# OPTIMIZATION OF BIOCHAR YIELD USING HYDROTHERMAL CARBONIZATION USING RESPONSE SURFACE METHODOLOGY FOR THE ADSORPTION OF METHYLENE BLUE

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**THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SAFETY, HEALTH AND ENVIRONMENT ENGINEERING**

**FACULTY OF ENGINEERING**
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## ABSTRACT

The objective of this research study is to produce and optimise the biochar yield using DOE. In order to achieve the objective of this study, the treated separator sludge that had undergone submerged fermentation was added into a hydrothermal autoclave reactor to produce biochar with varying temperatures (150-220ºC) and holding times (0.5-2.0 hours) and the yield was calculated and tabulated. The biochar was then used to study the reduction efficiency of methylene blue solution with the concentration of 50mg/L. Based on the study, it was found that the optimised condition for this research work was at temperature 150ºC and holding time of 0.5 hours, where the yield produced was 74%. At these optimised conditions, adsorption studies with different concentration of methylene blue solution were conducted, where the reduction was above 90% and remained constant at 150mg/L, thereafter. As for the statistical analysis, the reaction temperature and the holding time shows significant reliability to the biochar yield produced as the p-values obtained was less than 0.05.

## ABSTRAK

Objektif penyelidikan ini adalah untuk menghasilkan dan mengoptimumkan hasil biochar dengan menggunakan DOE. Bagi mencapai matlamat kajian ini, biochar telah dihasilkan dengan menggunakan *hydrothermal autoclave reactor* pada suhu (150-220$^oC$) dan masa (0.5 – 2 jam) yang berbeza dan hasil biochar yang telah dihasilkan telah direkodkan. Seterusnya, biochar tersebut telah digunakan untuk mengkaji proses penjerapan dengan satu kepekatan (50mg/L) biru metilena. Berdasarkan hasil kajian ini, suhu dan masa yang optimum untuk menghasilkan biochar yang terbaik adalah pada 150$^oC$ dan 0.5jam, di mana pengeluaran biochar telah mencecah 74% dan ke-atas. Dengan menggunakan suhu dan masa optimum, proses penjerapan dengan beberapa kepekatan metilena biru telah dikaji, di mana 90% pengurangan pada metilena biru telah dicapai dan pada kepekatan selepas 150mg/L, pengurangan tersebut telah kekal malar. Bagi analisis statistic, suhu dan masa telah menunjukkan kesan saintifik dalam menghasilkan disebabkan nilai P (*p-value*) yang kurang dari 0.05.

## ACKNOWLEDGEMENTS

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# CHAPTER 1.0

# INTRODUCTION

## 1.1 Background of Study

Sludge from wastewater treatment plants is a nutrient-dense by-product (WWTP). The majority of the sewage produced there is moistened, transferred to landfills, or burned, emitting greenhouse gases and consuming nutrients. (Huezo et al., 2021). In accordance to Merzari et al. (2020), he had reported that sludge is a complex and universal compound of organic compounds such as proteins, peptides, polysaccharides, phenols, aliphatic, aromatic and furan compounds and nutrients (phosphorus, potassium, nitrogen), silica, heavy metals, pathogens and other microbial contaminants. He had also added that anaerobic digestion (AD) is the most widely used waste management technique. This technique converts organic solids to oxygen (mainly $CH4$ and $CO2$) by hydrolysis, acid formation, estogenesis and methanogenesis.

Heavy metals are produced in various industries, such as industrial production, sewage irrigation, agricultural activities, textile industries and many more. Toxic heavy metals in the environment pose a potential danger to the environment, public health and safety due to their toxicity and carcinogenicity according to Ii et al. (2015). Therefore, they must be removed from the aqueous solution before discharging. As stated by Suma et al. (2021), many methods can be used to treat dye effluents, including ozone oxidation, freezing, advanced oxygenation, and biological treatment. Among these methods mentioned, adsorption is not a complex process and has great potential in the treatment of dyes. Therefore, it is increasingly used for dye treatment in sewage.

Suma et al. (2021), had also reported that activated carbon is often used as a conventional adsorbent due to its high porosity, but its regeneration is more expensive, and losses its efficiency during regeneration. Recent studies had shown that some natural biomaterials that can accumulate high concentration of heavy metals on their body. In a recent study conducted by Jian et al. (2018), he had concluded that biochar, a solid end-product derived from the thermochemical conversion of biomass, has been used in wastewater treatment and contaminated soil restoration because of its high surface area, high porosity, cation exchange capacity, and pH buffering ability. There are various methods used for producing biochar such as gasification, microwave pyrolysis, carbonization, torrefaction, hydrothermal carbonization and many more. Hydrothermal carbonization (HTC) was chosen to produce the biochar in this research work. In pursuant to Jian et al. (2018), HTC is a thermochemical conversion of pre-treatment by placing the biomass in an inert atmosphere at temperatures of 180 to 280°C at a pressure of 2 to 10 MPa. At lower temperatures, hydrothermal carbonization generates more solid, while at higher temperatures, the solid yield is lower and the liquid oil is higher.

### 1.2 Problem Statement

Textile dyes are materials used to dye fabrics. Dyes were soaked in the fabric, chemically modify and reapply to stabilize the colour. Dyes can be synthetic, which means they were created using chemicals in a lab, or natural, which means they were created using natural materials. Adsorption is commonly used technique in removing dyes in the industrial phase. For the adsorption process, despite using biomass waste as a viable source of adsorbent, using bio-sludge from the wastewater streams could be another option, but due to the complexity of the structure, it was always neglected. The use of solids in the soil can be an important cause of greenhouse gas emissions and pollutants from mercury, lead, cadmium and copper on agricultural land, which contribute to the acidification of the environment. Microbial processes in sewage sludge leads to significant emissions of methane and nitroxide, as well as ammonia and nitrates. And the most frequently used technique to produce the biochar is the fast pyrolysis method such as the gasification process. The disadvantages of the gasification process are low yield produced at a shorter time span and requirement of high temperatures (700ºC - 900ºC) where it poses high energy requirement. Moreover, when dealing with high temperatures, the safety is the most concerned topic discussed as the safety measures should be taken care of at every usage.

**1.3 Objectives of Study**

The objectives of this research work are:

- To produce and optimize the biochar yield using DOE.
- To analyse biochar adsorption quality using methylene blue using Annova Analysis.
- To characterize the biochar produced.

**1.4 Scope of Study**

In order to achieve the objectives stated, the following parameters should be considered. The main parameters are:

- Temperature: 150-220ºC
- Holding/Residence Time: 0.5-2.0 hours

**1.5 Limitation of Study**

In this research work, the particle size was fixed throughout all the experimental runs. The particle sized was fixed throughout as it creates a porous structure which enables the adsorption process to function efficiently. A porous structure leads to better efficiency of the adsorption process; besides it had enabled the sorption process to give desire results and complete reduction of methylene blue was obtained

# CHAPTER 2.0

# LITERATURE REVIEW

## 2.1 Introduction to Oil Palm Industry in Malaysia

According to Basiron (2007), the Malaysian oil palm industry is one of the most well-organized sectors of any national agriculture system in the world. Palm oil is a major source of sustainable and renewable raw material for the food, oleochemical, and biofuel industries worldwide. The oil palm is credited with its high oil yield per unit area. It produces two types of oils from the same fruit which are palm oil from the flesh or mesocarp and palm kernel oil from the seed or kernel inside the hard-shell mesocarp. Many other biomass products generated by the oil palm plantations are often under-utilised commercially. Mills regularly generate large quantities of fibre-type products in the form of empty fruit bunches (EFB). Some amount of the fruit fibre and the kernel shell are burnt in boilers to generate steam and electricity for the mills. As the oils form about 10% of the total dry biomass produced by the palm, the other 90% of the biomass represents a further huge source of fibre and cellulosic materials which awaits further commercial exploitation. It has benefited citizens through annual foreign exchange earnings of some RM30 billion or about US$8 billion. The oil palm, being eco-friendly by its very nature, is a highly productive crop. Oil palm cultivation also uses comparatively less land to supply oils and fats for food and non-food uses, including biofuel, for the world.

## 2.2 Bio-Char from Bio-Sludge

Biochar is carbon-rich charcoal formed by thermal pyrolysis (300ºC-700ºC) of biomass (organic materials) under low or no oxygen conditions, according to Shiralian (2016). The process is similar to backing rather than burning or incinerating, that's why it also produces mixture of organic gaseous (syngas). Biochar is a key solid with very large pores and a surface structure that provides better habitat for microorganisms, increases bioavailability and is expected to rot for hundreds of years into an excellent reservoir for food and water pollutants. Bio-char also reduces the risk of crop yields during draughts, filters out contaminants from shallow soil water, reduces the need for chemical fertilizers containing nitrogen and phosphorus, removes heavy metals and acids from abandoned mines ponds, bind toxins and prevent their leaching into surface and ground water, facilitates the reestablishment of vegetation on typically sterile ground, inhibits the growth of moulds or mildews, retains nitrogen and sulphurs in soil , and reducing emissions of nitrogen oxide and sulphur oxides into the atmosphere (greenhouse effect reduction), and odor control.

