

**PREPARATION OF SODIUM BICARBONATE ACTIVATED
CARBON FROM *CHLORELLA PYRENOIDOSA* FOR
WASTEWATER TREATMENT**

BY

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MASTER OF SCIENCE

In

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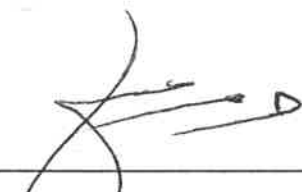
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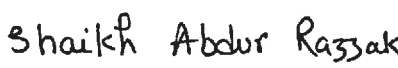
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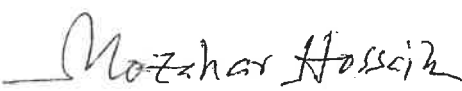

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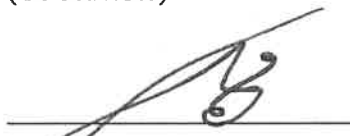



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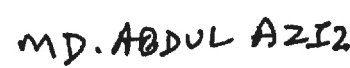
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| Dedicated To My Parents and My Family |

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LIST OF ABBREVIATIONS

ASTM	: American Society for Testing Material
BET	: Brunauer-Emmet-Teller
CM	: Cattle Manure
CO ₂	: Carbon Dioxide
DI Water	: Deionized Water
EMCR	: Extracted Marine <i>Chlorella Sp.</i> Residue
FTIR	: Fourier Transform Infrared Spectrophotometry
GC/MS	: Gas Chromatography/Mass Spectrophotometry
HCl	: Hydrochloric Acid
HHV	: Higher Heating Value
HR	: Heating Rate
HTL	: Hydrothermal Liquefaction
ICP-AES	: Inductively Coupled Plasma Atomic Emissions Spectrophotometry
NaHCO ₃	: Sodium Bicarbonate
NER	: Net energy ratio
NH ₃	: Ammonia
NO _x	: Nitrogen Oxides
PMS	: Papermill Sludge
PZC	: Point of Zero Charge
RS	: Rice Straw
RT	: Reaction Time
SCWG	: Supercritical Water Gasification
SEM	: Scanning Electron Microscopy
Syngas	: Synthesis Gas
TGA	: Thermogravimetric Analysis
WW	: Willow Wood
XRD	: X-Ray Diffraction

ABSTRACT

Full Name :Gus Ali Nur Rohman

Thesis Title :*Preparation of Sodium Bicarbonate Activated Carbon from Chlorella Pyrenoidosa for Wastewater Treatment*

Major Field :Chemical Engineering

Date of Degree :June 2024

In this research, a highly porous sodium bicarbonate activated carbon was produced by the fast pyrolysis of *Chlorella pyrenoidosa* biomass. The biochar without modification showed non-porous material characteristics based on the results of N₂ isotherm adsorption-desorption. The modification with sodium bicarbonate successfully increased the BET specific surface area of biochar to 1282 m²/g, with a microporous surface area of 871 m²/g and an external surface area of 411 m²/g. This result was obtained at a temperature of 750°C. XRD characterization showed broad peak around 24° which indicates amorphous carbon structure that is favorable for adsorption purposes. FTIR characterization after pyrolysis showed an important functional group that should enhance the adsorption process. Following that, a batch adsorption technique of lead synthetic wastewater is used to conduct more tests on its performance. The maximum adsorption capacity of Lead (Pb²⁺) based on Langmuir model of activated carbon ($q_{\max}$) is 159.071 ± 23.4008 mg/g. The heterogeneity factor (hf) based on Freundlich model is 0.4671 ± 0.06394 , which mainly indicates the physical adsorption. The separation factor (R_L) is nearly zero, indicating irreversible nature. The pseudo second order kinetic model showed that the rate of adsorption (k_2) for activated carbon is 0.00931 ± 0.00222 g.mg⁻¹.min⁻¹. Overall, the results demonstrated that in terms of technological feasibility, activated carbon from *Chlorella pyrenoidosa* met the standards of commercial activated carbon, either based on characterization data or performance results.

خلاصة

- الاسم الكامل : جوس علي نور الرحمن
- عنوان الرسالة : تحضير الكربون المنشط ببيكربونات الصوديوم من شلوريلا بيرينويدوسا لمعالجة مياه الصرف الصحي
- الدراسة المجال الرئيسي : هندسة كيميائية
- تاريخ الدرجة : يونيو 2024

في هذا البحث، تم إنتاج الكربون المنشط ببيكربونات الصوديوم عالي المسامية عن طريق الانحلال الحراري السريع للكتلة الحيوية لكلوريلا بيرينويدوسا. أظهر الفحم الحيوي دون تعديل خصائص المواد غير المسامية بناءً على نتائج نجاح التعديل باستخدام ببيكربونات الصوديوم في زيادة المساحة السطحية. N₂ امتصاص - امتزاز متساوي الحرارة إلى 1282 م²/جم، مع مساحة سطحية صغيرة المسام تبلغ 871 م²/جم ومساحة سطح BET المحددة للفحم الحيوي XRD خارجية تبلغ 411 م²/جم. تم الحصول على هذه النتيجة عند درجة حرارة 750 درجة مئوية. أظهر توصيف ذروة واسعة تبلغ حوالي 24 درجة مما يشير إلى بنية الكربون غير المتبلورة الملائمة لأغراض الامتزاز. أظهر بعد الانحلال الحراري مجموعة وظيفية مهمة من شأنها تعزيز عملية الامتزاز. بعد ذلك، يتم FTIR توصيف استخدام تقنية الامتزاز الدفعي لمياه الصرف الصحي الاصطناعية لإجراء المزيد من الاختبارات على أدائها. الحد هو $159.071 \pm q_{\max}$ على أساس نموذج لانجميور للكربون المنشط (Pb²⁺) الأقصى لقدرة الامتزاز للرصاص على أساس نموذج فروندليتش هو 0.4671 ± 0.06394 ، والذي (hf) 23.4008 ملجم/جم. عامل التجانس يقترب من الصفر، مما يشير إلى طبيعة لا رجعة (R_L) يشير بشكل رئيسي إلى الامتزاز المادي. عامل الانفصال للكربون المنشط هو $0.00931 \pm k_2$ فيها. النموذج الحركي من الدرجة الثانية الزائفة أظهر أن معدل الامتزاز بشكل عام، أظهرت النتائج أنه من حيث الجدوى التكنولوجية، فإن الكربون المنشط من 0.00222 g.mg⁻¹.min⁻¹. يلبي معايير الكربون المنشط التجاري، إما بناءً على بيانات التوصيف أو نتائج الأداء *Chlorella pyrenoidosa*

CHAPTER 1

INTRODUCTION

1.1 Background

Almost all industrial sector in the Kingdom of Saudi Arabia produce wastewater[1]. It is a residual of industrial operation in the form of water[1]. Without a proper treatment that is conducted before its discharge to environment, wastewater could contain many kinds of hazardous chemicals including heavy metal (such as Cd, Cr, Cu, Pb, Hg, Ni, Ag, Zn)[2]. If heavy metal spreads across aquatic ecosystem, it will be consumed by human-being and bring severe health issues for them[2]. Several methods have already proven to be successful on removing heavy metal from wastewater, and the most efficient and reliable method is adsorption process with activated carbon[3]. Adsorption with activated carbon is a promising method to remove heavy metal from wastewater because it has a high efficiency and relatively low cost compared to other methods[3]. The main mechanism of heavy metal adsorption using activated carbon could be a physical adsorption using pore volume in the adsorbent, electrostatic interaction, or complexation reaction of heavy metal with nitrogen contained and/or oxygen contained functional group [4,5]. To obtain a better adsorption performance, it is necessary to produce activated carbon with high surface area and to obtain a more graphitic-N functional group. A high surface area is needed to increase potential physical adsorption, while nitrogen and oxygen contained functional group is needed to increase the probability of complexation reaction [6].

Research about thermochemical conversion on micro algae started in the 1970s when there is energy crisis due to shortage of supply crude oil from the middle east [7]. Many researcher look

into microalgae as a potential feedstock for renewable energy source[8]. The initiation process to extract oil from microalgae is using solvent which is expensive and ineffective method from economical point of view[9]. Then thermochemical process like pyrolysis, gasification, liquefaction and torrefaction starting to gain attention in the 1980s because it is relatively cheap compared to solvent extraction and give several benefit over solvent extraction[10,11]. There are different products that can be generated from microalgae such as biofuel, biochar, syngas, and many others. This process is relatively environment friendly because it uses renewable source and the feedstock can be reproduced in a high scale cultivation method[12–17]. Those findings in energy sector give encouragement for researcher to dig more about thermochemical process on microalgae since 1980s[10,11]. Researchers first looked into using microalgae biomass to make biochar, which can increase soil fertility and store carbon, in the 1990s[18,19].

Microalgae cultivation is well-known as sustainable bioremediation media. Cultivation of microalgae consumed several pollutants such as carbon dioxide as its main carbon source and nitrogen and phosphorus pollutant as its nutrients. Simultaneous consumption of pollutants gives microalgae advantages as promising solution to solve carbon emissions problems and achieve net zero carbon emissions[20].

Microalgae have emerged as a promising feedstock for bioenergy production in response to the rising need for renewable energy and sustainable development [21–26]. Due to its benefits, *Chlorella pyrenoidosa* has attracted a lot of interest among many microalgae species. *Chlorella pyrenoidosa* is a viable potential candidate for a variety of applications, including the generation of biofuels, chemicals, and charcoal. It has a number of benefits over other biomass feedstocks[27]. *Chlorella pyrenoidosa* is a cost-effective feedstock for the production of bioenergy and charcoal because it can be grown in large-scale outdoor systems. [28–31]. *Chlorella pyrenoidosa* also has

a high growth rate in the cultivation and has potential to generate high amount of biomass. Because of that, *Chlorella pyrenoidosa* has a high potential for sustainable and renewable biomass resource [32–39]. Moreover, *Chlorella pyrenoidosa* contains high amount of lipids which are useful in the biodiesel production [40–44]. Beside lipid content, *Chlorella pyrenoidosa* also has a high protein content that makes it valuable as high protein food or animal feed applications [38,45–51]. For another application, adsorbents made of *Chlorella pyrenoidosa* biomass have been proven to be efficient at removing heavy metals and dyes from wastewater [52,53]. Furthermore, due to high concentration of cellulose and lignin, *Chlorella pyrenoidosa* can produce biochar with high stability[32,54–57]. Biochar-derived from *Chlorella pyrenoidosa* also demonstrates excellent outcomes in increasing soil fertility and carbon sequestration[58–61].

Two thermochemical conversion processes, such as pyrolysis and torrefaction, can be utilized to create adsorbent from microalgae biomass, including *Chlorella pyrenoidosa*. The process of pyrolysis involves heating the biomass in the absence of oxygen to create syngas, charcoal, and bio-oil [62–67]. In order to remove contaminants from water and wastewater, pyrolyzed biochar can be utilized as an adsorbent because it is porous and has a large surface area[68–76]. Torrefaction, on the other hand, is a method that includes heating biomass in the absence of oxygen at a lower temperature than pyrolysis, usually below 300°C[77–84]. Torrefaction is a process used to transform biomass into a solid with increased energy content and better qualities for combustion and gasification by removing moisture and volatile components[83,85–91].

Several aspects need to be considered when comparing pyrolysis and torrefaction for the synthesis of adsorbent from microalgae biomass. First off, pyrolysis, as opposed to torrefaction, can provide biochar with a greater surface area and porosity. This is due to the fact that pyrolysis uses a higher operating temperature and a longer residence period, which causes the biomass to carbonize more

thoroughly [92–98]. Additionally, pyrolysis-produced biochar is more effective than torrefaction at removing contaminants from water and wastewater [95,99–104].

However, recent research on pyrolysis of *Chlorella pyrenoidosa* is heavily focused on renewable energy application. another application of biochar derived from *Chlorella pyrenoidosa* needs to be studied thoroughly. The objective of this research work is to provide in depth observation in the potential of *Chlorella pyrenoidosa* for precursor of adsorbent material, and furthermore, to determine optimum operational condition to produce high performance activated carbon. High performance activated carbon is needed to tackle a lead heavy metal problem in wastewater treatment applications.

1.2 Scope of This Work

This study focuses on the synthesis of novel activated carbon from *Chlorella pyrenoidosa* and observes the effect of activating agent and acid treatment on the characteristics of activated carbon. Product activated carbon and raw *Chlorella pyrenoidosa* will be characterized using thermogravimetric analysis (TGA), Nitrogen adsorption/desorption isotherm Brunauer-Emmett-Teller (BET) Model, Scanning Electron Microscopy (SEM), X-ray Diffractogram (XRD), Fourier Transform Infrared Spectrophotometry (FTIR), and Elemental Analysis.

The rationale for this work can be concluded as the followings:

- Synthesis of activated carbon from *Chlorella pyrenoidosa* with fast pyrolysis process
- Characterization of activated carbon (thermal characterization, chemical characterization, and physical characterization)
- Performance test of activated carbon produced.

