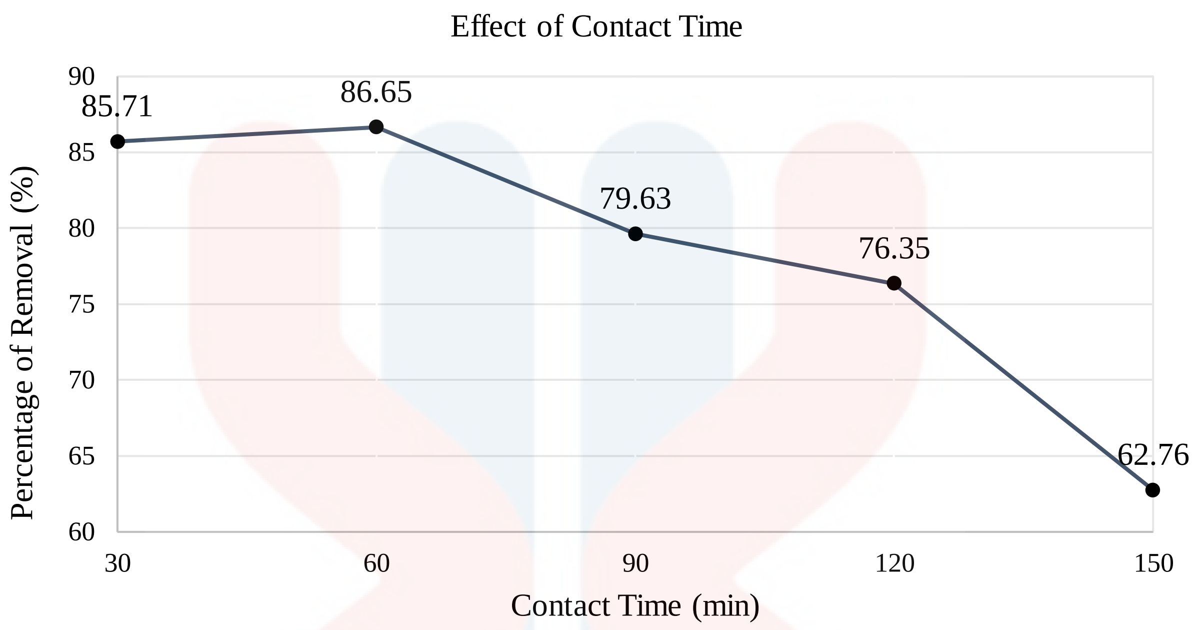


**Figure 4.3:** Effect of contact time on the removal of metamifop by activated carbon

The efficiency of the activated carbon for the adsorption of metamifop solution increases at the contact time of 30 minutes to 60 minutes. The metamifop solution was rapidly removed by the adsorption of activated carbon at the initial contact time due to the high availability of adsorption sites and strong attractive forces between the molecules of the metamifop and the adsorbent (Tesfaye & Semegn, 2014). However, The adsorption of metamifop by activated carbon become slower towards the final contact time. The adsorption efficiency were moderately decreases at the contact time of 90 minutes to 150 minutes. An equilibrium between the amount of metamifop adsorbed by the activated carbon and amount of metamifop that remained in the solution was not reached. This result indicates that the adsorbent sites were fully occupied by the metamifop molecules. The collision between the molecules of metamifop and the activated carbon become bigger as the contact time increases (Ahmad et al, 2014).

Contact time of 60 minutes recorded the highest percentage of metamifop removal which was 86.65% while contact time of 150 minutes recorded the lowest percentage of metamifop removal which was 62.76%. 60 minutes was chosen as the optimum contact time for the subsequent experiment.

### 4.2.3 Effect of Initial Metamifop Concentration

The effect of the initial metamifop concentration on the adsorption efficiency of activated carbon from foxtail palm fruits for the removal of metamifop was conducted. Activated carbon was loaded into the metamifop solution with different initial concentration of 10, 12, 14, 16 and 18 ppm. The initial adsorbent dose of and the contact time were fixed at 3g and 60 minutes respectively. Figure 4.4 shows the effect of initial metamifop concentration on the removal of metamifop by activated carbon.