Precisely, biochar produced from bio-sludge had deeply impacted the chemical characteristics of biochar. Similarly, studies have concluded that thermal decomposition of biosolids at 300 ° C increases the yield due to the decrease in molar ratios of H / C, O C / and N / C in the production of biochar which leads to the aromatization in the structure. Besides that, it is possible to make biochars from bio-sludge that are suitable for use in acidic or alkaline soils by adjusting the pyrolysis temperature.

## 2.3 Conversion of Various Agro-Waste into Biochar

As known, production of biochar had various approaches till date. Some of the known approaches are gasification process, microwave pyrolysis, torrefaction and others. All these stated approaches are operated in a stipulated conditions/parameter. Table 2.1 shows the different approaches by researchers to produce biochar from different biomass wastes.

**Table 2.1: Review of Various Approaches in Conversion of Biomass into Biochar**

| Technique Used | Waste Involved | Operating Conditions/Parameters | Yield Produced (%) | Author (Year) |
|---|---|---|---|---|
| Carbonization Process | POME | - Purified Nitrogen Flowrate: 300ml/min<br>- Pyrolysis Temperature: 300-600ºC<br>- Holding Time: 60-180 min | 80 | (Bashir et al., 2017) |
| Pyrolysis | Sewage Sludge of Concentrated Natural Rubber Latex | - Temperature: 300-700ºC<br>- Heating rate: 10 ºC/min | 85 | (Phoungthong & Suwunwong, 2020) |
| Pyrolysis | Kitchen Waste Residue | - Pyrolysis Temperature: 300-600 ºC<br>- Heating rate: 4 ºC/min<br>- Nitrogen flow is | 87 | (C. Xu et al., 2021) |

| | | | | |
|---|---|---|---|---|
| | | constant. | | |
| Carbonization | Sterculia Foetida | - Pyrolysis Temperature: 500 ºC ± 2 ºC for 2 hours.<br>- Oven-dried: 100 ºC (overnight) | 90 | (Barman et al., 2021) |
| Pyrolysis | Aqueous Solution of Rice Husk | - Purified Nitrogen (99.995%)<br>- Flow Rate: $100cm^3/min$<br>- Heating Rate: 7 ºC/min | 85 | (Saeed et al., 2021) |
| Microwave Pyrolysis | Olive Pomace | - Temperature: 900ºC<br>- $N_2$ flowrate: 100ml/min | 75 | (Kostas et al., 2019) |
| Microwave Pyrolysis | Rice Husk | - $N_2$ gas: 0.2L/min for 15 mins<br>- Power: 900W, | 75 | (Shukla et al., 2019) |

| | | | | |
|---|---|---|---|---|
| | | Temperature: 600ºC | | |
| Microwave Pyrolysis | Corn Cob | - Time: 5 mins & 10 mins<br>- Power: 450W & 700W | 73 | (Lawas et al., 2019) |
| Microwave Pyrolysis | Coconut Shell | - Power: 550W, 600W, 650W<br>- Time: 15-25 mins | 76 | (Nuryana et al., 2020) |
| Microwave Pyrolysis | Oil Palm Fiber | - Power: 800W<br>- Frequency: 2.45 GHz<br>- $N_2$ gas: 1-10 L/min | 75 | (Abas et al., 2018) |
| Microwave Heating | Oil Palm Shell | - Power: 300W, 450W, 600W<br>- $N_2$ gas: 5 L/min | 74 | (Moshood & Nasir, 2015) |
| Microwave Pyrolysis | Sewage Biosolids | - Power: 600W<br>- Temperature: 600ºC<br>- $N_2$ gas: 99% purity; unknown flowrate | 74 | (Antunes et al., 2017) |

| | | | | |
|---|---|---|---|---|
| | | - Frequency: 2.45 GHz | | |
| Microwave Pyrolysis | Oil Palm Fibers | - Temperature: 450ºC-700 ºC<br>- Power: 400W-900W<br>- $N_2$ gas: 200-1200 $cm^3$/min | 76 | (Arafat Hossain et al., 2017) |
| Microwave Pyrolysis | Olive pruning residue | - Power: 3 kW<br>- Temperature: 450ºC – 705ºC<br>- Time: 15-36 mins | 73 | (Bartoli et al., 2019) |
| Microwave Pyrolysis | Water Hyacinth | - Power: 0.8MW, 0.86MW, 0.9MW, 0.95MW<br>- Temperature (ºC): 300, 480, 580, 680<br>- Biomass to Microwave Absorber Ratio | 70 | (Abd et al., 2018) |

| | | | | |
|---|---|---|---|---|
| | | - Particle Size (mm) | | |
| Microwave Pyrolysis | Rice straw, rice husk, corn stover, sugarcane bagasse, sugarcane peel, waste coffee grounds, and bamboo leaves | - $N_2$ gas: 50 mL/min<br>- Power: 500 W<br>- Temperature: 45 °C to 300 °C | 75 | (Lo et al., 2017) |
| Microwave Carbonization | Agricultural Wastes | - Power: 1000W<br>- Frequency: 2450Hz<br>- $N_2$ gas: 100 mL/min<br>- Temperature: : 245 °C to 390 °C | 75 | (Wahi et al., 2015) |
| Microwave Pyrolysis | Softwood chips (spruce–fir mix) & Hemp stalk | - Power: 2100, 2400, and 2700 W<br>- Operating time: 10 mins | 77 | (Wallace et al., 2019) |

## 2.4 Hydrothermal Carbonization/Hydro char

Hydrothermal carbonization (HTC) is a thermochemical pretreatment technology that uses hot compressed water to produce hydrochar from biomass as stated by Reza et al. (2014). Adding on, Reza et al. (2014), had also  that, in 1958, Leibniz was the first to explain the theory of HTC utilising hot compressed water. He demonstrated the significance of water in the reaction. Besides that, he discovered that Van Krevelen demonstrated that different plant species may yield different lithotypes in coal and that the medium had an effect on the result. Putra et al., (2018) had defined HTC as a thermochemical process that mimics the natural coalization of biomass. He had also added that HTC is formed via a series of reactions that include hydrolysis, condensation, decarboxylation, and dehydration. Besides, in terms of sustainability, not only the process temperature but also the type of feedstock must be taken into account. Many researchers have debated the use of the HTC process to various types of biomass/bio sludge. Table 2.1 and 2.2 discusses on various optimization studies conducted by using numerous biomass/biosludge using different types of pyrolysis methods to produce biochar/hydrochar.

**Table 2.2: Optimization Study of Different Biomass/Bio sludge Using Hydrothermal Carbonization Process to Produce Biochar**

| Biomass/ Sludge | Input | Output | Author (Year) |
|---|---|---|---|
| A-SS, T-SS (sludge) from Southern Spain | T: 200 ºC, 260ºC<br>H.T: 0.5h and 3h | a) 200 ºC<br>→ High plant growth, Less energy consumption | (Paneque et al., 2019) |
| EFB | T: 150 ºC-350 ºC<br>H.T: 1h | a) 300 ºC<br>→ High Yield, Heating Value is high | (Inoue, 2010) |
| Banana Peel | T: 190 ºC, 210 ºC, 230 ºC<br>H.T: 1h, 0.5h | a) 190 ºC<br>→Yield = 64.21 | (Putra et al., 2018) |
| Eucommia ulmoides | T: 180 ºC - 320 ºC<br>H.T: 0.5h | a) Required low temperature<br>b) Yield of HC drops after 260 ºC | (Y. Wang et al., 2019) |
| Municipal Sewage | T: 180 ºC, 240 ºC, | a) Sludge hydrochar yields drops from | (F. Wang et al., 2021) |

| | | | |
|---|---|---|---|
| Sludge | 300 °C<br>H.T: 2h, 6h, 10h, 15h | 81.8% of $HC_{180-2}$ to 65.9% of $HC_{300-15}$. | |
| Urban sludge | T: 180 °C, 210 °C, 240 °C, 270 °C, 300 °C | a) Yield decreases at 300 °C to 52.65%.<br>b) At 180 °C, the yield is 92.04% | (X. Xu & Jiang, 2017) |
| Sewage sludge | T: 200 °C - 300 °C<br>H.T: 0.5h -8h | a) Hydrochar at 260 °C – 4h had maximum 26.23 MJ/kg with highest energy density 1.43. | (H. Zhang et al., 2021) |
| Sewage sludge | T: 180, 200, 220, and 240 °C<br>H.T: 3h | a) The optimal condition for dewatering sludge was pH = 5.0 and residence time of 4 h at the reaction temperature of 180 °C.<br>b) Hydrothermal carbonization time higher than 4 h and reaction temperature higher than 180 °C did not improve sludge dewatering performance. This was due to the fact that sludge broke down more thoroughly at this time and temperature, and although the viscosity of sludge started to decrease, the sludge particles were very fine and clogged the | (Jian et al., 2018) |