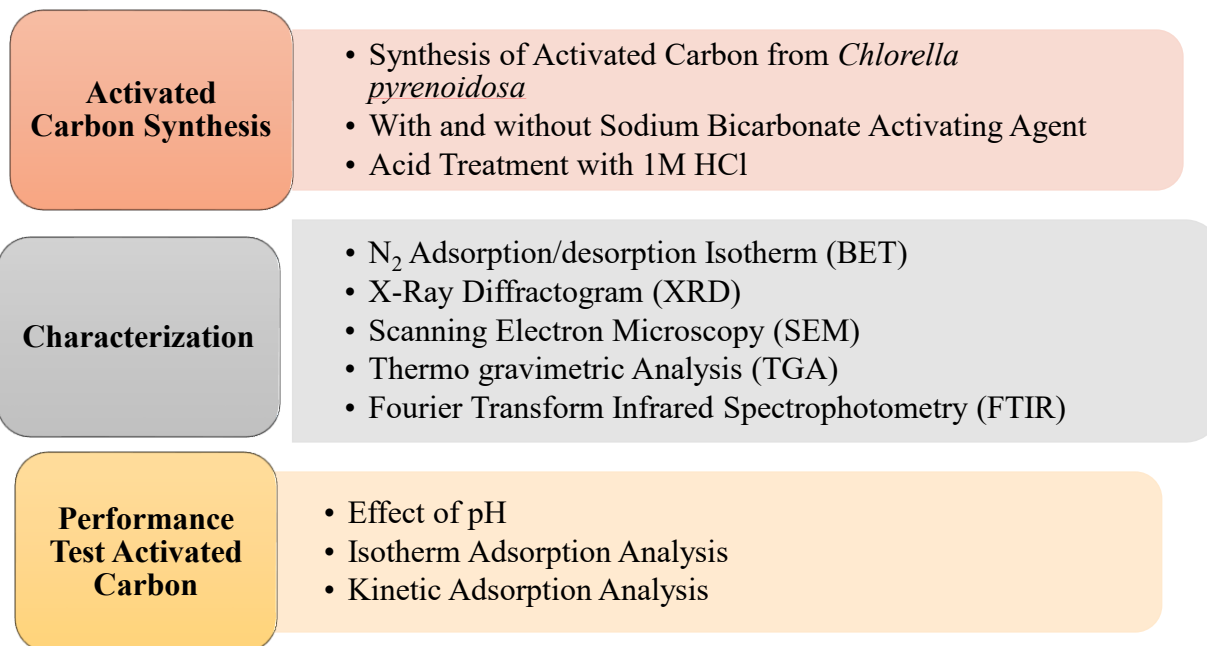


Figure 1 Schematic diagram of activated carbon synthesis and characterization.

1.3 Structure of Thesis

This Thesis is arranged as follows:

- **Chapter 1** consists of background information, problem statement, proposed solution, and motivation of the work. In addition, the scope of this study has been addressed properly in this chapter.
- **Chapter 2** presents an important review of the prevailing literature on synthesis of activated carbon from several sources and potential applications for activated carbon.
- **Chapter 3** concise the overall and specific objectives of this Thesis work.
- **Chapter 4** This chapter describes the experimental procedure and design as well as the experiments carried out for achieving the required goals of this study.
- **Chapter 5 and 6** include the result of the experiment and discussion of characterization.
- **Chapter 7** includes the performance test for heavy metal adsorption in wastewater.

- **Chapter 8** presents the concluding remarks and suggestions for further studies.

1.4 Completion Timeline

TASK	MONTHS											
	01	02	03	04	05	06	07	08	09	10	11	12
Experimental work												
Characterization												
Data Analysis												
Report writing												
Manuscript writing for Publication												

CHAPTER 2

LITERATURE REVIEW

2.1 History of Research on Microalgae

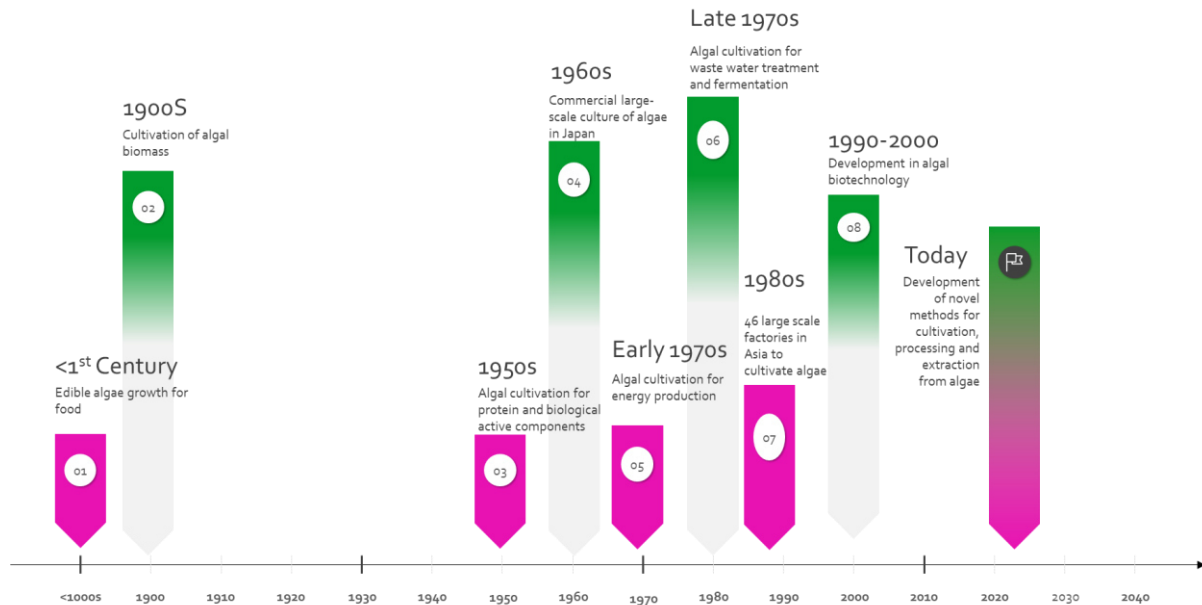


Figure 2 Timeline of Research on Microalgae

Algae biomass has begun to be considered as edible food since before 1st century based on archaeological evidence in Chile, China and Ireland [105]. The term of cultivation was first introduced in 1850 by Ferdinand Cohn when he successfully keeping *Haematococcus* in his laboratory in Poland. Then, Famintzin at 1871 also successfully grows green algae *Chlorococcum infusionum* and *Protococcus viridis* with inorganic salt solution as a media of cultivation [106].

In Asia, algae was already used for source of high-protein food since 1950 [107]. In 1960s, the first attempt to cultivate *Spirulina* (*Chlorella* and *Arthrospira*) commercially as special food with high protein source was conducted in Japan by Tokugawa Institute of Biological Research

[108,109]. Energy crisis at early 1970s triggered intensive research of microalgae as renewable resource and new option for fuel demand because there was a disruption of oil supply and high price of oil from middle east [7].

During space race between United States and Uni Soviet in 1955-1975, there was also intensive research to use algae for waste treatment in life support system in space. Implementation of algae as waste treatment in life support system took form as semi-batch photobioreactor that US Navy Aerospace Medical Labs called by “Algatron” [110]. Algatron recycled CO₂ and Ammonium from urinary waste and produce O₂ from photosynthesis at excess amount of water [111].

After the space race ended in the early 1970s, research of microalgae continues for waste treatment especially for wastewater treatment. The concept of algal technology for sanitary engineering was introduced by Soeder (1980). Soeder combined the concept of microalgae cultivation that is capital intensive and the new paradigm to cultivate microalgae as by-product of wastewater treatment process [112]. By 1980, there was around 1000kg/month of spirulina (mainly *chlorella*) produced by forty-six large-scale factories in Asia. Furthermore, in 1996 a trade of *chlorella* was reported to reach up to 2000 ton for Japan only. [113].

Chaumont (1993) explained that open raceway photobioreactor which is commonly used for commercial plant cannot get high efficiency of photosynthesis because there are a lot of uncontrolled variables that make specific product of microalgae difficult to get. Furthermore, he explained that closed system photobioreactor is better in term of photosynthesis efficiency, diversity of microalgae culture, and quality of microalgae product. However, closed-system photobioreactor is more capital intensive, therefore it is only applicable for high value product like pharmaceutical, phycobilin protein and cosmetic product[114].

Microalgae started gaining attention for carbon production in 2011. Gierson et al., starting synthesis carbon from *Tetraselmis chui* via slow pyrolysis process. This research focuses on the application of carbon from microalgae for agriculture nutrient. It showed that carbon from *Tetraselmis chui* has high cation exchange capacity, large concentration of nitrogen and low carbon to nitrogen ratio. Addition of carbon from *Tetraselmis chui* into soil can be expected stable up to 9%wt. of the original feed. This will ultimately leading to a potential net reduction of CO₂ emissions in atmosphere [115].

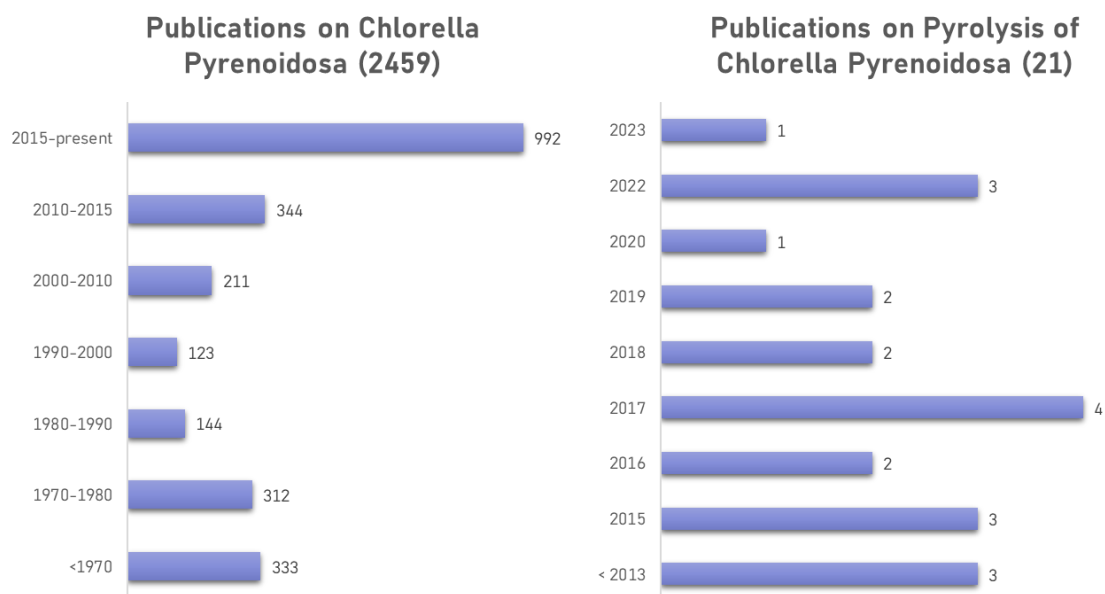


Figure 3 Research Related to *Chlorella pyrenoidosa*.

Lately *Chlorella pyrenoidosa* has been gaining a lot of attention from researchers. Around 992 papers have already been published in the Scopus from 2015 until now, significantly higher compared to the number of research published since 1970 to 2015. From those recent papers, only 21 publications that explains pyrolysis process of *Chlorella pyrenoidosa*. And by exploring its keyword we can see that there is still no paper that focuses on the effect of activating agent and carbonate salt for pyrolysis of *Chlorella pyrenoidosa*

2.2 Thermochemical Conversion

Thermochemical conversion is one of the most simple and reliable methods to convert microalgae to various products. Generally, thermochemical conversion of microalgae is divided into 2 mechanisms, which are High Pressure Thermochemical Conversion Mechanism and Atmospheric Pressure Thermochemical Conversion Mechanism[116]. High Pressure Thermochemical Conversion Mechanism developed to eliminate requirement of dewatering or drying process for feedstock. 2 pathways in High Pressure Thermochemical Conversion are Hydrothermal Liquefaction (HTL) and Supercritical Water Gasification (SCWG). Atmospheric Pressure Thermochemical Conversion is conventional way to processing algal biomass, which are Gasification, Pyrolysis, and Torrefaction.[13]

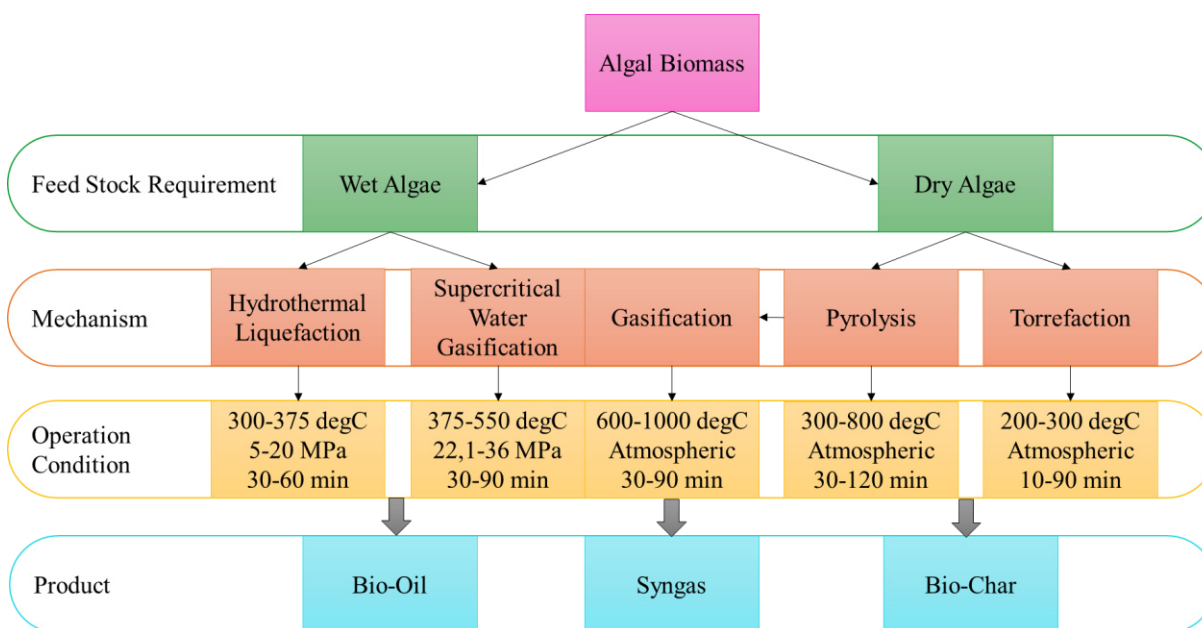


Figure 4 Various Mechanism of Thermochemical Conversion[116]

2.2.1 Hydrothermal Liquefaction

Hydrothermal Liquefaction is mostly used to generate high yield of bio-oil to accommodate high moisture content in feedstock. Another advantage to use Hydrothermal Liquefaction is its high

compatibility to use acid or base based catalyst that is easily solved in water as reaction medium[13].