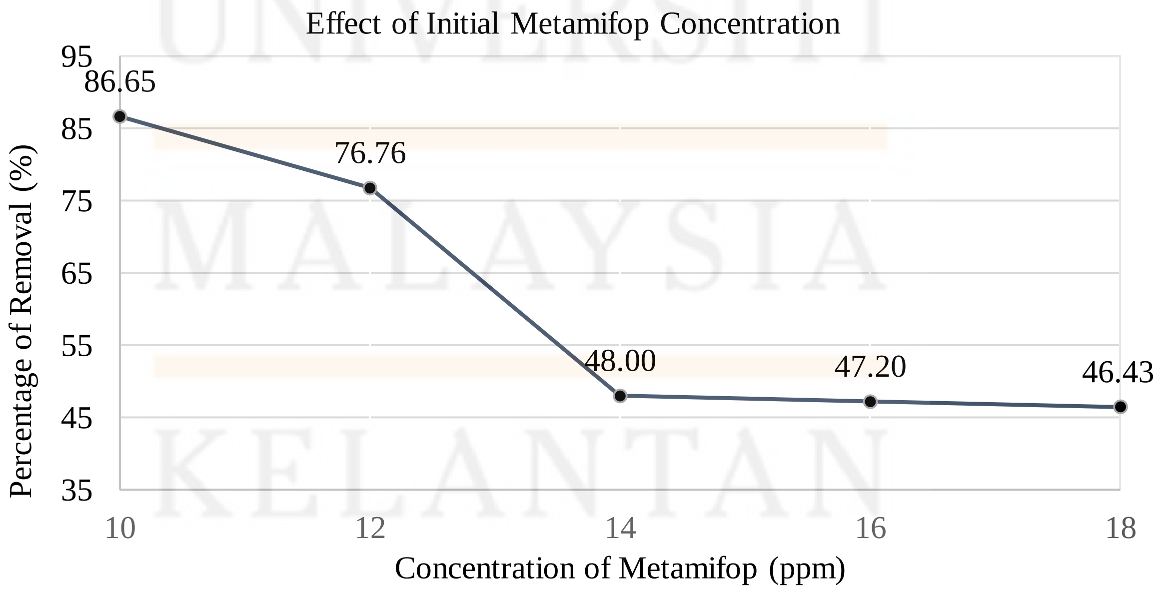


**Figure 4.4:** Effect of initial metamifop concentration on the removal of metamifop by activated carbon

The efficiency of the activated carbon for the adsorption of metamifop solution decreases as the initial concentration of metamifop solution increases. At the lowest initial concentration of metamifop which was 10 ppm, the metamifop molecules were easily adsorbed due to the larger surface area and the higher availability of adsorption sites of the activated carbon (Tesfaye & Semegn, 2014). Thus, the interaction between molecules of metamifop with the adsorbent made the available active sites on the surface of the activated carbon to fully occupied. At the highest initial concentration of metamifop which were 12 ppm, 14 ppm, 16 ppm and 18 ppm, the adsorption of metamifop by the activated carbon were restricted due to limited adsorption sites (Tesfaye & Semegn, 2014).

Initial concentration of metamifop at 10 ppm recorded the highest percentage of metamifop removal which was 86.65% while initial concentration of metamifop at 18 ppm recorded the lowest percentage of metamifop removal which was 46.43%. Thus, 10 ppm was chosen as the optimum initial concentration of metamifop that is efficient for the removal of metamifop by activated carbon made from foxtail palm fruits.

# CHAPTER 5

# CONCLUSION AND RECOMMENDATIONS

## 5.1 Conclusion

In this study, the activated carbon produced from the foxtail palm fruits through the chemical activation process with $HNO_3$ was utilized for the removal of metamifop. The effect of adsorbent dose, contact time and initial metamifop concentration toward the efficiency of prepared activated carbon in removing metamifop was conducted. From the study, the optimum adsorbent dose, contact time and initial metamifop concentration were obtained at 3 g, 60 minutes and 10 ppm respectively and has recorded the highest percentage of metamifop removal of 86.65%. Thus, based on the results of this study, the activated carbon produced from foxtail palm fruits have the potential to be commercialized for the treatment of water that has been contaminated with metamifop.