| | | | |
|---|---|---|---|
| | | filter. Therefore, sludge dewatering performance deteriorated. | |
| Barley, Maize, Sewage | T: 200ºC<br>H.T: 6h | a) HTC increased carbon contents and higher heating values (HHV) by 1.4–14.4% and 13–36%, respectively.<br>b) The evolution of the H/C and O/C atomic ratios indicated that dehydration and decarboxylation occurred during hydrothermal carbonization for all samples.<br>c) Furthermore, a significant synergistic enhancement was observed for HHV and carbon content. | (Seyedsadr et al., 2018) |
| Date Seeds | Biomass/ Water Ratio: 1/10<br>H.T: 40-140 min<br>T: 200-600ºC | a) The optimized hydro char (OHC-Ds) was obtained under optimal conditions (200°C,120 min, 20 mg) and characterized by a mass yield (%) and carbon retention rate (%) of 59.71% and 75.84%, respectively. | (El Ouadrhiri et al., 2021) |
| Anaerobic Digested Effluent | T: 180-260 ºC<br>H.T: 30-70 mins | a) Hydrochar yields from ADE at original and modified pH ranged from 70 to 80% and 62% to73%, respectively. | (Huezo et al., 2021) |

| | | | |
|---|---|---|---|
| | | b) Higher temperatures resulted in lower hydrochar and liquor yields. The obtained hydrochar had a low carbon content, high ash content, high H/C ratio, and low higher heating value, suggesting that it has little potential as solid fuel, and more potential as soil amendment.<br>c) The liquor's composition and chemical oxygen demand indicate a potential for recirculation into anaerobic digestion. | |
| Lemon Peels | T: 180, 220, 250 ºC<br>H.T: 1h | a) PW recirculation led to a solid mass yield increase and the effect was more pronounced at lower HTC temperature.<br>b) The increase of solid mass yield, after recirculation steps (maximum increase of about 6% at 180 C), also led to a significant energy yield enhancement. | (Picone et al., 2021) |
| Microalage | T:200 ºC | a) Employing relatively moderate conditions of temperature (ca. 200 _C), time (<1 h) and pressure (<2 MPa), microalgae can be converted in an energy efficient manner into an algal | (Heilmann et al., 2010) |

| | | | |
|---|---|---|---|
| | | char product that is of bituminous coal quality. | |
| Rice husk | T:200 ºC<br>H.T: 7h | a) The results reveal that the prepared hydro chars have carbon contents ranging from 45.01 to 58.71%, BET specific areas between 13.23 and 45.97 m2/g, and rich O-containing functional groups on the surfaces. | (Y. Li et al., 2021) |
| Harvested Wheat Straw | T: 180, 220, 250 ºC<br>H.T: 10,20,30 mins | a) The results indicated that the carbon microspheres appeared on the surface of hydrochar from 220 °C for 10 min.<br>b) The combustion characteristics under 180 and 220 °C were better than those under 260 °C. The slagging tendency of hydrochar pellets was lower than that of wheat straw pellets.<br>c) Activation energies were moderate under 220 °C for 10, 20, and 30 min.<br>d) Hydrochar pellets had high fuel efficiency under 220 °C for 10, 20, and 30 min. | (X. Zhang et al., 2020) |
| Spent coffee | T: 180 to 220 ºC<br>H.T: 1-5 hours | a) At optimal conditions of 216ºC and 1hr, guided by the RSM, a maximal | (Afolabi et al., 2020) |

| | | | |
|---|---|---|---|
| grounds | | hydrochar yield of 64% and a calorific value of 31.6 MJ/kg are feasible. | |

## 2.5 Challenges

Biochar's prospects are theoretically viable and attractive, but the path to full technological and market maturity is still a long way off. As a recent article published by Golisano Institute for Sustainability (January, 2021), had mentioned that the challenges can be grouped into 2 prospects; policy and logistics.

Policy

Any technology's viability is strongly reliant on the existence of supportive regulations that allow it to flourish and mature. This is especially true in the realm of thermochemical-conversion technology, which is still in its infancy in terms of sustainability. Among enthusiasts of bioenergy with carbon capture and storage, thermochemical processing has garnered the most traction (BECCS). When it comes to rewarding climate-friendly economic growth, BECCS is a catch-all term for "negative-emission" processes and technologies. Many policymakers are looking to BECCS as an alternative to carbon-credit trading ("cap and trade") or carbon taxes. Biochar is an ideal use of BECCS, according to proponents of sustainable thermochemical conversion, because it both sequesters carbon and turns otherwise troublesome waste into economic value. As part of a BECCS strategy, other thermochemical conversion technologies, such as gasification, can be integrated with biological processes, such as anaerobic digestion. The Climate Leadership and Community Protection Act of 2019 (CLCPA) in New York State, for example, states that the state's efforts must incorporate bioenergy and BECCS technologies. While low- or zero-carbon fuels like biogas and biodiesel can be produced by gasification and anaerobic digestion, the CLCPA does not accept pyrolysis as a BECCS method. Biochar proponents are concerned that this will have a knock-on effect, leaving biochar out of any policy resulting from the bill, despite the fact that it might provide significant benefits.

Logistics

When deciding where to locate facilities, regional geography is very significant. Poultry manure, for example, contains a significant amount of phosphorus that can be retrieved indefinitely through thermochemical conversion (rather than mined). Phosphorus has a market: large-scale farmers rely on it for their crops. Biochar-based goods' potential value must be matched to manufacturing capacity and market demand. It's a balancing act that all firms face, but it's more difficult when developing new, sustainable technologies. In order to provide value to consumers and businesses up and down the supply chain, thermochemical conversion plants must be equipped with technology that allows them to be flexible in what they create. In reality, this may mean making biochar for farmers to utilise in their soil while also being able to "upgrade" it into activated carbon for industrial use.

**2.6 Sustainable Application of Biochar**

Biochar has emerged as a very promising solution for effectively addressing multiple multifaceted concerns. In parallel with this statement, Kumar & Bhattacharya (2021) had stated that biochar helps to minimize heavy metal pollution by reducing the bioavailability of heavy metals in soil and water. Thus, it improves the quality of contaminated soil and water at the same time. Besides, Biochar has been found to help combat climate change by removing co2 from the atmosphere and reducing greenhouse gas emissions like nitrous oxide and methane. It can help with biofuel production, hence reducing the demand for fossil fuels.

Furthermore, the use of biochar can help to improve soil productivity, which is necessary for increasing crop yield. However, according to Jatav et al. (2021), The real impact of this amendment is determined by the type of biochar used, the production conditions, the soil condition, and the amount of biochar used. The biochar's internal surface has a negative electrical charge, which works as a cation exchange resin, attracting metal cations from the soil solution. As a result, the concentration of metal and organic pollutants in soil might be efficiently lowered. In addition, biochar helps to improve the fertility status of the soil. This was well explained by Jatav et al. (2021), whereby he had stated that when compared to commercial fertilisers, solid digestate formed during anaerobic digestion provides a possible feed stock for making biochar, which is effective in boosting and maintaining soil fertility while creating high soil organic matter and providing long-term micronutrient release.

**2.7 Chapter Conclusion**

In a nutshell, this research work is mainly on producing biochar using hydrothermal carbonization process from fermented separator sludge. Based on the previous research works that had been discussed, these studies had been chosen to study the removal efficiency of methylene blue as no research had been studied using treated separated sludge and its removal efficiencies.

# CHAPTER 3.0

# RESEARCH METHODOLOGY

## 3.1 Flowchart of Experimental Procedure

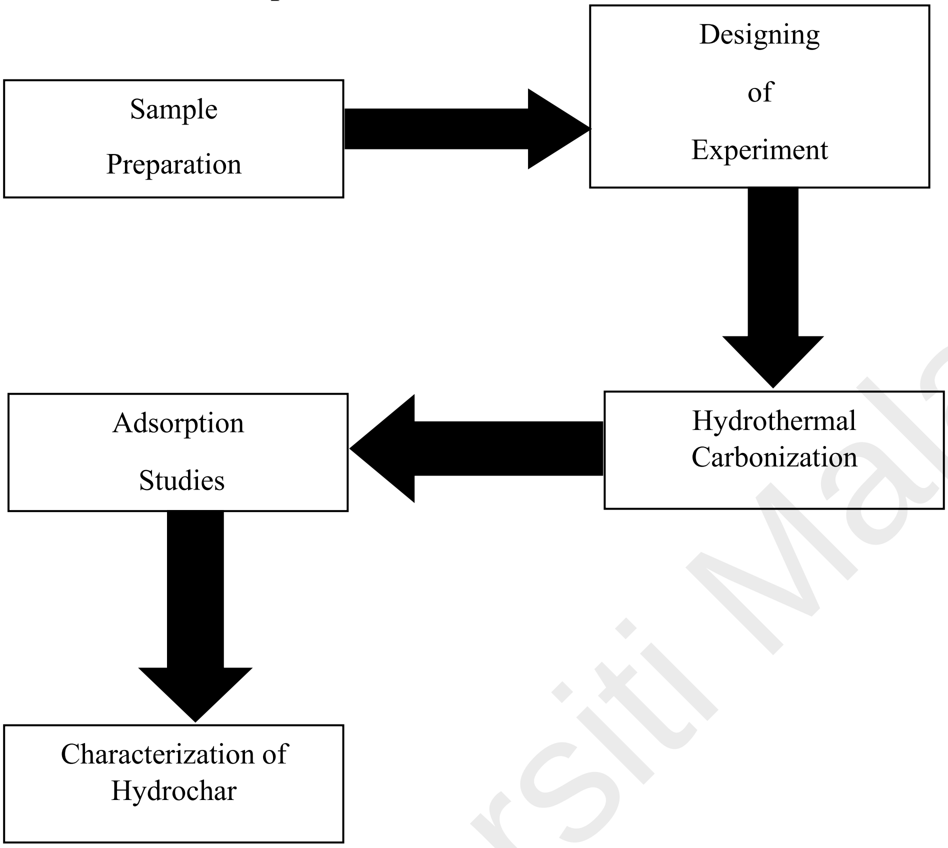



**Figure 3.1: Experimental Procedure**

## 3.2 Materials and Apparatus

**Table 3.1: Materials and Apparatus/Equipment Used**

| Materials | Apparatus/Equipment |
|---|---|
| • Treated Separator Sludge<br>• Methylene Blue<br>• Distilled Water | • Oven<br>• Hydrothermal Autoclave Reactor<br>• Teflon Chamber<br>• Spatula<br>• Volumetric Flask |

| | |
|---|---|
| | • UV-Vis Spectrophotometer<br>• Analytical Balance<br>• pH meter<br>• Centrifugal tubes<br>• Conical Flasks<br>• Beakers<br>• Filter Papers<br>• Filter Funnels<br>• Pipette |