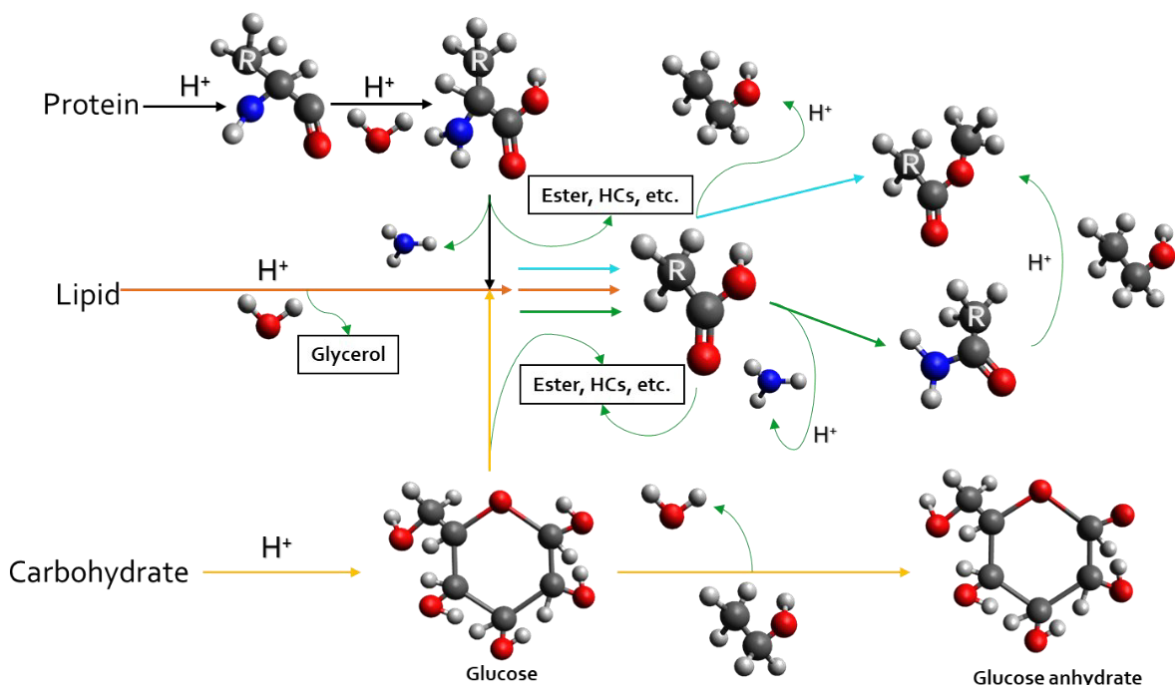


Figure 5 Mechanical Pathway of Algal biomass to Bio-Oil by Hydrothermal Liquefaction[13]

Zhang et al explained about mechanical pathway to produce bio-oil from microalgae by HTL mechanism. Protein, Lipid and Carbohydrate will be broken-down to monomers. After that, the monomer will undergo decomposition to corresponding intermediate product. Amino acids will undergo decarboxylation to form keto acids and deamination to form NH_3 or amines. Ketones will be formed by decarboxylation of keto acids and fatty acids. Aliphatic hydrocarbons will be formed by decarboxylation of fatty acids. There are also possibilities that fatty acid will undergo esterification and acylation reaction to form amides and fatty ester. Melanoidin and nitrogenous compounds will be formed by mailiard's chemistry of amino acids and monomers. Monosaccharides will decompose into smaller carboxylic acid and furfurals. Polymerization of

phenol and furfurals will generate solid products. Volatile products formation will be reduced because of stable ester suppressing decarboxylation reaction[117].

2.2.2 Supercritical Water Gasification (SCWG)

Supercritical Water Gasification is a new development of gasification process by eliminating the drying and dewatering process of feedstock algal biomass. Supercritical water gasification mechanism is usually conducted on $>374\text{ }^{\circ}\text{C}$ in temperature and $>22.4\text{ MPa}$ in pressure. On this condition, water as medium of gasification will have properties of gaseous and liquid phase. Liquid viscosity and diffusivity will be like gaseous phase so it will help gasification process[13].

2.2.3 Pyrolysis

Pyrolysis or devolatilizations is thermochemical mechanism that works by decomposing organic substance to produce volatile gas, condensable liquids, and solid residue by low concentration of oxygen or oxygen-free process at atmospheric pressure and high temperature. With further refining and post-treatment, condensable liquids and solid residue can be used as bio-oil and bio-char[13].

Fast Pyrolysis

Fast pyrolysis can be a catalytic or a non-catalytic process that uses fluidized bed reactor with high heating rate. A fluidized bed is used because it has high heat transfer coefficient and relatively similar in temperature along with length of reactor. Typically, heating rate for Fast or Flash Pyrolysis is around $1\text{-}200^{\circ}\text{K/s}$ with residence time around $0\text{-}0.5\text{ s}$ [13].

Hemberger et al. in 2017 proposed mechanism for catalytic fast pyrolysis of lignin monomer guaiacol by tracking the potential intermediate product that in catalyst surface. Mainly, there are three sub-process that occur in fast pyrolysis, which are transmethylation, deoxygenation and hydration-dehydration[118].

The first sub-process is deoxygenation. It means that one or two oxygen atom release from biomass and produce intermediate products such as phenol, cyclopentadiene, pulvinone and fulvene. Deoxygenation triggered by instability of carbon monoxide, water and carbon dioxide formation in biomass[118].

The second sub-process is transmethylation. It is proven by Hemberger et al. using py-iPEPICO spectra and py-GC/MS that found some group of methyl formation distributed in the final product. There is high probability that formation of methyl-cyclopentadiene, cresols, and methyl-pulvinones from guaiacol because of transmethylation in fast pyrolysis process[118].

Third sub-process is hydration-dehydration. From transmethylation, guaiacol converts into catechol as intermediate product. And from dehydration of catechol, it produces pulvinone ketene that has high reactivity as main species in reaction mechanism. Pulvinone then branched into cyclopentadiene and phenol because of radical hydrogenation. There is also possibility of hydration of pulvinone that produce cyclopentadiene followed by CO₂ release[118].

Slow Pyrolysis

Slow pyrolysis is also called conventional pyrolysis and carbonization. Slow pyrolysis can be a catalytic or a non-catalytic process that uses a fixed bed reactor with low heating rate. Typically, heating rate for slow Pyrolysis is around 0.1-1°K/s with minutes or hours residence time [13].

Catalytic Pyrolysis

Catalytic pyrolysis is a term for pyrolysis which is enhanced by catalyst to get volatile gas and solid residue faster. Catalytic pyrolysis can use either fluidized bed reactor (fast pyrolysis) or fixed bed reactor (conventional pyrolysis) [13].

Microwave Assisted Pyrolysis

Microwave assisted pyrolysis is a term for pyrolysis process that uses internal heating process which resulted from microwave. Microwave pyrolysis eliminates heat loss from conventional pyrolysis because the direction of heating process from internal molecule of feedstock to environment, so there is no heat losses by heating up reactor [13].

2.2.4 Torrefactions

Torrefaction is one of the mechanisms to produce biochar from microalgae biomass. Torrefaction uses mild temperature pyrolysis (200-300°C) mechanism with atmospheric pressure in low oxygen condition to convert dry biomass to get solid biofuel or biochar. Generally, torrefaction is divided into 3 pathways based on operation temperature, which are light torrefaction (200-235 °C), mild torrefaction (235-275 °C) and severe torrefaction (275-300 °C). Torrefaction is highly dependent on operating temperature. The higher the operating temperature, the higher the quality of bio-char produced, but if temperature is too high, it become an energy intensive process and reduce energy yield from torrefaction process[13].

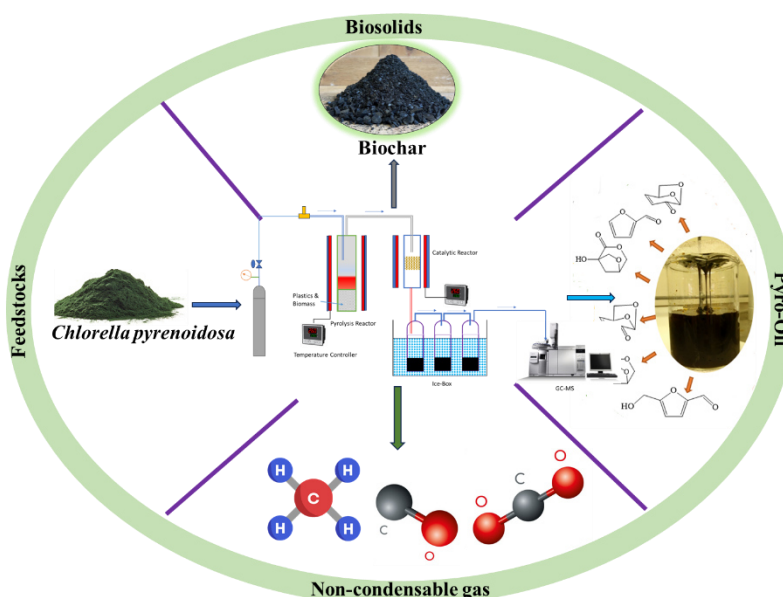


Figure 6 Potential Product of Thermochemical Conversion of Microalgae

2.3 Characteristics of *Chlorella pyrenoidosa*

2.3.1 Physical Characteristics

Chlorella is a small, unicellular green algae that is spherical in shape, with a diameter of 3-10 µm[119]. The cell wall is made of cellulose, pectin, and other polysaccharides and is rather thin[120,121]. A single cup-shaped chloroplast with a pyrenoid is present in the cytoplasm and is near to the cell surface [122–124]. The chloroplast of many green algae, including *Chlorella pyrenoidosa*, contains a unique component called a pyrenoid[125,126]. It participates in carbon fixation and is essential for the algae's capacity for photosynthetic growth[127–131]. A starch coating that surrounds the pyrenoid works to shield it from environmental stressors[132–134]. *Chlorella pyrenoidosa* also has a nucleus, mitochondria, and other organelles that are typical of eukaryotic cells in addition to the chloroplast and pyrenoid[135,136]. The cytoplasm is granular and packed with many tiny vacuoles[124,137,138]. *Chlorella pyrenoidosa* has a simpler morphology than most other kinds of algae and higher plants. Though it is an essential model organism for research in fields like photosynthesis, biotechnology, and environmental science due to its distinctive characteristics like the pyrenoid and the capacity to develop quickly and survive a wide range of environmental circumstances.

2.3.2 Growth Conditions

Depending on the strain and intended use, *Chlorella pyrenoidosa*'s ideal development circumstances may change. Here are some broad circumstances that have been discovered to promote growth:

- 1) Light intensity: *Chlorella pyrenoidosa* needs sufficient light to flourish, with the best growth taking place at light levels between moderate and high. Typically, the optimum range of light intensity is between 6000 and 8000 lux[139].

- 2) Temperature: Although some strains of *Chlorella pyrenoidosa* may survive temperatures outside of this range, the best temperature range for this organism to grow is often between 25°C and 35°C[140].
- 3) pH: Depending on the strain, the ideal pH for growth is often between 5.7 and 6.5[29].
- 4) Nutrient availability: For growth, *Chlorella pyrenoidosa* needs a variety of nutrients, such as nitrogen, phosphorus, and several trace elements. Depending on the strain and intended use, different nutritional amounts and ratios may be best. Culture media with optimum 15:1 N/P atomic ratio is needed to avoid nitrogen limitation. However, the ratio may change based on the rate of dilution[141].
- 5) Carbon source: several carbon sources, like CO₂, glucose, and other organic compounds is already proven to enhance the output biomass product of *Chlorella pyrenoidosa* [142,143]. But the optimal carbon source and concentration depend on the growing circumstances and intended usage.

2.3.3 Thermogravimetric Analysis of *Chlorella pyrenoidosa*

Table 1 Ultimate Analysis, Chemical Composition, and Proximate Analysis

Ultimate Analysis, %					
C	H	N	O	S	References
51.2	6.8	11.3	30.7	-	Gai et al., 2013
51.42	7.45	6.87	-	1.63	Chen and Wu, 2017
48.56	6.8	8.39	41.29	1.76	Hu et al., 2015
47.2	6.4	7.5	-	2.7	Chen et al., 2017
56.6	7.3	11.2	24.1	0.8	Cano-Pleite et al., 2020
Chemical Composition, %					
		Protein	Lipid	Carbohydrate	References
		71.5	0.2	22.5	Gai et al. 2013
		67.42	1.83	24.07	Hu et al., 2015
		63.3	3.6	19.4	Chen et al., 2017
Proximate Analysis, %					
Moisture	Volatile Matter	Fixed Carbon	Ash Content	LHV, MJ/kg	References
9.94	70.62	16.23	3.21	16.87	Chen and Wu, 2017
5.78	66.51	15.98	5.95	17.24	Hu et al., 2015
8.4	70.4	14.9	6.3	-	Chen et al., 2017

2.4 Recent Research

2.4.1 Research of Pyrolysis *Chlorella pyrenoidosa*

Previous research on pyrolysis of *Chlorella pyrenoidosa* mainly focuses on the renewable energy application rather than broad potential application of pyrolysis of *Chlorella pyrenoidosa*. Dong et al, 2013 conducted a two-steps catalytic pyrolysis process of *Chlorella pyrenoidosa* to study its activity result. Zeolite base catalyst shows a high concentration of light olefins from these methods. This result shows the promising potential of *Chlorella pyrenoidosa* to produce light olefine throughout a two-step pyrolysis process using ZSM-5 catalyst. His finding shows remarkable improvement of carbon yield of high olefins at 650°C around 31.9%wt with main product of ethylene, propene and butene. This result is almost three times the carbon yield from one step pyrolysis process. His finding also includes comparison of carrier gas in the two-step catalytic pyrolysis process. It shows that the steam carrier gas producing higher yield of light olefine compared to nitrogen carrier gas at inert environment [144].