## 5.2 Recommendations

In this research, the efficiency of activated carbon produced from foxtail palm fruits for the removal of metamifop was studied. Based on the results, the activated carbon have the potential to be commercialized for the treatment of water that has been contaminated with metamifop. However, there are some recommendations that should be addressed to enhance the efficiency of activated carbon for a more significant result for future research. The first recommendation is to study the effect of other parameters such as temperature, pH value and the size of particle on the adsorption efficiency of the activated carbon in removing metamifop. Besides that, further study can be done on the characterization of the adsorbents using Scanning Electron Microscopy (SEM) to describe the morphology of activated carbon produced from the foxtail palm fruits. In future research, different chemicals can be utilized during the process of chemical activation such as zinc chloride or phosphoric acid to increase the effectiveness on the decomposition of the raw material structure and thus, producing a lot of micropores.

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# APPENDIX

## Appendix A: Calculation for the preparation of metamifop stock solution

To prepare 1000 ppm of metamifop solution, the total solution weight of Nominee-M was calculated as shown below. Nominee-M consists of 9.5% of metamifop as the active ingredient. Thus, (1000 ppm = 1000 mg/L = 1 g/L)

9.5% in 100% = 9.5 g in 100 g

$\frac{100\ g}{9.5\ g}$ = 10.5 g of Nominee-M formulation was required to prepare 1000 ppm from 9.5% of metamifop.

10.5 g of Nominee-M formulation was dissolved with 1000 ml of deionized water in 1000 ml volumetric flask. The stock solution was covered with aluminium foil and stored in the refrigerator at 4˚C to prevent the solution from degraded by the surrounding light.

Standard solution of metamifop was prepared from 1000 ppm of stock solution through dilution method. The standard solution was calculated as shown in the formula below,

$$M_1 V_1 = M_2 V_2$$

Where,

$M_1$ = Molarity of concentrated solution

$V_1$ = Volume of concentrated solution

$M_2$ = Molarity of diluted solution

$V_2$ = Volume of diluted solution

**Appendix B: Absorbance value of metamifop solution from UV-Visible Spectrophotometer**

Standard metamifop solutions of 2 ppm, 4 ppm, 6 ppm, 8 ppm, 10 ppm and 12 ppm were prepared for the selection of analytical wavelength. The standard solutions were scanned by the UV-Visible Spectrophotometer in the wavelength range from 200-800 nm. Based on the maximum wavelength, 500 nm was chosen for the analysis of metamifop. At 500 nm, a calibration curve (Figure 4.1) was generated which indicates the value of absorbance against the concentration of the metamifop at 2 ppm, 4 ppm, 6 ppm, 8 ppm, 10 ppm and 12 ppm. The data was collected for the calibration curve as shown in Table B1.

**Table B1**: The absorbance values of each concentration of metamifop solution (2-12 ppm)

| Concentration of metamifop (ppm) | Absorbance value (Abs) |
|---|---|
| Blank | 0.000 |
| 2 | 0.214 |
| 4 | 0.263 |
| 6 | 0.318 |
| 8 | 0.380 |
| 10 | 0.427 |
| 12 | 0.486 |

## Appendix C: Results on the percentage of metamifop removal

i. Effect of adsorbent dose

**Table C1:** Effect of adsorbent dose on the percentage removal of metamifop

| Adsorbent dose (g) | Initial absorbance | Final absorbance | Percentage of metamifop removal (%) |
|---|---|---|---|
| 1 | 0.427 | 0.094 | 77.99 |
| 2 | | 0.064 | 85.01 |
| 3 | | 0.061 | 85.71 |
| 4 | | 0.077 | 81.97 |
| 5 | | 0.069 | 83.48 |

ii. Effect of contact time

**Table C2:** Effect of contact time on the percentage removal of metamifop

| Time (min) | Initial absorbance | Final absorbance | Percentage of metamifop removal (%) |
|---|---|---|---|
| 30 | 0.427 | 0.061 | 85.71 |
| 60 | | 0.057 | 86.65 |
| 90 | | 0.087 | 79.63 |
| 120 | | 0.101 | 76.35 |
| 150 | | 0.159 | 62.76 |

iii. Effect of initial metamifop concentration

**Table C3:** Effect of initial metamifop concentration on the percentage removal of metamifop

| Initial concentration (ppm) | Initial absorbance | Final absorbance | Percentage of metamifop removal (%) |
|---|---|---|---|
| 10 | 0.427 | 0.057 | 86.65 |
| 12 | 0.482 | 0.112 | 76.76 |
| 14 | 0.550 | 0.286 | 48.00 |
| 16 | 0.625 | 0.330 | 47.20 |
| 18 | 0.672 | 0.360 | 46.43 |