### 3.3 Sample Preparation

The fermentation process was carried out in conical flask with a volume of 250 ml with 100ml of fermentation medium (separator sludge). 1 ml of Aspergillus niger spore suspension was injected into each flask and incubated in a rotary shaker at 37 ° C at 100 rpm for 6.5 days. The fermented broth was collected and centrifuged at 10,000rpm for 15 minutes at 4°C. The solid obtained was used to make biochar.

### 3.4 Designing of Experiment

DoE- Version 13 was used to fit a response, primarily hydrochar yield, as a function of two parameters, namely HTC reaction temperature (ºC), and residence time (hours), using a faced-centred central composite factorial design (FCCD). To provide excellent prediction and improve model reliability, the CCF design included a total of 13 runs: four factorial points, four axial points, and five centre points. The temperature of the carbonisation reaction (Factor A) was thus marked as 150°C, 185°C, and 220°C, while the residence temperature (Factor B) was coded as 0.5h, 1.25h, and 2h. Figure 3.2 shows the experimental runs that had been designed for this research work whereas Table 3.2 shows the yield produced according to the experimental runs proposed by the software.

| Std | Run | Factor 1 A:Temperature C | Factor 2 B:Holding Time hour |
|---|---|---|---|
| 12 | 1 | 185 | 1.25 |
| 4 | 2 | 220 | 2 |
| 9 | 3 | 185 | 1.25 |
| 5 | 4 | 150 | 1.25 |
| 1 | 5 | 150 | 0.5 |
| 11 | 6 | 185 | 1.25 |
| 6 | 7 | 220 | 1.25 |
| 10 | 8 | 185 | 1.25 |
| 3 | 9 | 150 | 2 |
| 8 | 10 | 185 | 2 |
| 7 | 11 | 185 | 0.5 |
| 13 | 12 | 185 | 1.25 |
| 2 | 13 | 220 | 0.5 |
| 14 | 14 | 185 | 1.25 |
| 15 | 15 | 220 | 2 |
| 16 | 16 | 185 | 1.25 |
| 17 | 17 | 150 | 1.25 |
| 18 | 18 | 150 | 0.5 |
| 19 | 19 | 185 | 1.25 |
| 20 | 20 | 220 | 1.25 |
| 21 | 21 | 185 | 1.25 |
| 22 | 22 | 150 | 2 |
| 23 | 23 | 185 | 2 |
| 24 | 24 | 185 | 0.5 |
| 25 | 25 | 185 | 1.25 |
| 26 | 26 | 220 | 0.5 |
| 27 | 27 | 185 | 1.25 |
| 28 | 28 | 220 | 2 |
| 29 | 29 | 185 | 1.25 |
| 30 | 30 | 150 | 1.25 |
| 31 | 31 | 150 | 0.5 |
| 32 | 32 | 185 | 1.25 |
| 33 | 33 | 220 | 1.25 |
| 34 | 34 | 185 | 1.25 |
| 35 | 35 | 150 | 2 |
| 36 | 36 | 185 | 2 |
| 37 | 37 | 185 | 0.5 |
| 38 | 38 | 185 | 1.25 |
| 39 | 39 | 220 | 0.5 |

**Figure 3.2: Proposed Total Runs based on DOE**

**Table 3.2: Biochar Yield Produced**

| Temperature (°C) | Holding Time (hour) | W1 (g) | Y1 (%) | W2 (g) | Y2 (%) | W3 (g) | Y3 (%) |
|---|---|---|---|---|---|---|---|
| 150 | 0.5 | 0.5553 | 76.96 | 0.5547 | 76.88 | 0.5545 | 76.85 |
| | 1.25 | 0.5228 | 72.46 | 0.5215 | 72.28 | 0.5203 | 72.11 |
| | 2.0 | 0.5113 | 70.87 | 0.5106 | 70.77 | 0.5104 | 70.74 |
| 185 | 0.5 | 0.5068 | 70.24 | 0.4998 | 69.27 | 0.498 | 69.02 |
| | 1.25 | 0.4182 | 57.96 | 0.4041 | 56 | 0.4027 | 55.81 |
| | 1.25 | 0.4039 | 55.98 | 0.3972 | 55.05 | 0.3968 | 55 |
| | 1.25 | 0.4024 | 55.77 | 0.401 | 55.58 | 0.4007 | 55.54 |
| | 1.25 | 0.4021 | 55.73 | 0.4003 | 55.48 | 0.4001 | 55.45 |
| | 1.25 | 0.4116 | 57.04 | 0.411 | 56.96 | 0.4005 | 55.51 |
| | 2.0 | 0.4736 | 65.64 | 0.4651 | 64.46 | 0.4649 | 64.44 |
| 220 | 0.5 | 0.5437 | 74.54 | 0.5427 | 74.53 | 0.5426 | 74.53 |
| | 1.25 | 0.4829 | 66.93 | 0.4815 | 66.74 | 0.4801 | 66.54 |
| | 2.0 | 0.4675 | 64.8 | 0.4643 | 64.35 | 0.422 | 58.49 |

### 3.5 Hydrothermal Carbonization

The hydrothermal reactor consisted of a 100ml stainless steel stirred and a pressurized reactor was used to produce the biochar. To control the reaction, the method's reaction temperature and holding time were manipulated. About 10 g of wet sludge (with 90% moisture content) was mixed with 70 ml of distilled water (ratio of wet sludge to distilled water = 1:7) and thoroughly mixed to ensure consistent mixing of the mixtures. According to the randomise run proposed by FCCD, Temperatures of 150, 185, and 220ºC were set. The reaction was carried out in triplicate for 0.5, 1.25, and 2.0 hours at each temperature which was proposed by FCCD. To cool down the reactor, the heater was turned off when the reaction was done. Once the temperature had cooled to room temperature, the reactor was opened to collect the solid and liquid products. The solid product (hydrochar) was filtered using filter paper. With about 150ml of distilled water, the contaminants in the hydrochar were removed by extensive washing. The hyrochar was then dried at 60°C for overnight. After the drying process, the hydrochar was weighed to calculate the yield produced. The hydrochar yield was calculated using the formula proposed by Picone et al. (2021):

$$Hydrochar\ Yield\ (\%) = \frac{Dry\ Weight\ (g) of\ Hydrochar}{Dry\ Weight\ (g) of\ Sludge}$$ ..................Picone et al. (2021)

### 3.6 Adsorption Studies

#### 3.6.1 Standard Methylene Blue Calibration Curve

A stock solution of 1000 mg/L of methylene blue solution was prepared in a volumetric flask. Various concentrations of methylene blue solution, ranging from 20 mg/L to 400 mg/L was prepared. A UV-Vis Spectrophotometer was calibrated to wavelength 664 nm was used to measure the absorbance of methylene blue. The recorded absorbance from the spectrophotometer was plotted against the prepared solution concentration to create a standard curve.

#### 3.6.2 Adsorption Studies of Methylene Blue

For roughly an hour, 10ml of 50mg/L methylene blue solution was agitated with 0.2g of hydrochar at 100 rpm. The solution was set to rest after the agitation process. A filter paper was then used to filter the solution. The absorbance of the remaining methylene blue solution was determined using the UV-Vis Spectrophotometer at the wavelength of 664nm.

### 3.7 Characterisation of Biochar

In line with Lee et al. (2019), SEM-EDX was used to study the surface morphology of hydrochar samples. The elements distribution on the samples' surface was studied using the integrated EDX detector. With the use of a razor blade, a little amount of dried hydrochar was cut into the desired shape before being evenly dispersed onto a carbon conductive pad on top of an aluminium stub. The stubs were placed on a sample rack in the microscope test chamber. An electron beam of 15kV was used to create images of the hydrochar.

According to (Li et al. (2021), a Fourier transform infrared spectrometer was used to investigate the sample's functional group structure. Under the equipment, wavenumber scanning was performed in the range of 4000–400 $cm^{-1}$. The samples' microcrystalline structures were determined using X-ray diffraction.

# CHAPTER 4.0

# RESULTS AND DISCUSSIONS

## 4.1 Design of Experiment (DOE)

### 4.1.1 Annova Analysis

This study's design allowed us to explore the impact of temperatures on the hydrothermal treatment of treated sludge throughout a range of residence times. As reported by Xu et al. (2018), had revealed that the reaction temperature and residence time largely determined the rate of hydrothermal carbonization reactions. He also stated that temperature has the greatest impact on hydrothermal carbonization solid yield and carbonization. This had been illustrated in Figure 4.1 from the information extracted from the DOE software.