Other research on pyrolysis of *Chlorella pyrenoidosa* is conducted by Duan et al., 2013. His study focuses in the product distribution of hydro pyrolysis of *Chlorella pyrenoidosa*. Hydro pyrolysis uses hydrogen as carrier gas instead of nitrogen with an inert atmosphere. From his study it can be concluded that temperature is the most influential factor in product distribution. The optimum temperature to produce bio-oil is achieved at 310°C with retention time of 60 minutes at moderate hydrogen pressure (3MPa). At this hydrogen pressure, Duan et al., 2013 obtained higher yield of bio-oil than hydrothermal liquefaction (HTL) process. At optimum conditions, the highest yield of bio-oil is 53.2%, following by 18.5% of non-condensable gas and 12.3% of biochar [145]. Following his previous research on hydro pyrolysis, Duan et al., 2015 expand his area of research on upgrading the quality of bio-oil using catalytic hydrothermal liquefaction (HTL). His research

revealed a remarkable result that by using 10% Ru/C+Mo₂C Catalyst, resulted on the bio-oil produced from *Chlorella pyrenoidosa* that has a high energy density and good stability in thermal and storage. Duan et al., 2015 got the optimum conditions for HTL at 400°C, 22 MPa and 240 minutes of holding time. At optimum conditions, the product distribution shows a high yield of bio-oil (51.5%) followed by 10.5% of biochar and 4.3% of non-condensable gas [146].

Research on Catalytic hydro pyrolysis of *Chlorella pyrenoidosa* was also conducted by Chang et al., 2015. Using 20%wt. Mo₂C catalyst, the optimum condition is achieved at temperature 310°C and 20 minutes holding time. At this optimum condition, the yield of bio-oil increases compared to non-catalytic hydro pyrolysis. The maximum yield of bio-oil from this condition achieved around 54.4%wt. From this result, calculated energy recovery can be estimated around 87.5%. His finding also shows that temperature is still the most important variable either for quality or quantity of bio-oil produced through this method [147].

Recent research on pyrolysis of *Chlorella pyrenoidosa* is conducted by Li et al., 2019. His research is focusing on the environmental aspect of bio-oil produced from microalgae. His research showed that bio-oil produced from *Chlorella pyrenoidosa* has high concentrations of carbon and nitrogen. This can potentially lead to production of NO_x pollution if bio-oil from *Chlorella pyrenoidosa* is used in direct combustion without proper treatment. His finding shows that *Schizochtrium limacinum* produced higher yield of bio-oil, higher HHV, and lower concentration of carbon and nitrogen [148].

Table 2 Summary Literature of Pyrolysis *Chlorella pyrenoidosa*

Method	Catalyst	T, °C	RT, min	Product Distribution, %wt.			Remark	Ref.
				Biochar	Bio-oil	Gas		
Two-step Catalytic Pyrolysis	35%wt. ZSM-5 Zeolite+65% clay	650		-	-	31.9%	A two-step pyrolysis process with modified ZSM-5 catalyst produces 31.9%wt. carbon yield in the form of light olefins (ethylene, propene, butene). It is almost three times the carbon yield compared to one-step pyrolysis process.	[144]
Hydro-pyrolysis	-	310	60	12.3%	53.2%	18.5%	In hydro-pyrolysis, temperature is the most influential factor for product distribution. Moderate hydrogen pressure (3MPa) is needed	[149]

							to produce a higher bio-oil yield at lower temperature than hydrothermal liquefaction	
Catalytic hydro-pyrolysis	20%wt. Mo ₂ C	310	20	-	54.4%	-	Catalytic hydro-pyrolysis is proven to increase yield of bio-oil compared to non-catalytic hydro-pyrolysis. Highest energy recovery achieved for this method is 87.5%	[147]
Catalytic hydrothermal	10%wt. (1:1) Ru/C + Mo ₂ C	400	240	10.5%	51.5%	4.3%	HTL produce upgraded bio-oil with high energy density and have thermal and storage stability.	[150]
Pyrolizer-GC/MS	-	350		-	44.32 %	-	Bio-oil produced from <i>C. pyrenoidosa</i> contains a high concentration of Carbon and Nitrogen. Bio-oil produced from <i>Schizochytrium limacinum</i> have higher yield (60.99%wt.), higher HHV and lower concentration of Carbon and Nitrogen.	[46]

2.4.2 Research of Activation Process

Recent research regarding the activation process of activated carbon is generally divided into two sub-categories, which are in-situ and ex-situ activation process. Activation itself can be defined as an enhancing process to either increase the specific surface area or to adding certain functional group. Both of these purposes are to increase its ability or capacity to remove pollutant such as heavy metal in the wastewater. In-situ activation process generally uses solid activator such as carbonate salt and ex-situ activation process generally used solution or gaseous activator. In-situ activation process means that the activation process itself is embedded with carbonization process. The advantages of in-situ activation process are that it is a straightforward process that includes only mixing the raw material and solid activator, then directly sending it to carbonization process. However, the downside of in-situ activation process is that it needs post treatment purification using solution to remove the remaining solid activator. On the other hand, ex-situ activation process is relatively an easier process than in-situ because the separation between activated carbon and activator is much simpler. The different state between solid activated carbon and fluid activator can reduce the cost of post treatment purification. On the ex-situ process, the activation process can be at pre-carbonization or post carbonization. But in the case of functional group addition, the ex-situ activation process is conducted in the post-treatment to avoid destruction of functional group throughout carbonization process. The downside of ex-situ activation process is that the increase of surface area is much lower compared to in-situ activation. It is because the in-situ activation process focuses to enhance the decomposition process and increasing the specific surface area throughout the carbonization process. While the ex-situ activation process generally focuses on the addition of specific functional group to maximize its potential to capture specific sorbent. In general, for multi-purpose application, in-situ activation process is more favorable

because the utilization of high specific surface area is more versatile for different applications. On the other hand, for specific applications, ex-situ activation can be beneficial for certain applications such as capture of noble gold or specific high value products [151].

Recent research on the activation process using acid and base solution is conducted by Giron et al., 2015, Hijab et al., 2021, and Bergna et al., 2022. From that research it shows the significant increase of specific surface area. Activated carbon produced from Eucalyptus Globulus with NaOH activator can achieve 2108 m²/g specific surface area, Waste date stone with phosphoric acid activator can achieve 909 m²/g specific surface area and hydrolysis of lignin with KOH activator can achieve 2054 m²/g specific surface area. The other type of activator that is generally used in the in-situ activation process is carbonate salt. Recent research that uses carbonate salt as its activator agent is conducted by Sevilla et al., 2017, Satayeva et al., 2018, Dao and Le Luu., 2020, Liu et al., 2021, Song et al., 2021 and Bergna et al., 2022. *Spirulina plantesis* with Calcium carbonate at 750°C shows promising result with high specific surface area around 3053 m²/g. The other research that used Potassium carbonate also produced promising results of specific surface area: rice husk 1330 m²/g, macademia nutshell 459.8 m²/g, rice straw 2800 m²/g, cattail fiber 1016 m²/g and hydrolysis lignin 514 m²/g.

The other carbonate salt that still has little utilization on in-situ activation process is Sodium bicarbonate. Sodium bicarbonate is well known for Baking Soda in the baking industry for leavening agent. By mimicking its mechanism as leavening agent, Sodium bicarbonate is a promising activator for producing activated carbon. By the effect of CO₂ gas release in decomposition, Sodium bicarbonate can rise the baking dough at high temperatures and this ability is potentially used to increase the volume of activated carbon and reduce its density that ultimately increases the specific surface area [152].

Table 3 Summary Literature of Activating Agent

Material	Activating Agent	Result	Reference
<i>Eucalyptus Globulus</i>	NaOH	S: 2108 m ² /g	[153]
<i>Spirulina plantesis</i>	Potassium oxalate & Calcium Carbonate	MA-750 S:3053 m ² /g; N:2.1%	[154]
Rice Husk	Potassium Carbonate	S: 1330 m ² /g	[155]
Macademia Nutshell	Sulfuric Acid & Potassium Carbonate	K ₂ CO ₃ S: 459.8 m ² /g	[156]
Waste date stone	Phosphoric Acid	activated S:909 m ² /g. non-activated:86 m ² /g	[157]
Rice straw	Urea & Potassium Carbonate	S: 2800 m ² /g; N: 1.65%	[158]
Cattail fiber	Potassium Carbonate	S:1016 m ² /g	[159]
Hydrolysis Lignin	KOH, ZnCl ₂ , Sodium Carbonate	800_KOH S:2054 m ² /g; 800_Na ₂ CO ₃ S:514 m ² /g; 500_ZnCl ₂ S:1626 m ² /g	[160]

2.4.3 Research of Heavy Metal Adsorption

Biochar is a well-known material that can be used as adsorption material. Several research on biochar as adsorbent material is shown in **Table 4**. Based on **Table 4**, several factors that affect adsorption performance are temperature[161], purging gas that is used[162], activation method[161], pH of point of zero charge (PZC) [163], specific surface area[163,164], type of functional group appeared on the surface[164] of adsorption material and method of adsorption[164].

Research by Islam et al shows that papermill sludge (PMS) biochar from pyrolysis process at 600 °C and heating rate of 15 °C/min had a high adsorption capacity for heavy metal like Ni (II), Cu (II) and Pb (II). Meanwhile, Rice Straw (RS) biochar had a high adsorption capacity for Cd (II). Compared to the effect of feedstock type, carrier gas that is used has less impact in the performance of biochar on adsorption process. PMS biochar had a higher affinity for multiple heavy metal because it has a larger surface area and has more carboxyl and hydroxyl functional group in the surface of biochar compared to RS biochar. Hydroxyl and Carboxyl functional group promotes electrostatic interaction and complexation reaction between heavy metal and biochar, hence it has a great impact in adsorption process[162].

Wang et al. also conducted an experiment about biochar for adsorption of heavy metal purposes. Biochar preparation used drum carbonizer with pyrolysis process at 550 °C for 2h. The same treatment is applicable for willow wood (WW) and cattle manure (CM). The result concluded that the primary mechanism in heavy metal removal using biochar is surface interaction with carboxyl (-COOH) functional group. Carboxylic functional group promotes complexation reaction between heavy metal and the surface of biochar, then enhance the adsorption capacity. Large specific

surface area and lower pH of point of zero charge also have a great contribution on the physical adsorption and electrostatic interaction[163].

Kwak et al focuses on the application of biochar on lead (II) heavy metal adsorption on wastewater. Biochar preparation used muffle furnace with variable of temperature (300, 500, and 700 °C) followed with/without steam activation process for 1h. Heating rate 10 °C/min was used with reaction time of 2h at inert environments. Those conditions are applicable for all raw material (canola straw, manure pellet, sawdust, and wheat straw). Kwak et al. found that by increasing pyrolysis temperatures, there will be an increase of pH, ash content and surface area of biochar and finally leads to positive impact on adsorption capacity of lead (II). Best raw material that Kwak et al. found for Lead (II) heavy metal adsorption is biochar from canola straw and the worst is sawdust because of its low adsorption capacity[161].

Amin and Chetpattananondh conducted an experiment using extracted marine *Chlorella sp.* (EMCR) Residue to produce biochar for adsorption material purposes. Biochar preparation used tube furnace with inert environment with constant temperature of 450 °C, heating rate of 10 °C/min and reaction time of 60 min. Biochar derived from EMCR is used for adsorption of Cr (VI), Zn (II) and Ni (II) with variable of conventional adsorption and ultrasonic adsorption. Amin and Chetpattananondh observed the effect of adsorption method in the adsorption capacity of heavy metal on biochar derived from EMCR with Langmuir isotherm model. The result shows that for both conventional and ultrasonic adsorption, biochar derived from EMCR has the highest adsorption capacity for Ni (II) heavy metal. Amin and Chetpattananondh also found that ultrasonic adsorption method can enhance adsorption capacity of heavy metal for 10-30%[164].