## Appendix D: Process during experiments in the laboratory



**Figure D1:** Fresh foxtail palm fruits before being dried.

**Figure D2:** Foxtail palm fruits after being dried.

**Figure D3:** Sieved foxtail palm fruits powder.


**Figure D4:** Chemical activation of foxtail palm fruits powder using $HNO_3$.



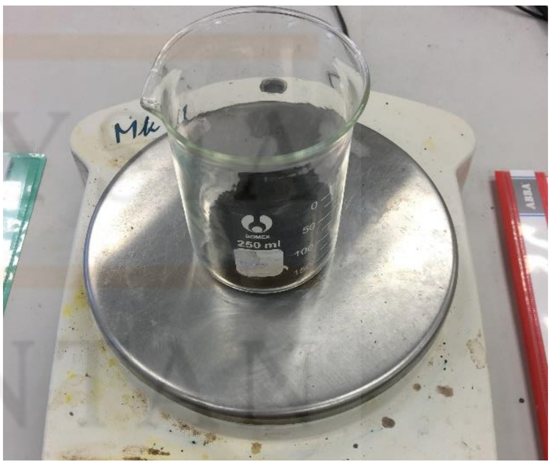


**Figure D5:** Carbonized carbon of chemically activated foxtail palm fruits powder.

**Figure D6:** Activated carbon.

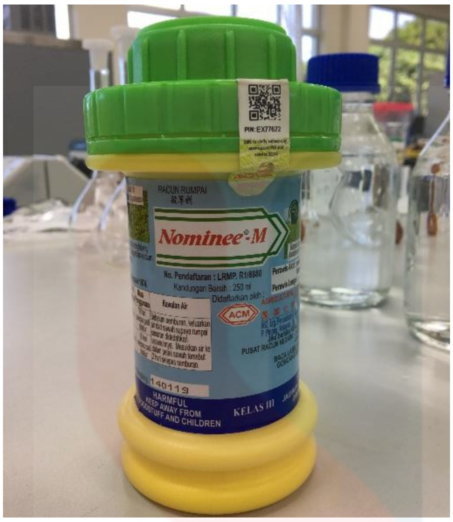


**Figure D7:** Nominee-M.

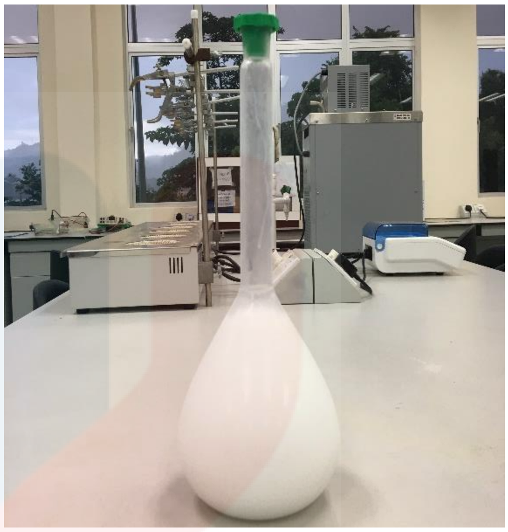

**Figure D8:** 1000 ppm of metamifop stock solution.

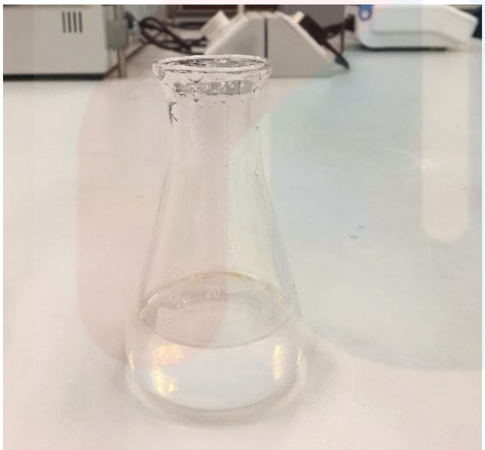

**Figure D9:** Diluted metamifop solution.


**Figure D10:** Metamifop after being treated by activated carbon.

**Figure D11:** Filtered activated carbon.

**Figure D12:** Filtrate of metamifop after being treated by activated carbon.