**Response 1: Biochar Yield**

| Source | Sum of Squares | df | Mean Square | F-value | p-value | |
|---|---|---|---|---|---|---|
| **Model** | 2473.36 | 5 | 494.67 | 69.64 | < 0.0001 | significant |
| A-Temperature | 58.39 | 1 | 58.39 | 8.22 | 0.0072 | |
| B-Holding Time | 394.90 | 1 | 394.90 | 55.60 | < 0.0001 | |
| AB | 94.64 | 1 | 94.64 | 13.32 | 0.0009 | |
| $A^2$ | 765.33 | 1 | 765.33 | 107.75 | < 0.0001 | |
| $B^2$ | 439.03 | 1 | 439.03 | 61.81 | < 0.0001 | |
| **Residual** | 234.40 | 33 | 7.10 | | | |
| Lack of Fit | 198.59 | 3 | 66.20 | 55.45 | < 0.0001 | significant |
| Pure Error | 35.81 | 30 | 1.19 | | | |
| **Cor Total** | 2707.76 | 38 | | | | |

**Figure 4.1: Reliability of Operating Parameters**

From the figure it can be deduced that, both the operating parameters which had been varied throughout the experiment, had a significant impact on producing a greater biochar yield using hydrothermal treatment. This is because both the p-values obtained for both of the operating parameters, are less than 0.05 which indicates that the model of study is significant.

### 4.1.2 Model Graphs

Figure 4.2 shows the response surface plot obtained biochar yield produced illustrating the impact of reaction temperature and residence time.

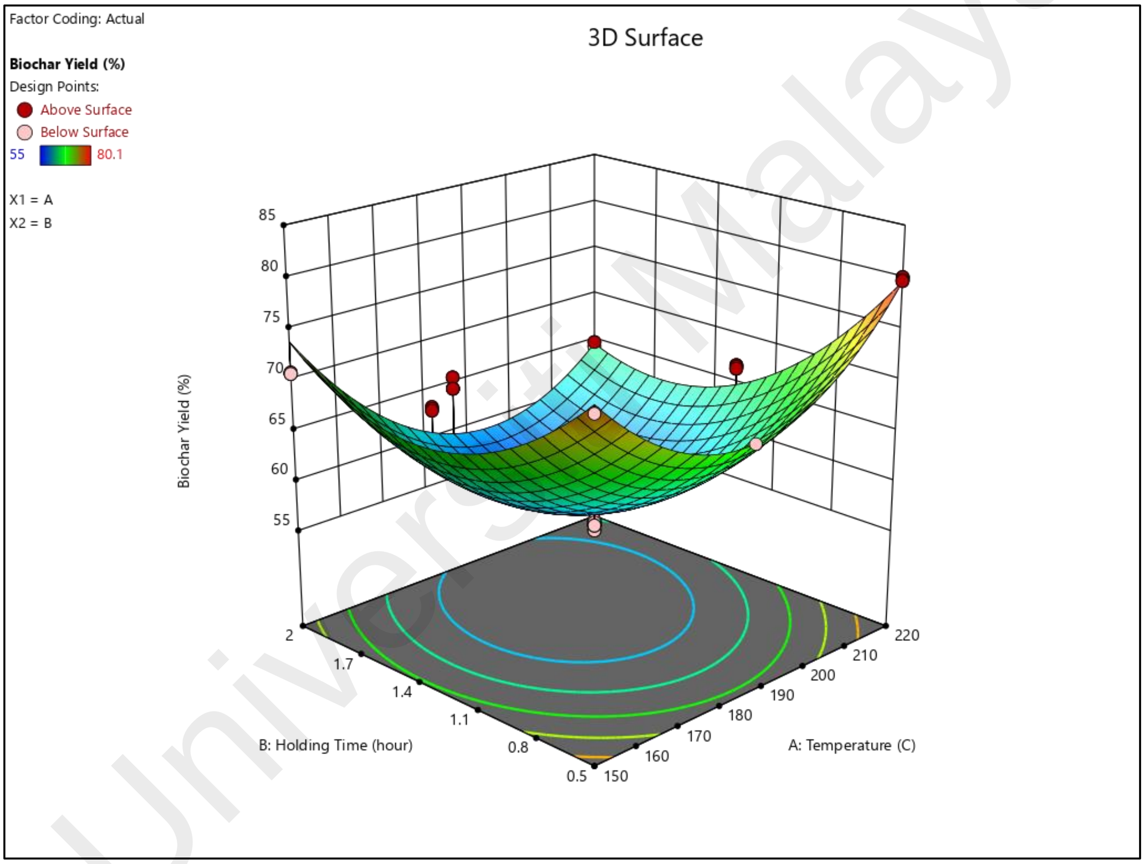



**Figure 4.2 Response Surface Plot**

As observed in Figure 4.2, in the surface plots, both reaction temperature and residence time exhibit slopes, showing that both factors influenced the yield of hydrochar. The surface plot could be summarised in which, the yield of biochar increases when the reaction temperature increases while the residence time decreases or the when the both reaction temperatures and residence time increases. For an example, at reaction temperature of 220ºC and holding time of 30 minutes, the yield produced was 75%, besides, at the temperature of 150ºC and holding time of 30 minutes, the yield produces was 75% too.

Table 4.3 shows the predicted versus actual graph of the experimental model.

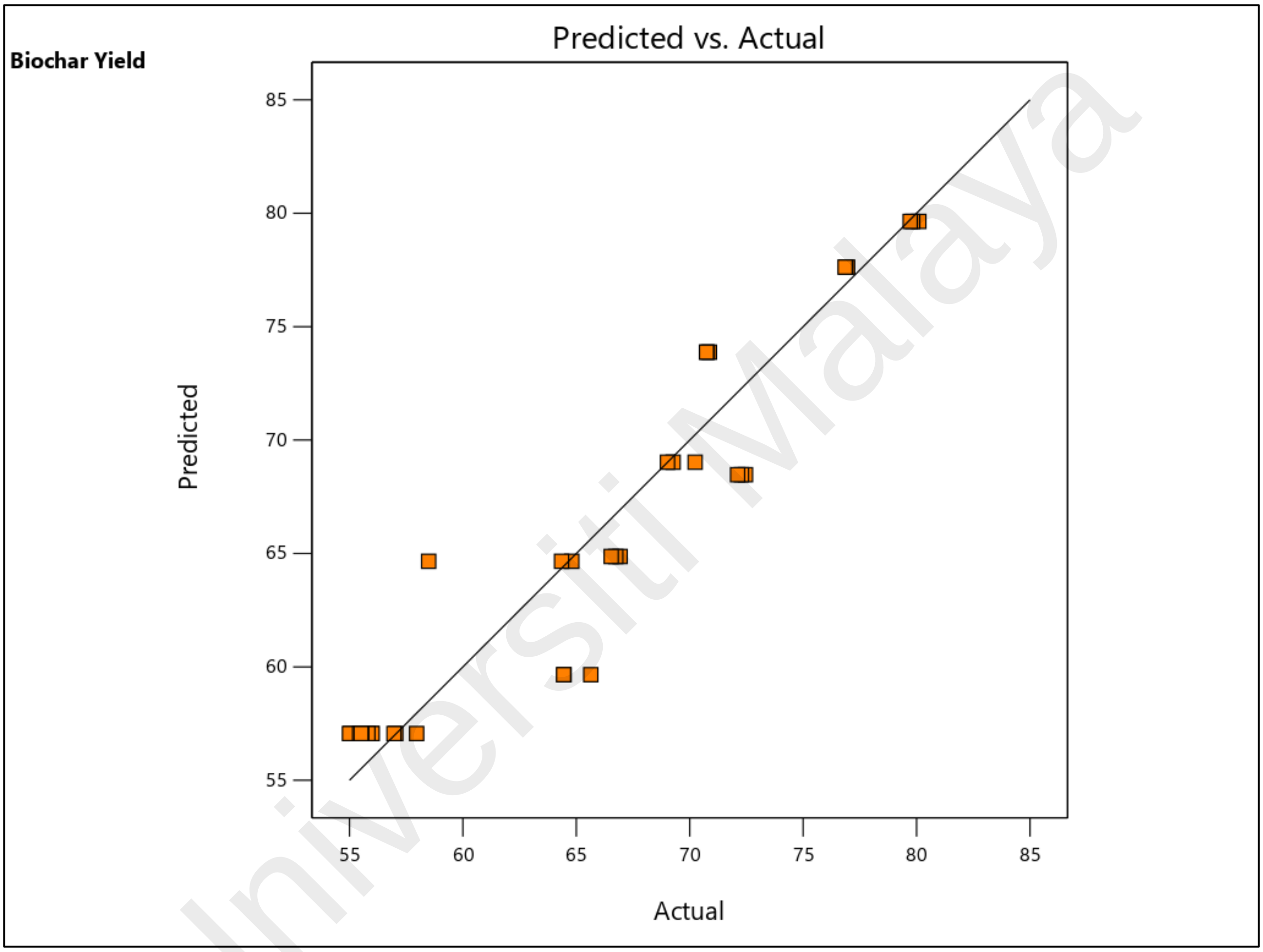



**Table 4.3: Actual-Predicted Graph**

As seen in Figure 4.3, almost all the point lies on the straight line indicating the percentage of error found was less than 5%. For an example, at the temperature of 185ºC and holding time of 1.25 hours, the actual yield was 57.96% whereas the predicted value was 57.06%. The percentage of error found was 1% (error < 5%). Hence, this proves that this experimental model is significantly reliable.