Table 4 Summary Literature of Heavy Metal Adsorption using Biomass based Activated Carbon

Material	Adsorption Capacity	Remark	Reference
Pulp Mill Sludge (PMS) and Rice Straw (RS)	PMS: 256.4 mg/g for Lead (II) RS: 133.3 mg/g for Lead (II)	Lead (II) adsorption is higher with nitrogen purge than carbon dioxide purge. Biochar from PMS performed better than RS for adsorption of lead (II) heavy metal	[162]
Willow wood (WW) and Cattle Manure (CM)	WW: 76.4 mg/g for Cd CM: 37.5 mg/g for Cd	Biochar from WW has a higher adsorption capacity than from CM. A higher specific surface area and a lower pH of point of zero charge (PZC) are major contributing factors for removal capacity.	[163]
Sawdust, canola, and wheat straw	Canola: 195 mg/g for Lead (II)	At 700 °C and steam activation, biochar from canola has the highest adsorption capacity for Lead (II). Steam activation increased surface area for most biochar	[161]
Extracted marine <i>Chlorella sp.</i> Residue (EMCR)	EMCR: 27.45 mg/g for Ni (II)	Biochar from EMCR has a high surface area (266 m ² /g) and a rich O-functional group that has a high contribution on heavy metal adsorption. Ultrasonication adsorption (UA) increases heavy metal efficiency by 10-30%	[164]

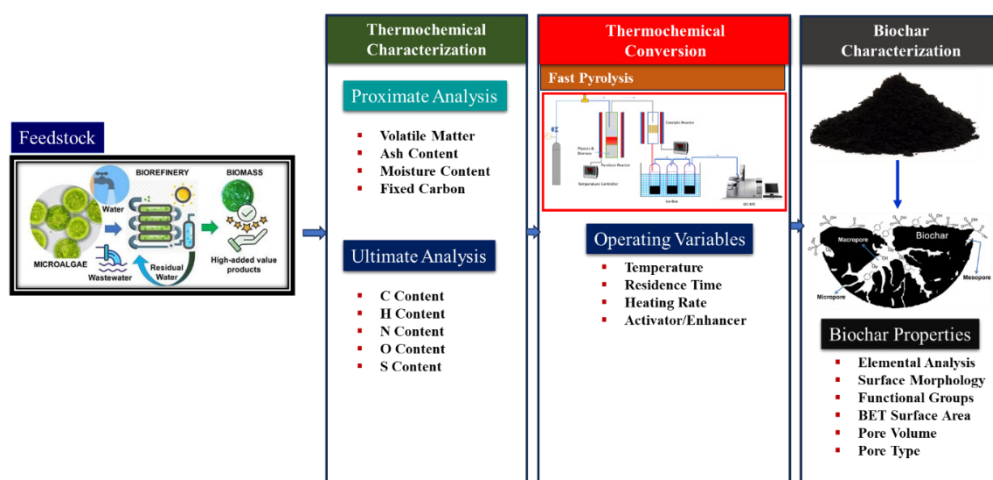


Figure 7 Biochar production from *Chlorella pyrenoidosa* via pyrolysis process.

2.5 Research Gap

Recent studies on the topic of pyrolysis of *Chlorella pyrenoidosa* heavily focus on the renewable energy application. Non condensable gas and pyro-oil are still the main product that are targeted in those researches. Furthermore, until early 2023, only 21 papers published on Scopus indexed journal that specifically discuss about pyrolysis of *Chlorella pyrenoidosa*. Additionally, the research on the activation process and application of activated carbon for heavy metal removal shows the promising area to increase the value of biochar produced from pyrolysis of *Chlorella pyrenoidosa*. Biochar from pyrolysis process shows much lower energy density compared to biochar from torrefaction. Hence, throughout the activation process biochar will be comparable with activated carbon in terms of value and usability.

This research attempts to fill this gap by focusing on producing high performance activated carbon from pyrolysis of *Chlorella pyrenoidosa* through pyrolysis process. By utilization of Sodium bicarbonate as activating agent, this study will contribute to enriching the literature on in-situ activating process with carbonate salt. This will motivate another researcher to explore more topics in this area of research.

CHAPTER 3

RESEARCH OBJECTIVES

The main objective of this study is to develop and synthesize novel activated carbon from *Chlorella pyrenoidosa* microalgae with a high surface area for Lead wastewater treatment applications. High surface area is one of the main characteristics of adsorption material with high performance. Therefore, this research aims to fill the gap of research on the precursor option and condition to produce high performance activated carbon for wastewater treatment application.

The following are the specific objectives of this Thesis:

- i. To investigate the potential of *Chlorella pyrenoidosa* and synthesis activated carbon with high performance characteristics.
- ii. To study the performance of activated carbon derived from *Chlorella pyrenoidosa* for Lead removal in the wastewater.

CHAPTER 4

MATERIALS AND METHOD

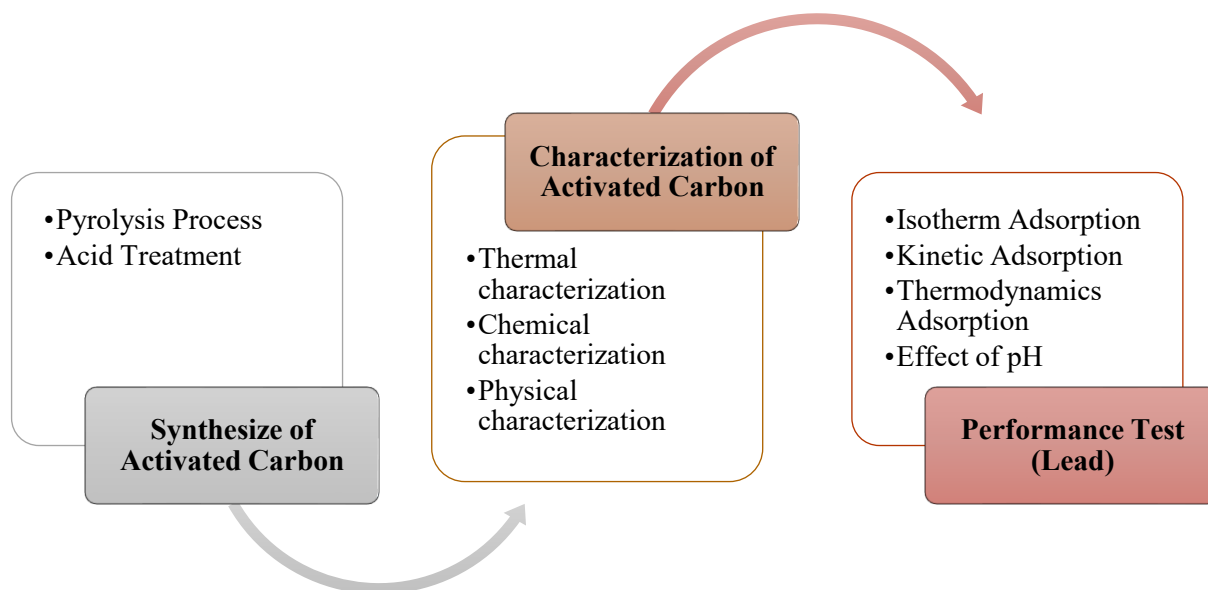


Figure 8 Major steps to produce activated carbon from microalgae.

To synthesize novel activated carbon from microalgae there are several steps that need to be done. These steps are introduced in **Figure 8**. Synthesis process starts with drying sample to remove moisture in the microalgae. Dry microalgae will be divided into two group samples. The first group sample uses sodium bicarbonate (activating agent) while the second one does not use activating agent. Each group sample is set for different pyrolysis temperature.

4.1 Chemicals and Materials

The microalgae species *Chlorella pyrenoidosa* powder was obtained from Organic Tradition Company with its headquarters in the Wilmington, Delaware, 19803, United States. The activating agent that was used is Sodium Bicarbonate (NaHCO_3), while Hydrochloric Acid (HCl) 1M is used for Acid Treatment. Heavy metal reagents that are used for synthetic wastewater are lead diluted from $\text{Pb}(\text{NO}_3)_2$. All the reagent was without further purification.

4.2 Carbon Preparation

4.2.1 Pyrolysis Process

Microalgae samples with and without activating agent (Sodium Bicarbonate) were processed in pyrolysis process. Pyrolysis is one of thermochemical process that can produce porous material with a high surface area. Optimum heating rate used was $10\text{ }^\circ\text{C}/\text{min}$ [165] and the retention time was 180 min [166]. Variable of temperature that was used in this experiment was around 550-750 $^\circ\text{C}$.

4.2.2 Acid Treatment

Biochar produced from pyrolysis process needs further process with acid treatment to clean the porous and the remaining of sodium bicarbonate. Acid treatment with HCl is proven to decrease active acidic group and enhances the adsorption of larger molecules[167]. Carbon was mixed with 1M Hydrochloric Acid (HCl), and the mixture was further processed in the ultrasonic bath for 1 h. After that, the mixture was settled overnight to separate the carbon from the solution. The carbon was separated from the solution with decantation process and washed with Deionized (DI) Water twice before filtering it. The drying was $80\text{ }^\circ\text{C}$ overnight.

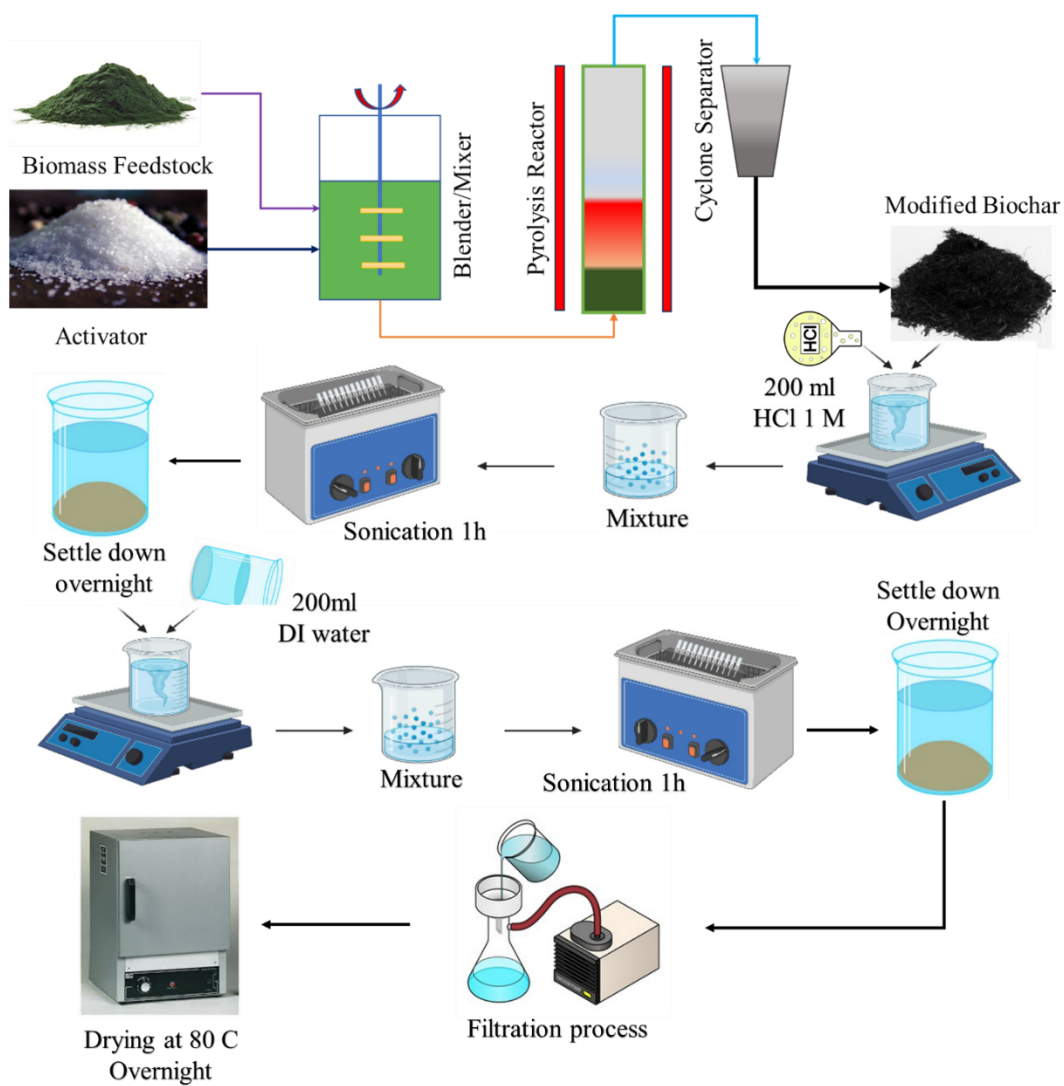


Figure 9 Schematic of Pyrolysis Process and Acid Treatment

4.3 Characterization of Activated Carbon from *Chlorella pyrenoidosa*

4.3.1 Thermal Characterization

The most common method for thermal characterization is Thermogravimetric analysis (TGA). TGA is an assessment property of material using mass difference as a function of temperature and its derivative. Mass difference data represent the decomposition stages of material. Meanwhile, its derivative data represent the composition of material that decomposes for every temperature. Thermogravimetric analysis was generally used in inert environment (Nitrogen) and air environment. Air environment was used to check thermal stability of activated carbon and composition of ash in the end of analysis. Inert environment was used for proximate analysis of microalgae, and to predict kinetic parameters in the pyrolysis process. From kinetic parameter, conversion of microalgae biomass in the pyrolysis process can be estimated[168].

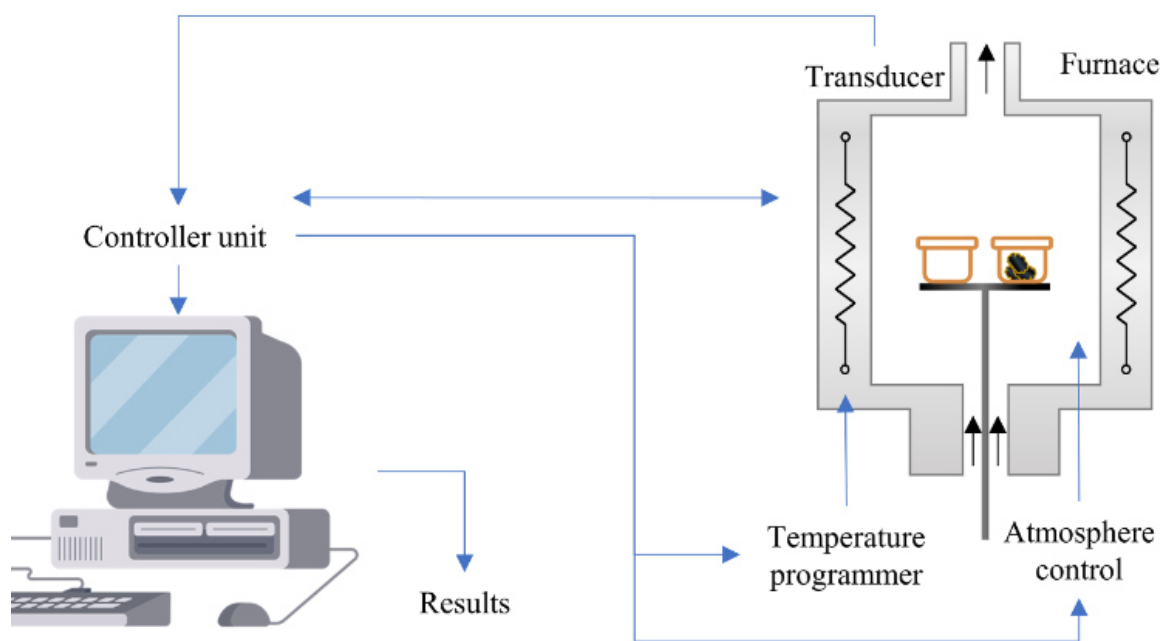


Figure 10 Schematic Process of Thermogravimetric analysis.

4.3.2 Chemical Characterization

X-ray Diffraction (XRD) Analysis is commonly used for observation of crystallite structure of material. X-ray beams will deliver light at a certain degree of angle and the result will be received by detector. With this method, the type of crystallite can be identified based on its corresponding peaks[168]. It is also needed to check graphite peak in the activated carbon. Commonly, activated carbon is represented by 002 planar and 100 planar from XRD result. The narrower and the higher the (002) peak, the better the orientation of the aromatic layer slice. The narrower and the higher the (100) peak, the larger the size of the aromatic layer slice[169].

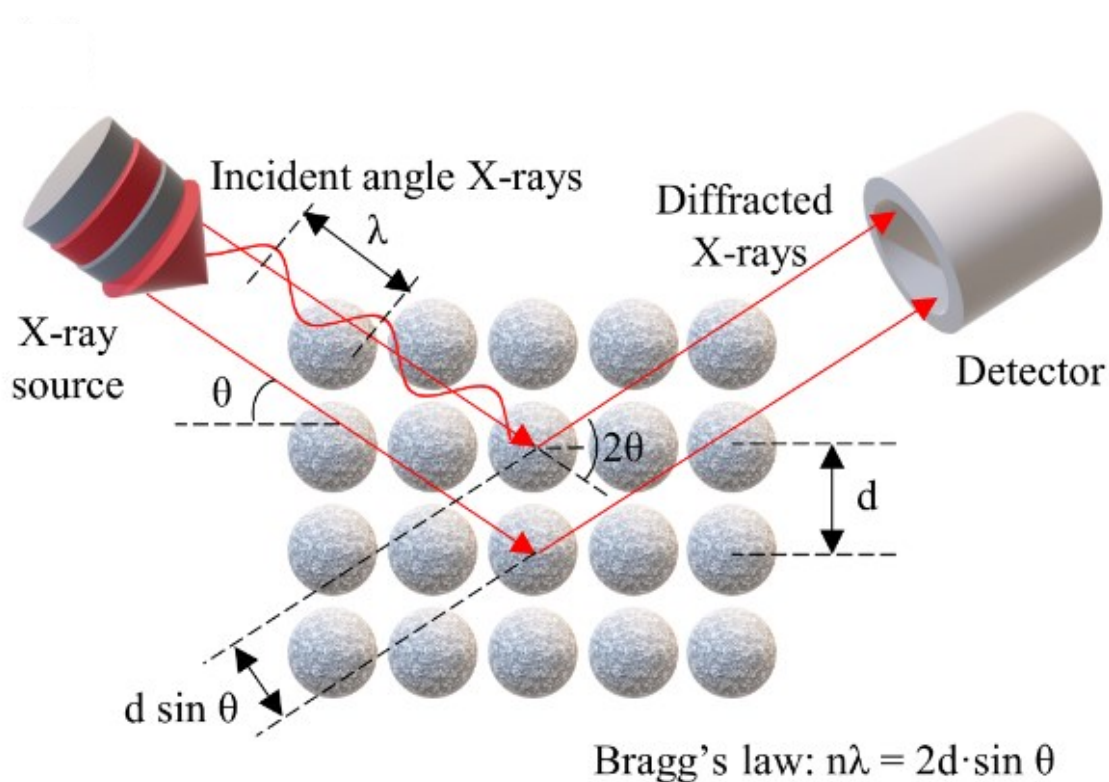


Figure 11 Schematic process of XRD Analysis

Fourier Transform Infrared Spectrophotometry (FTIR) is one of the most informative techniques that gives information from material about its chemical composition, functional group, isomorphic substitution, and structural modification. Moreover, it can determine the different interaction between materials. Infra-red radiation causes a vibration in the molecular bond because of excitation energy generated by it. Michelson interferometer is typically used for FTIR. Infrared from source is split by beam splitter to the mirror and from those two mirrors the infrared beam will be recombined and directed to the detector through the sample. Then, those signal that is received by detector is converted into plot of intensity function of wavenumber by Fourier transform mathematical method[168]. FTIR is needed to check functional groups and other characteristics in the surface of activated carbon. Graphitic-N functional group is a main functional group that is favorable in adsorption process because graphitic-N functional group increases the probability of complexation reaction.

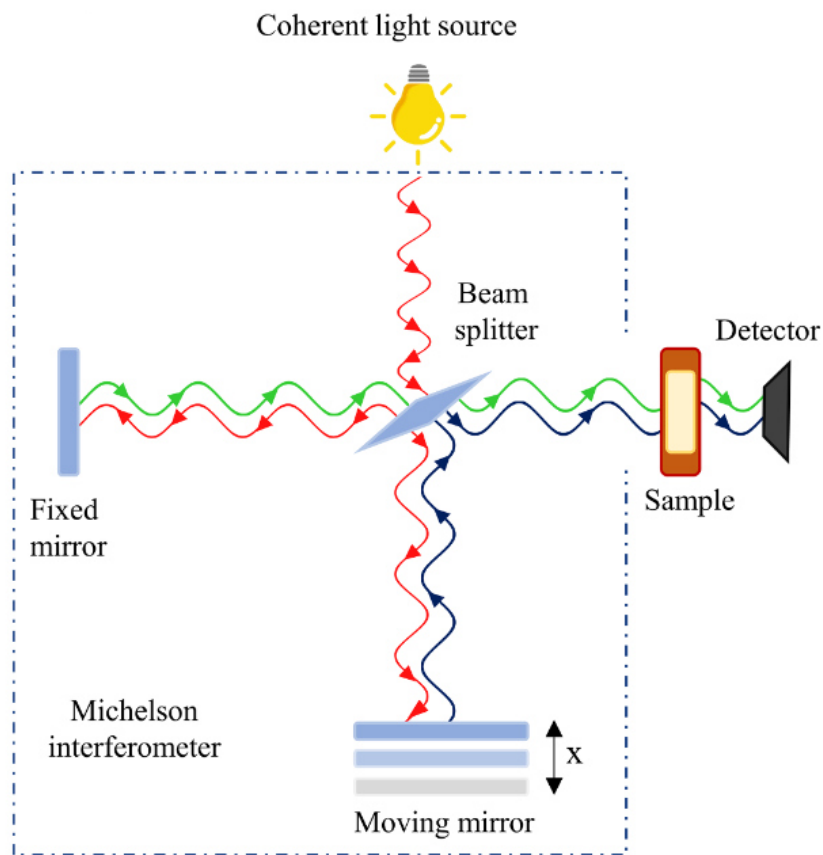


Figure 12 Schematic Process of FTIR analysis.

4.3.3 Physical Characterization

The Brunauer–Emmett–Teller (BET) Model is commonly used to determine physical properties of porous material. Data collected from its apparatus is mainly quantity of adsorbed nitrogen as a function of relative pressure. From isothermal Nitrogen adsorption/desorption process, it can estimate how much is the surface area, pore volume, pore diameter and nanoparticle size[168]. Also, from adsorption/desorption curve, hysteresis loop can interpret estimation of the pore shape of material[170]. Higher surface area is considered better in terms of adsorption process.

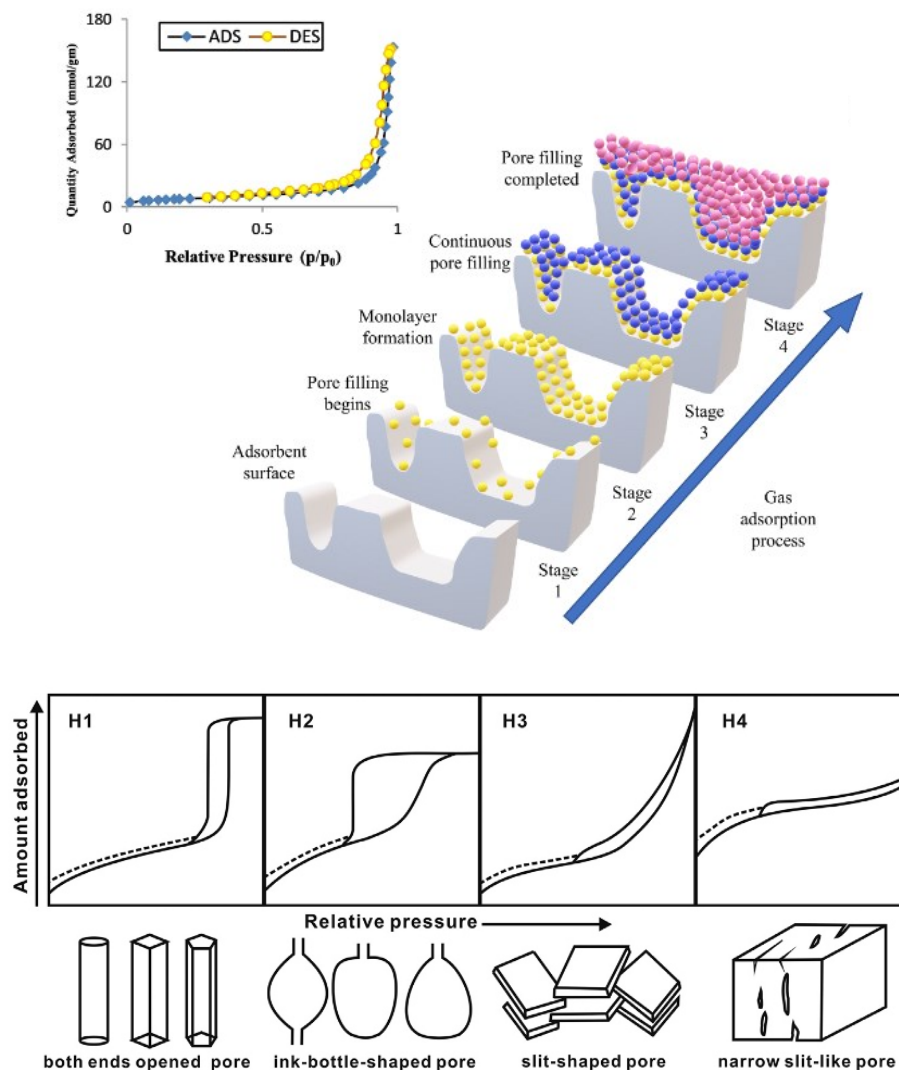


Figure 13 Schematic process of isothermal N₂ adsorption/desorption using BET Model and Hysteresis shape and its corresponding pore shape estimation.

Scanning Electron Microscopy (SEM) is usually needed to observe and study microstructure of activated carbon. It is also needed to verify the modification of microalgae to activate carbon. SEM uses excitation energy from electron beam that crosses a set of electromagnetic sample lenses then hits the sample. Sample releases secondary electrons that is captured by detector to generate image[168]. SEM is also used to visualize the surface structure of adsorption material and to verify

heavy metal particles in the surface of activated carbon after heavy metal adsorption performance test.

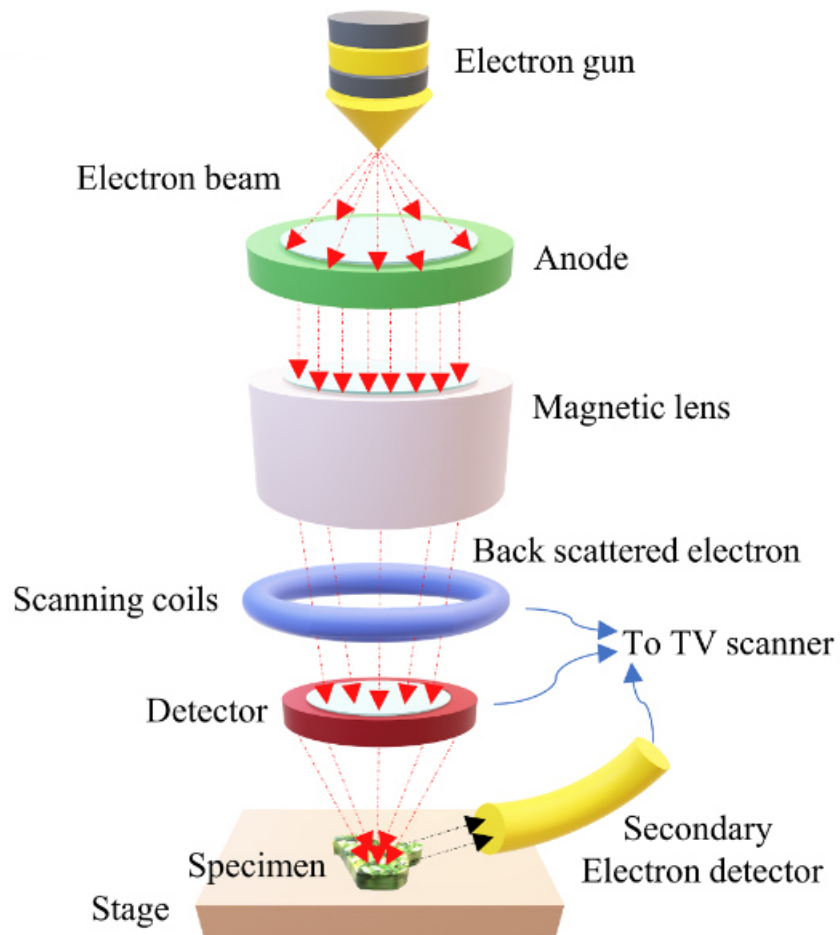


Figure 14 Schematic Process of SEM Analysis

4.4 Heavy Metal Removal Performance Test

Heavy metal removal performance test was conducted as explained in the **Figure 15**. Activated carbon with the most suitable characteristics was mixed with synthetic wastewater with heavy metal content and was mixed in the shaker at 180 rpm for 1h. After that, the solution was centrifuged to separate the solid carbon and supernatant. Supernatant was further checked to observe the metal content after performance test.