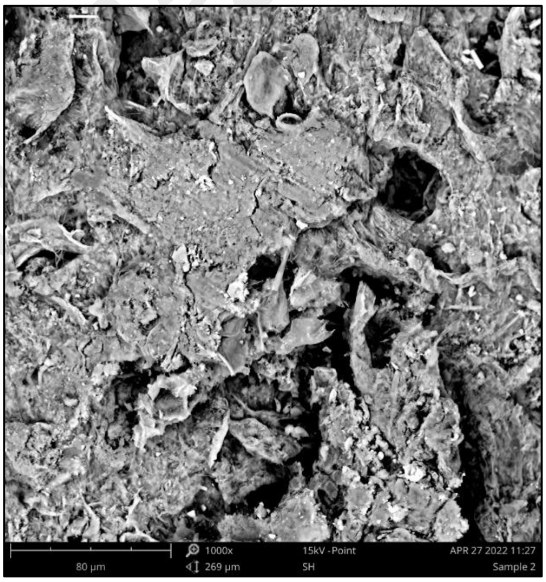
## 4.2 Characterisation of Biochar

### 4.2.1 SEM-EDX

The SEM-EDX analysis were performed on two different chars, i.e., Raw Pome char and Optimized Hydrochar. Figure 4.4 shows the SEM micrographs of both the chars at optimised condition.

Raw POME Char


Optimised Biochar



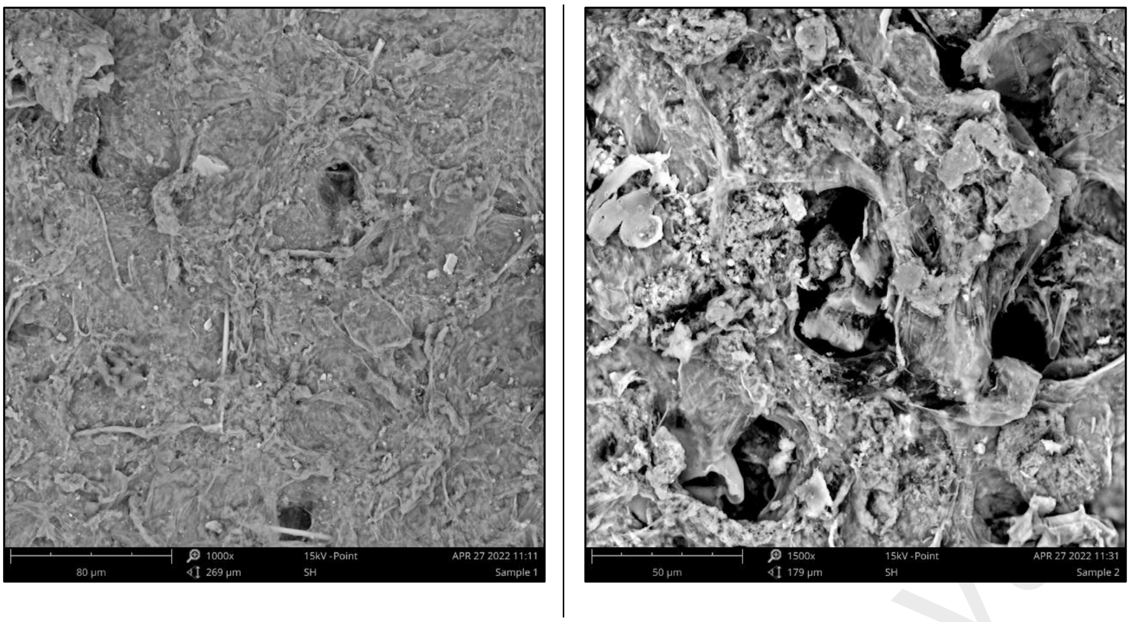



**Figure 4.4: SEM Images**

The purpose of performing SEM-EDX analysis is to study the inorganic salt formation or nutrient chemisorption (N, K, and P) on the hydrochar. Similarly, the effects of different nutrient amounts on hydrochar production were studied. From the figure above, it could be deduced that the optimised hydrochar had immensely large pores which makes it more deserving adsorbent to be chosen for adsorption process in line with Lee et al. (2019).

As for the EDX analysis, the graphs (Figure 4.5 & Figure 4.6) illustrate the composition of metals present in the chars.

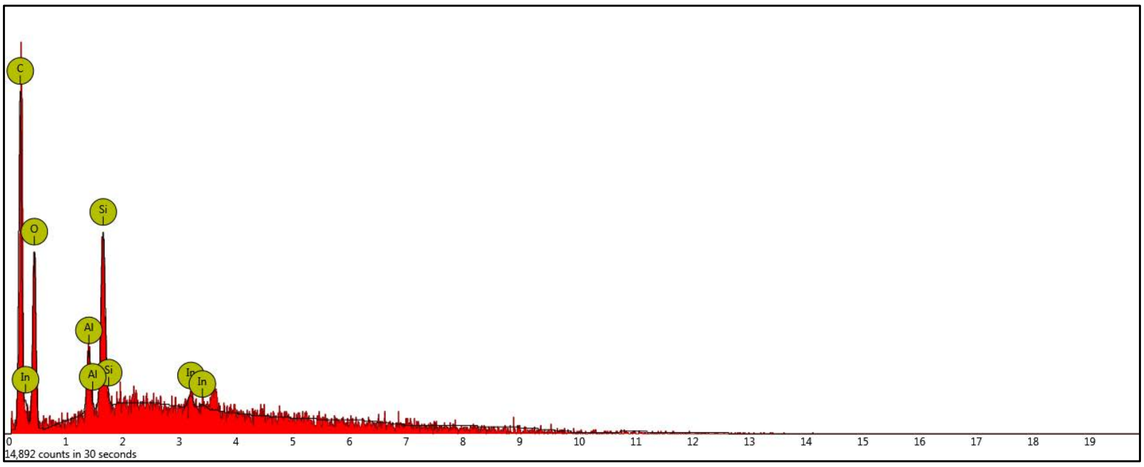



**Figure 4.5: EDX Analysis-POME Biochar**

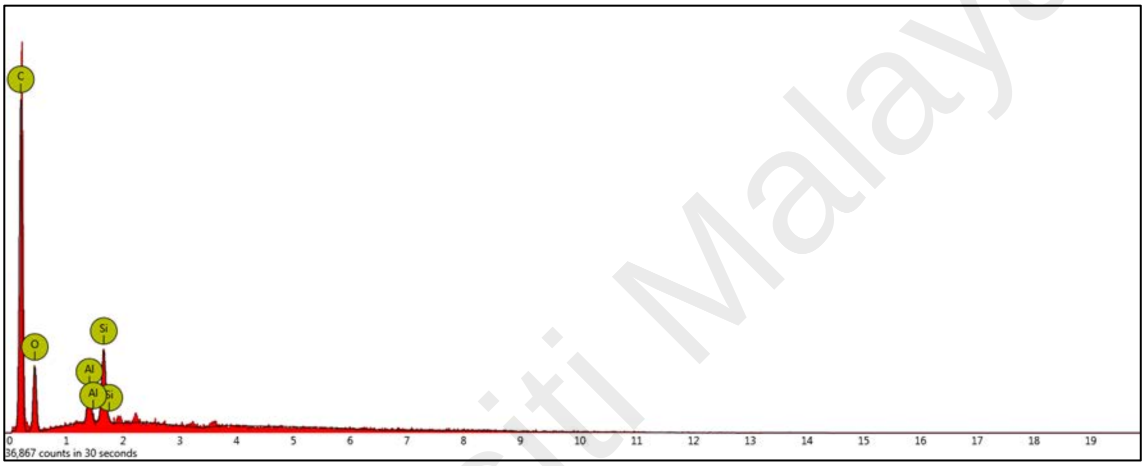



**Figure 4.6: EDX Analysis-Treated POME Biochar**

As observed in both figures, the inorganic elements discovered on the morphological surface of hydrochar. Surprisingly as explained by Lee et al. (2019), there is no clear association between inorganic element compositions and reaction temperature, showing that hydrothermal reactions only alter the composition of organic compounds. He had also added that polymeric component degradation, which contributes inorganics from solid compounds to the liquid, could explain the difference in inorganic element composition with reaction temperature. The plots show that C and O contributed the most to the hydrochar regardless of the hydrothermal reaction temperature at subcritical conditions.

### 4.2.2 FT-IR Analysis

Figure 4.7 and Figure 4.8 shows the FT-IR spectra for optimized hydrochar produced and its filtrate respectively.

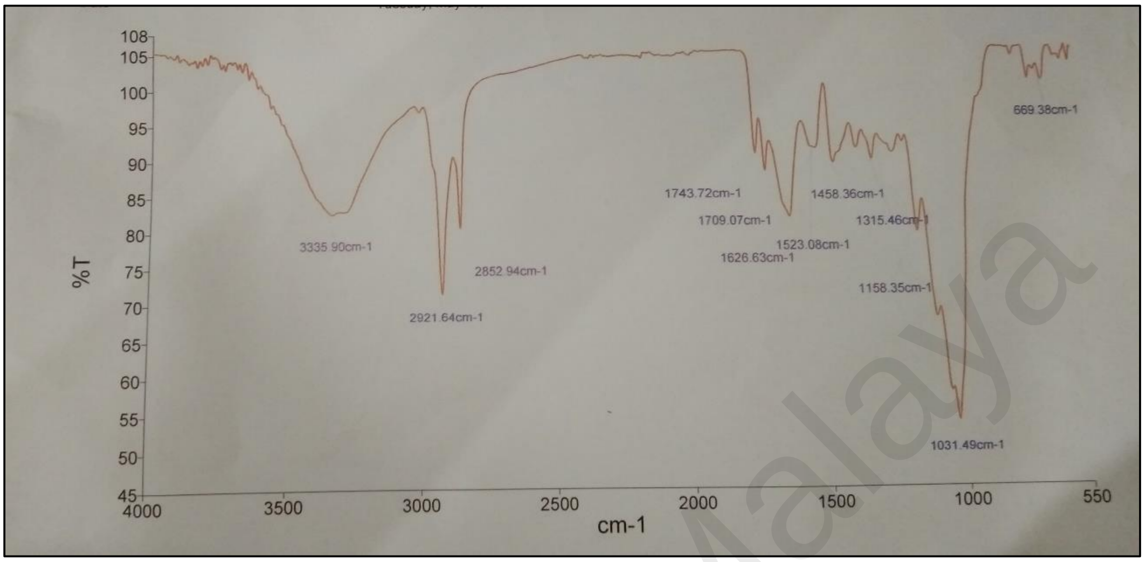



**Figure 4.7: FT-IR Spectra for Optimised Char**

From Figure 4.7, the peaks between 3200cm$^{-1}$ to 3500cm$^{-1}$ indicates that O-H stretching hydrogen bonded with hydroxyl group were evident in the hydrochars (Jian et al., 2018). Adding on, there is a sharp peak in between 2750cm$^{-1}$ and 3000cm$^{-1}$ which indicates the presence of C-H stretching of methylene groups, due to increasing reaction temperature. A peak is found at 1523cm$^{-1}$ which shows that presence of C-C stretching(Jian et al., 2018). And a peak at 1031cm$^{-1}$ is found that there is an evident presence of C-O bond (Jian et al., 2018).

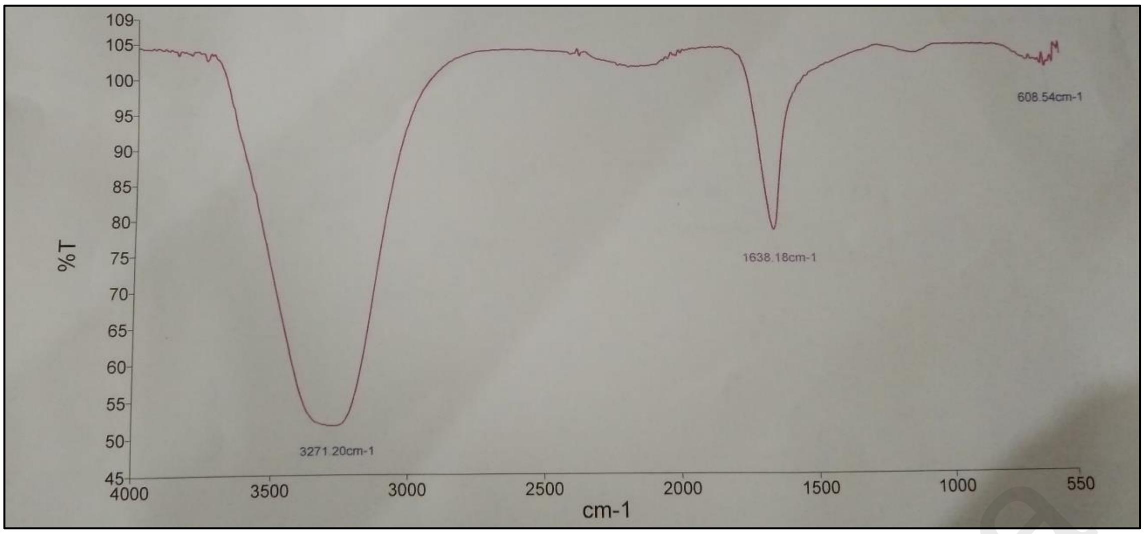



**Figure 4.8: FT-IR Spectra for Char Filterate**

From Figure 4.8, the peak formed at 3271cm-1 is an evident presence of O-H stretching hydrogen bonded with hydroxyl group. Besides, the peak at 1638cm-1 is indicating the presence of C-C stretching.

### 4.3 Optimisation Study

The optimisation study had been performed using the Design of Expert (DOE) Software. The results that had been tabulated in Table 3.2 was inserted into the software with the following criteria in Figure 4.9.

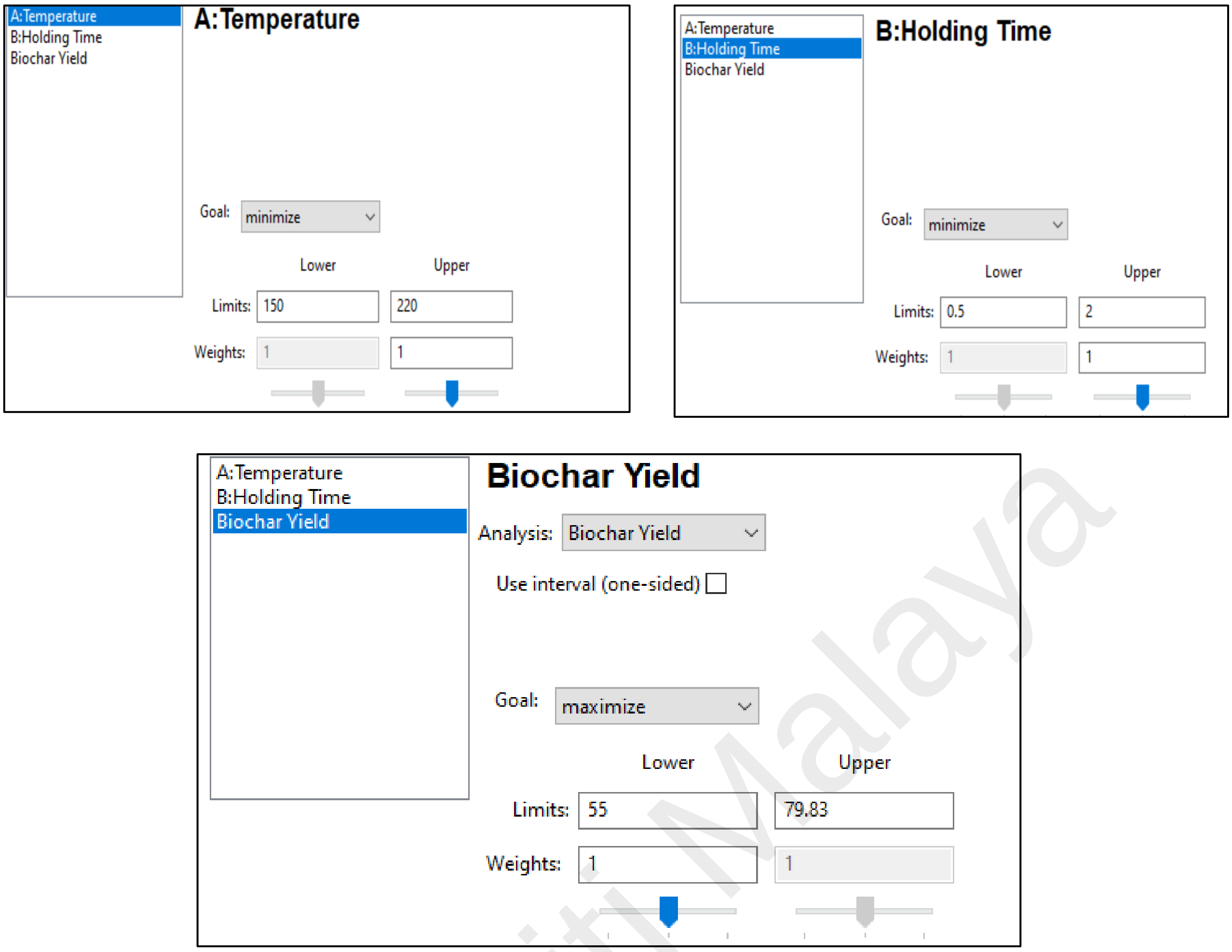



**Figure 4.9: Criteria Used**

From the criteria inserted, it had found that at reaction temperature 150ºC and at holding time of 0.5 hours, an optimised hydro char being produced. The optimised hydrochar is then further sent to study the adsorption capabilities using different prepared concentration. Table 4.1 shows the recorded reading of methylene blue reduction in concentration and the percentage of removal.