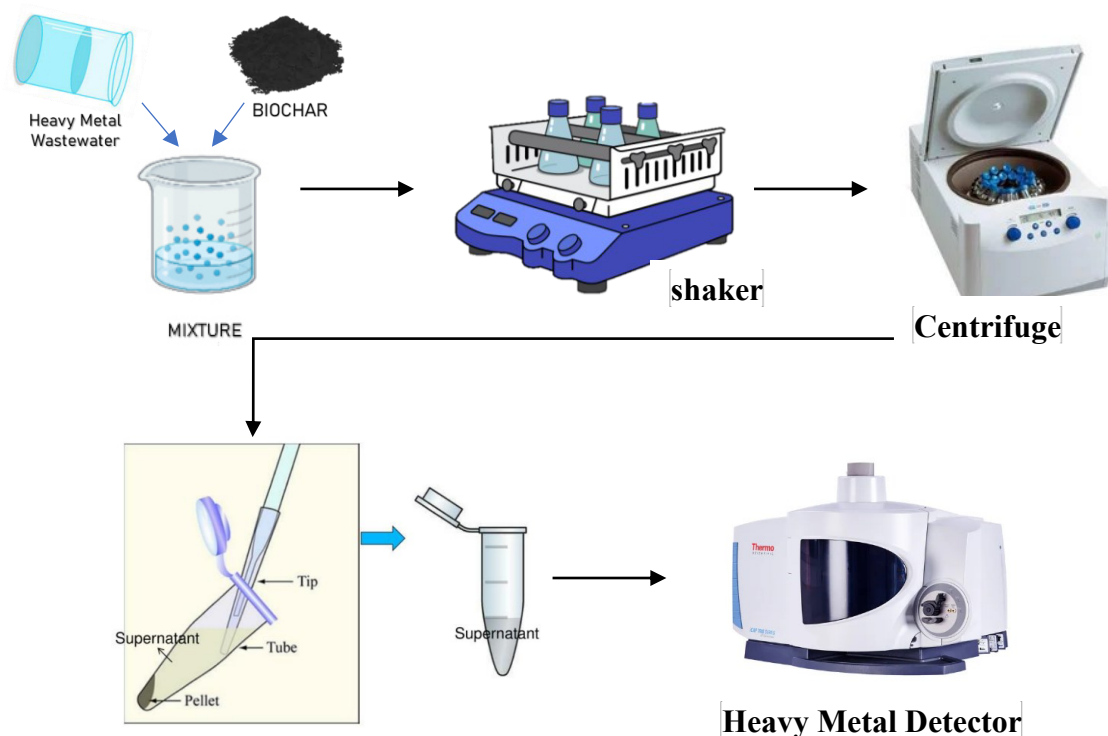


Figure 15 Schematic Process of Performance Test

CHAPTER 5

EXPLORING THE POTENTIAL OF CHLORELLA PYRENOIDOSA USING CHEMICAL CHARACTERIZATION AND THERMOGRAVIMETRIC ANALYSIS

5.1 Physicochemical Analysis Result

The plot of Thermogravimetric (TGA) and Derivative Thermogravimetric (DTG) of CP is shown in **Figure 16**. **Figure 16(a)** shows a summary of TGA and DTG plot for different heating rates. Peak in DTG plot represents the stage of decomposition of CP. It shows that in general, in a non-oxidative atmosphere, thermal decomposition of CP had 4 stages of decomposition. Stage I was between 100-200°C: moisture removal. In this stage all of moisture in the CP would evaporate. Stage 1 was represented by the first peak of DTG plot. Stage II was between 220-315°C: hemicellulose devolatilization. In this stage, hemicellulose was decomposed into light oxygenates, acetic acid, furfural and other components [171]. Stage III was between 300-600°C: cellulose devolatilization. In this stage, cellulose was decomposed into levoglucosan. Stage II and III were represented by broad twin peaks between 220-600°C. Stage IV was between 600-900°C: carbonization. After all volatile matter evaporates, the remaining organic compound was converted into fixed carbon and ash[172].

Figure 16 also indicates that at higher heating rate, more volatile matter was generated from thermal decomposition, but the temperature needed for decomposition of cellulose was slightly higher. It can be concluded that higher heating rate increased conversion of hemicellulose and

cellulose but the energy to decompose cellulose was slightly higher. It also shows that the devolatilization process was achieved better in the higher heating rate. At higher heating rate, area under the peak DTG of volatile matter was bigger than at higher heating rate which indicated higher concentrations of volatile matter released from the microalgae [173]

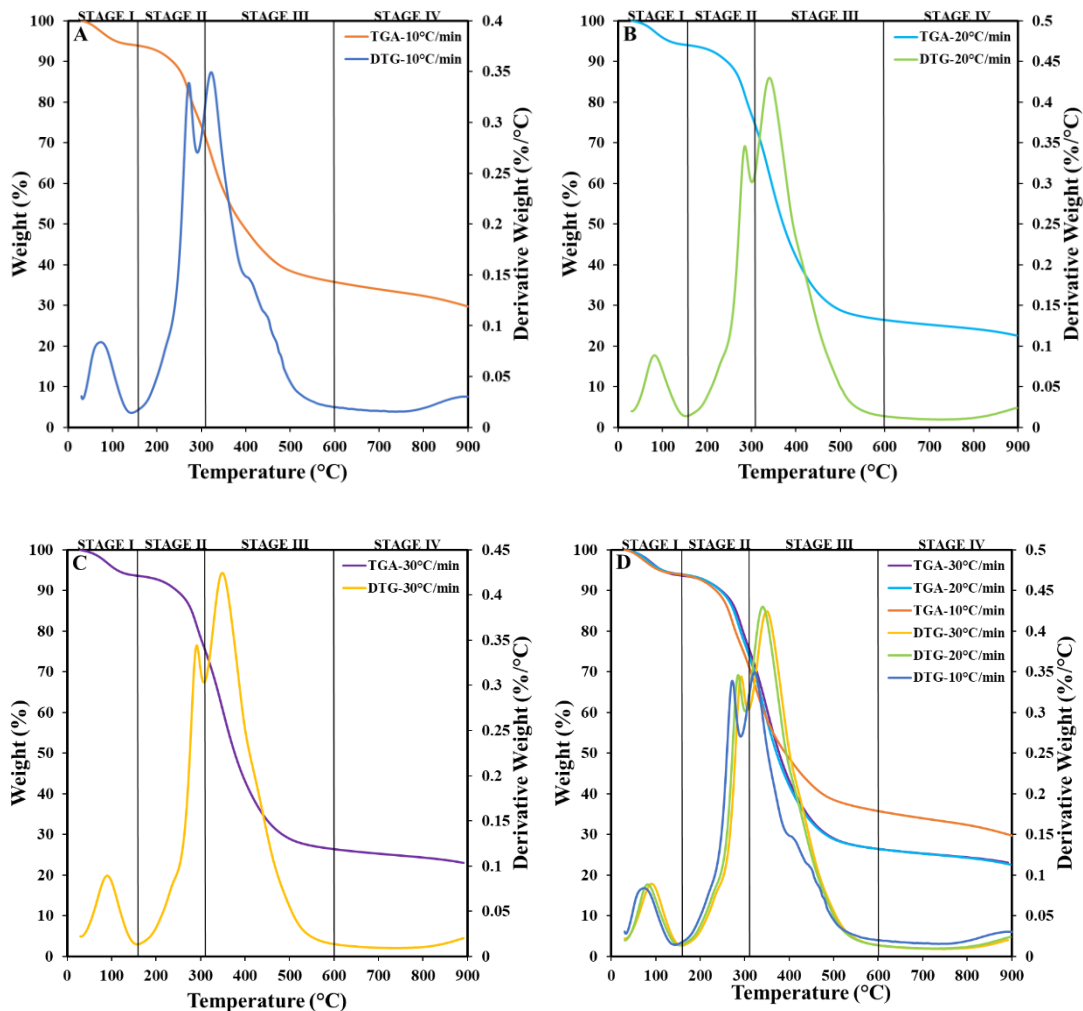


Figure 16 Result of Thermogravimetric and Derivative Thermogravimetric Analysis of *Chlorella pyrenoidosa*: a) Heating rate of 10°C/min, b) Heating rate of 20°C/min, c) Heating rate of 30°C/min and d) Summary result for different heating rate.

Table 5 Peak Temperature (T_m) for Different Heating Rates, Result of Proximate Analysis and Ultimate Analysis of CP.

Ultimate Analysis, %					
C	H	N	O	S	References
51.2	6.8	11.3	30.7	-	[174]
51.42	7.45	6.87	-	1.63	[175]
48.56	6.8	8.39	41.29	1.76	[176]
47.2	6.4	7.5	-	2.7	[177]
56.6	7.3	11.2	24.1	0.8	[178]
53.1	7.5	9.5	29.2	0.7	This Study
Proximate Analysis, %					
Moisture	Volatile Matter	Fixed Carbon	Ash Content	LHV, MJ/kg	References
9.94	70.62	16.23	3.21	16.87	[175]
5.78	66.51	15.98	5.95	17.24	[176]
8.4	70.4	14.9	6.3	-	[177]
2.19	69.35	25.04	3.42	19.7	This Study
Heating Rates (β)		Peak (%/°K)		T_m (°K)	
10		0.349434		595.2079	
20		0.429795		613.5025	
30		0.424507		622.2997	

5.2 XRD and FTIR Analysis

XRD and FTIR analysis is needed to identify the characteristics of lattice plane in the CP and functional group in the surface of biomass. **Figure 17(a)** shows the results of XRD analysis. It shows that broad peak around 20° corresponded to 021 lattice plane of cellulose. The broad peak in the XRD analysis indicated that the CP biomass tended to be more amorphous than crystalline. Amorphous characteristics tended to be more reactive than crystalline that made the biomass potentially feasible for adsorption applications [179,180]. **Figure 17(b)** shows the result of FTIR analysis. From this figure, several functional groups can be identified from its bending and stretching response after infrared radiation. It shows that CP biomass contained aromatic rings, alkanes, amines, nitrous, esters, ether, amides, alkenes and carboxyl functional group. This result shows the potential of CP as adsorbent material for several applications and has high potential in chemisorption mechanism. Several research shows that carboxyl functional group increase the performance of heavy metal removal [181] and CO_2 adsorption [182]. **Figure 17(c)** shows Van Krevelen diagram of CP biomass. It shows that in comparison with another biomass in the figure, CP had relatively low H/C and O/C atomic ratio. The lower H/C and O/C shows the potential of this biomass as bioenergy applications. Classification of energy density potential is described in journal published by Chacón-Patiño et al., It shows that material that can be easily converted into compound with high energy density usually has feature of $1.5 < \text{H/C} < 2$ and $\text{O/C} > 0.3$ [183]. It shows that CP biomass has potential to be converted into another molecule that has high energy density.