**Table 4.1: Methylene Blue Removal Using Optimised Hydrochar**

| Concentration (mg/L) | Concentration Reduction (mg/L) | Percentage Removal (%) |
|---|---|---|
| 10 | 6.2389 | 37.61 |
| 30 | 8.917 | 70.28 |
| 50 | 8.623 | 82.7 |
| 70 | 6.839 | 90.23 |
| 80 | 9.412 | 88.23 |
| 100 | 7.1291 | 92.27 |
| 150 | 11.1 | 92.6 |
| 200 | 9.204 | 95.3 |
| 250 | 17.342 | 93.06 |
| 300 | 15.735 | 94.76 |

From the table above, it can be concluded at optimized parameters, the removal capacity of methylene blue shows a value of <90% which leads to proving the biochar produced using hydrothermal treatment is a good source of adsorbent rather than the conventional adsorbents in the market.

Figure 4.10 shows a picturisation of the saturation point by the optimised hydrochar in removal of methylene blue.

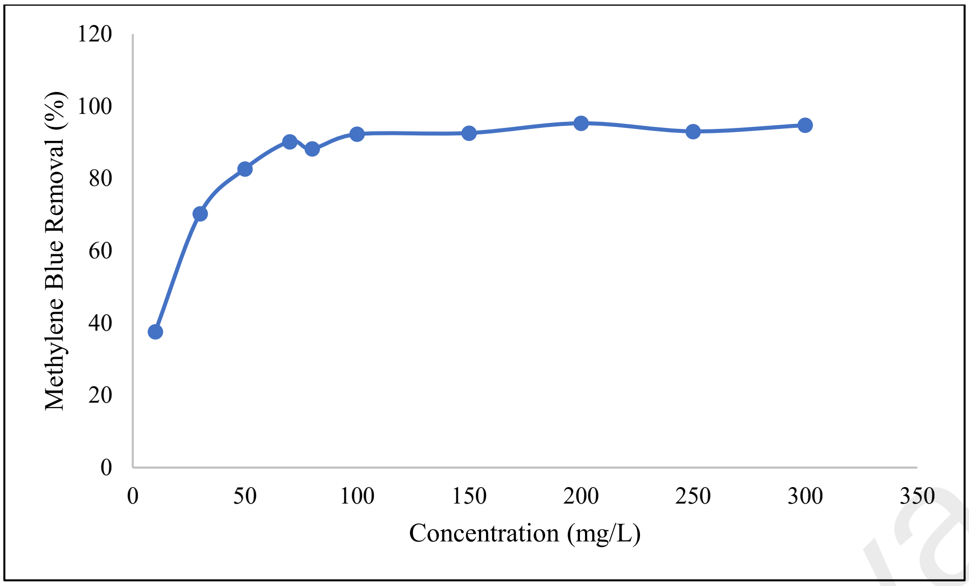



**Figure 4.10: Removal of Methylene Blue by Optimised Hydrochar**

At the optimised parameters, it is seen that at concentration of 100mg/L and above, the removal of methylene blue was found to be constant. This is because the hydrochar produced at the optimised temperature had reached its saturation point in removing the dye in the solution.

## 4.4 Biochar Yield

According to the design of experiment, the biochar was produced by varying the reaction temperature and the holding time in the reactor. Table 3.2 below shows the yield recorded for the respective biochar produced in the two parameters; i.e., reaction temperature and holding time.

From Table 3.2, it can be observed that at lowest reaction temperature and holding time, highest yield percentage had been obtained than the other reaction temperatures and holding times studied. This statement is in line with Niinipuu et al. (2020) in which he had stated that, the maximum yields were found at the lowest temperature, which is to be expected given that greater temperatures in HTC often result with lower yields. This is because organic matter dissolves and decomposes into gas and liquid fractions at higher temperatures, causing biochar yield to be decreased as the temperature rises (Huezo et al., 2021).

### 4.5 Adsorption Study of Methylene Blue

Biochar carbonised at temperatures ranging from 150 to 200ºC were used to remove methylene blue. Table 4.2 shows the maximum removal of methylene blue solution at its stipulated time and reaction temperature for a given concentration (50mg/L).

**Table 4.2: Methylene Blue Removal**

| Temperature (ºC) | Holding Time (hour) | Concentration Reduction (mg/L) | Methylene Blue Removal (%) |
|---|---|---|---|
| 150 | 0.5 | 8.623 | 82.70 |
| | 1.25 | 8.503 | 83.0 |
| | 2.0 | 8.729 | 82.5 |
| 185 | 0.5 | 8.55 | 82.9 |
| | 1.25 | 9.226 | 81.5 |
| | 1.25 | 8.30 | 83.4 |
| | 1.25 | 8.689 | 82.6 |
| | 1.25 | 8.567 | 82.9 |
| | 1.25 | 8.251 | 83.5 |
| | 2.0 | 8.775 | 82.45 |
| 220 | 0.5 | 8.559 | 82.9 |
| | 1.25 | 17.766 | 64.47 |
| | 2.0 | 9.040 | 81.92 |

As deduced from the table above, at varying reaction temperatures, biochar produced had a maximum methylene blue removal more than 80%. Hence, this proves that biochar produced from hydrothermal carbonization is a viable source for adsorption studies for heavy metal removal.

It is seen that, at 185ºC (reaction temperature) and 1.25 hours (holding time), the concentration had been reduced from 50mg/L to 8.251mg/L with maximum removal of 83.5%. The results are consistent as this is proved by Hamid and You (2021) whereby the researchers had found that with sewage sludge-derived hydrochar carbonised at 190 °C and 220 °C having the best methylene blue adsorption capabilities with >80% removal. This study revealed that hydrochars have increased methylene blue adsorption capabilities. In line with Jian et al. (2018), according to FT-IR measurements, the abundant functional groups on the surface of hydrochars may serve to enhance methylene blue complexation with the hydrochars as the adsorbent, and these functional groups may help to promote methylene blue complexation with the hydrochars as the adsorbent.

# CHAPTER 5.0

# CONCLUSION AND RECOMMENDATIONs

## 5.1 Conclusion

In a nutshell, the abundance of POME sludge being wrongly disposed leads to abundance of bio-waste which will affect the environment. The aim of this research work is to optimise the biochar yield produced using the hydrothermal carbonization treatment. Besides that, the objective of this work is to study the adsorption efficiencies of the biochar using methylene blue solution. At the starting of the experiment, the treated sludge was filtered and solid suspension was weighed approximately about 10g (with moisture content) and was placed into the hydrothermal reactor with 70ml of distilled water. The reactor was then sealed and kept in an oven at varying temperatures (150ºC, 185 ºC, 220 ºC) and at different holding times (0.5h, 1.25h, 2.0h). After reaction, the biochar was filtered, washed and dried at 60 ºC for overnight. Then, the run with methylene blue solution with concentration of 50mg/L was started by agitating 0.2g of biochar for about 1 hour. The steps were repeated with different reaction temperatures and holding times. The results were tabulated into the Design of Expert (DOE) Software and was found that the biochar was optimised at the temperature, 150ºC, and holding time of 30 minutes. The adsorption experiment was repeated with the optimised parameters and varying concentrations of methylene blue solution. A this point of time, it was found that the removal capacity increased as the concentration of methylene blue solution increases, and was approximately remained constant at around 150mg/L with removal capacity of 92.6%. According to the experimental results that had been tabulated in the DOE software, this experimental model was significantly reliable, as the p-values for both the operating parameters was less that 0.05. For the characterisation part, the SEM analysis shows immensely large pores for the biochar which leads to proving that biochar is a viable source for adsorption studies. Adding on, to the FT-IR analysis, due to sharp peaks in between 2750cm$^{-1}$ and 3000cm$^{-1}$, the presence of methylene groups methylene is so obvious enough, moreover, due to the increase of reaction temperature.

**5.2 Recommendations**

In order to examine the efficiency of the adsorption process of a certain adsorbate, a comparison of different biomass biochars as an adsorbent should be made. Biochars generated from rice husk and organic wastes, such as fruit peels, are examples of different biomass biochars. As a result, the adsorbent's adsorption uptake will be improved.

To measure the efficiency of the adsorbent in removing heavy metals from streams, different wastewaters should be tested with different adsorbents or vice versa. Future researchers might also alter the adsorbates by using wastewater from a variety of industries, including the food, pulp and paper, and iron and steel industries.

Adding on, future researchers might also conduct experimental study on the changes on Ph value using different reaction temperatures, holding times, raw materials, waste water streams. They could also propose on the reasons of changes occurred on Ph value.

Most of the time, the issue of disposal becomes the most talked about after the adsorption study. After the adsorption experiment, the biochar that had been adsorbed by methylene blue solution which was then should be thoroughly washed and sent for incineration. Kwapinski et al. (2010), had suggested that incineration is the best disposal technique for the used biochar to supply energy or used in high value goods. Biochar will make a significant contribution to ensuring a sustainable supply of green energy since it can efficiently maintain nutrients and produce a soil quality that will enhance plant growth by incinerating them.

Another method of disposal of biochar according to Berek and Hue (2016) is using as a soil amendment. This is because the most essential qualities of biochar were its calcium carbonate ($CaCO_3$) content, which was responsible for boosting acid soil productivity and plant growth. They had also reported that biochars generated from various feedstocks and processed under various conditions have variable physical and chemical properties, which means they could have varying effects when applied to soils.

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