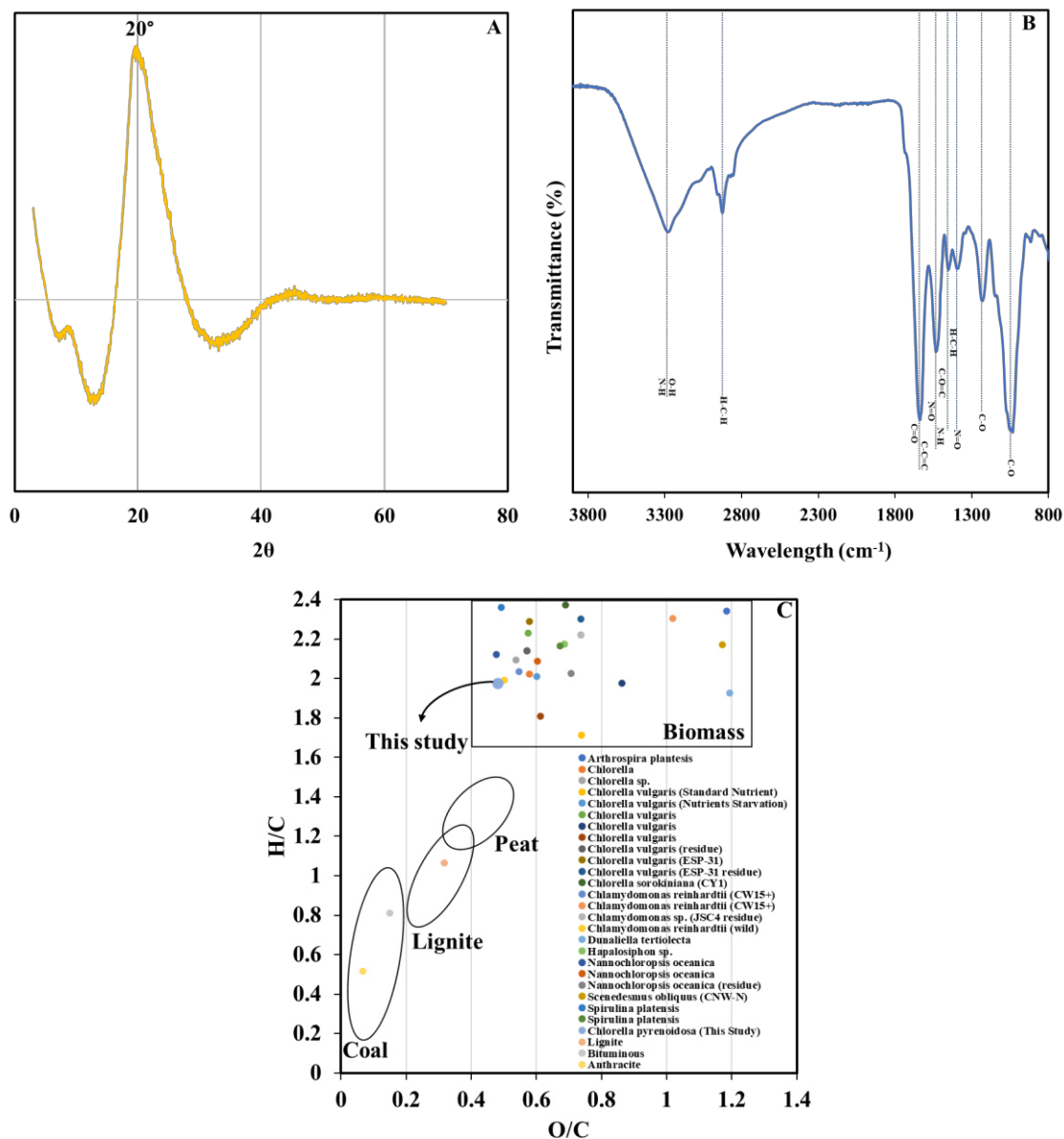


Figure 17 Chemical characterization of CP: a) XRD result, b) FTIR result, and c) Van Krevelen diagram result.

5.3 Kinetic Analysis

5.3.1 Iso-conversional Method

Iso-conversional methods utilize data from different heating rates (β) to obtain a good approximation of activation energy (E_a) and Arrhenius constant (A). In this study, heating rates

(β) of 10, 20 and 30°C/min were used to get consistency results. R-squared (R^2) shows how much the model can explain the experimental data[184]. The higher the indicated R^2 , the higher the ability of model in explaining the experiment result. **Table 6** shows result summary of thermo-kinetic parameter for different iso-conversional model at conversion range (α) between 0.1 and 0.7. The result indicated that all models had good consistency that was between 0.1 and 0.4 with $R^2 \geq 0.8$, but the activation result and pre-exponential Arrhenius constant ($\ln A$) were highly fluctuated ($E_\alpha = 162.68 - 550.21$ kJ/mol and $\ln A = 38.57 - 102.45$ min⁻¹). This result shows the limitation of iso-conversional model that some information cannot be captured at linearization and resulted in highly fluctuated estimation.

Analysis of variant (ANOVA) was used to get overall picture of approximation based on summary results of iso-conversional Model. ANOVA result shows the average of E_α and $\ln A$ with its standard error. Standard error indicates absolute measure of the distance between fitted value and the actual value of the data. R^2 is good for determining goodness of fit in the linear data, but it only tells as the relative measure of the percentage of variance that can be explained by the model without measuring the exact distance between data point and exact value. Hence, in this study standard error was utilized to measure the goodness of fit for the models[185]. The brief result of the E_α from the iso-conversional were 318.11±54.46 kJ/mol for Friedman, 277.48±45.14 kJ/mol for Flynn-Wall-Ozawa (FWO), 281.51±47.05 kJ/mol for Kissinger-Akahira-Sunose (KAS), and 281.7±47.03 kJ/mol for Starink. While the brief result of pre-exponential Arrhenius constant ($\ln A$) were 61.01±8.55 min⁻¹ for Friedman, 55.12±9.05 min⁻¹ for Flynn-Wall-Ozawa (FWO), 55.92±9.43 min⁻¹ for Kissinger-Akahira-Sunose (KAS), and 55.96±9.43 min⁻¹ for Starink. Precision analysis of iso-conversional model from ANOVA shows that FWO model gave the lowest standard error for activation energy (E_α), while Friedman gave the lowest standard error

for pre-exponential Arrhenius constant ($\ln A$). It was to be expected because FWO, KAS and Starink did not give explicit result of pre-exponential Arrhenius constant ($\ln A$) in the model, instead, it was obtained from the Kissinger equation based on activation energy (E_α) resulted from each models[186].

Figure 18(a) and 18(b) shows the plot of activation energy (E_α) and pre-exponential Arrhenius constant ($\ln A$) for different conversion. It shows that Friedman model for most of cases (except 10% of conversion) over-estimated the value of activation energy (E_α). While FWO, KAS and Starink model gave very similar results. This result supported the previous hypothesis from ANOVA that Friedman model showed the highest standard error compared with another iso-conversional model. It is also worth noting from **Figure 18(a) and 18(b)** that the increase of conversion led to the increase of activation energy (E_α) and pre-exponential Arrhenius constant ($\ln A$).

Figures 18(c), 18(d), 18(e) and 18(f) show the linear line for different models that determine the approximate activation energy (E_α). The activation energy is obtained from the slope of linear line from corresponding equations depending on the models. It shows that the data point was not too far away from the linear line for all iso-conversional models. It can be concluded that all iso conversional models that were used in this study gave good approximation of activation energy and pre-exponential Arrhenius constant ($\ln A$) for different heating rates of thermal decomposition of *CP*. However, further analysis with another method is needed to reconfirm that estimated activation energy (E_α) and pre-exponential Arrhenius constant ($\ln A$) parameter represent the actual thermal decomposition of *CP*.

Table 6 Summary Result of Iso-conversional Method

Conversio n	Friedman			Flynn-Wall-Ozawa			Kissinger-Akahira-Sunose			Starink		
	E_{α}	$\ln Af$	R^2	E_{α}	$\ln A$	R^2	E_{α}	$\ln A$	R^2	E_{α}	$\ln A$	R^2
0.1	162.7	38.57	0.91	177.39	35	1	178.07	35.2	0.96	178.27	35.19	0.96
0.2	182.2	40.83	0.97	160.22	32	1	159.24	31.3	1	159.48	31.37	1
0.3	248.4	52.21	0.98	222.13	44	1	223.81	44.4	1	224.03	44.44	1
0.4	482.7	95.56	0.98	345.73	69	0.8	353.38	70.4	0.8	353.51	70.42	0.8
0.5	251.4	48.83	0.97	222.44	44	0.6	223.24	44.3	0.64	223.49	44.33	0.64
0.6	349.2	63.02	0.95	313.89	62	0.8	318.83	63.5	0.86	319.03	63.52	0.86
0.7	550.2	88.09	0.72	500.54	100	0.9	513.99	102	0.96	514.08	102.5	0.96
Average	318.1	61.02	0.93	277.48	55	0.9	281.51	55.9	0.89	281.7	55.96	0.89
Std. Error	56.46	9	0.04	45.15	9	0.1	47.05	9.43	0.05	47.03	9.43	0.05

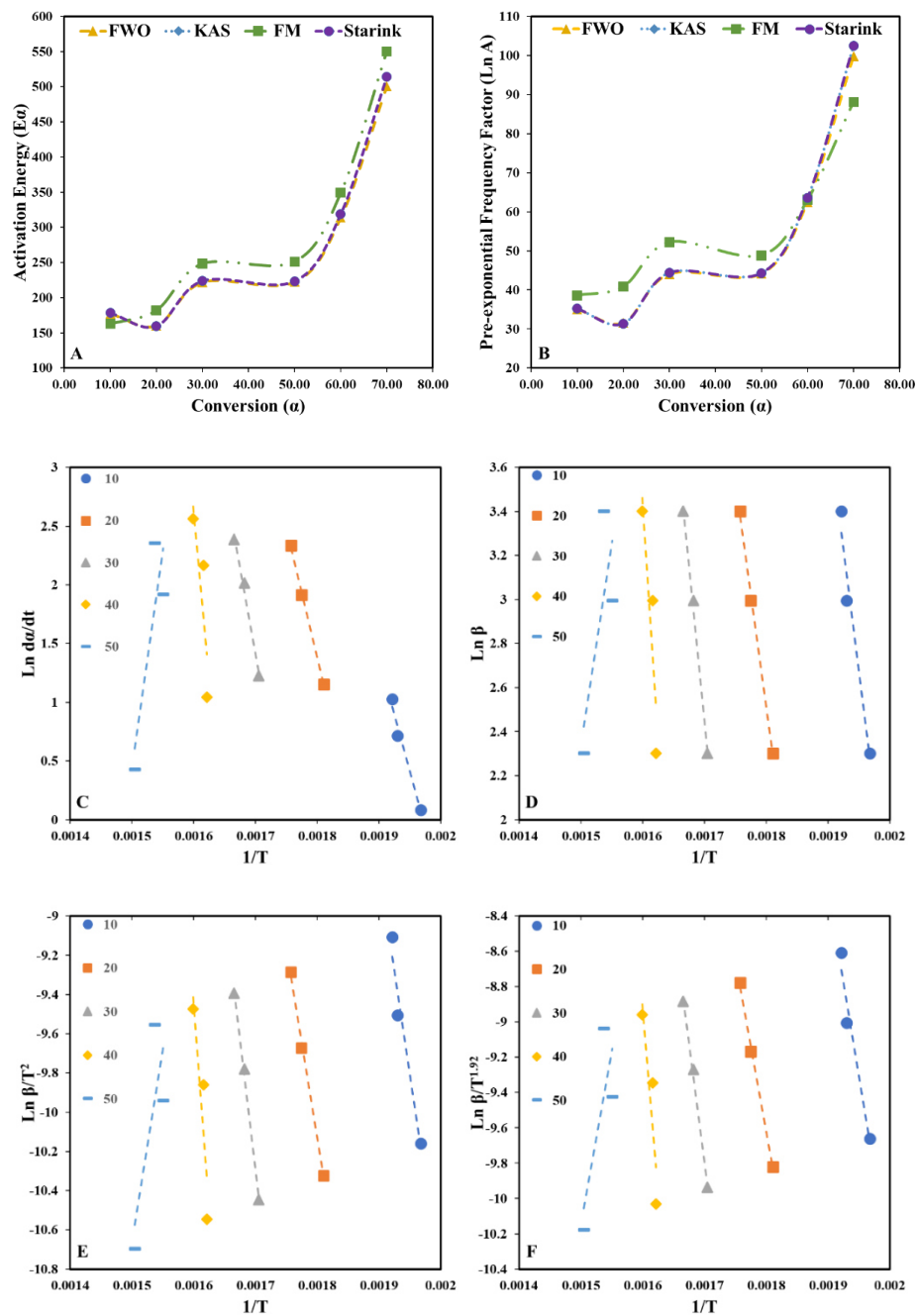


Figure 18 Result of iso-conversional method: a) Activation Energy (E_a) vs Conversion (α) for different Model, b) Pre-exponential Arrhenius constant ($\ln A$) vs Conversion (α) for different Model, c) Friedman Plot, d) FWO plot, e) KAS plot, and f) Starink plot.

5.3.2 Linear Regression Method

Based on model fitting method, linear regression is the simplest method to estimate thermo-kinetic parameters. Slightly different from the iso-conversional method, linear regression does not need multiple datasets to estimate activation energy (E_a) and pre-exponential Arrhenius constant. Each heating rate dataset produced its corresponding thermo-kinetic parameter. In this study all datasets were used to estimate activation energy (E_a) and pre-exponential Arrhenius ($\ln A$) constant. The purpose of using three different heating rates datasets was to minimize the error generated from consistency result between datasets. Maximize solver tools in excel were used to get maximum value of R^2 and by changing n and m value for all datasets, slope and intercept for each heating rate was obtained. While slope corresponds to activation energy, intercept corresponds to corrected pre-exponential Arrhenius constant ($\ln cA$). The result of activation energy (E_a) and corrected pre-exponential Arrhenius constant ($\ln cA$) is shown in **Table 7**. Activation energy obtained from linear regression model was around 262.78-311.48 kJ/mol, while corrected pre-exponential Arrhenius constant ($\ln cA$) was around 51.1-64.56min⁻¹. The standard error was relatively low and R^2 value from linear regression model was relatively high, and it indicated a desirable result for the linear model's goodness of fit. **Table 7** shows that the increase of heating rate resulted on the increase of activation energy and corrected pre-exponential Arrhenius constant ($\ln cA$). Similar results were found in the study of Saddawi *et al.*, 2010 that found positive correlation between heating rates and thermo-kinetic parameters[187]. Result of ANOVA in **Table 7** shows the activation energy (E_a) and corrected pre-exponential Arrhenius constant ($\ln cA$) from linear regression were 295±16.11 kJ/mol and 60±4.45 min⁻¹. Compared to the iso-conversional model, linear regression produced similar results with lower standard error for both activation energy and pre-exponential Arrhenius constant ($\ln A$).

Figure 19 shows the result of linear regression method for different heating rates (β). From **Figure 19(a), 19(b), 19(c) and 19(d)** it can be interpreted that the model for all heating rates was almost perfectly overlapping at the same line. It indicates that the model generated from linear regression was consistent for different condition and had good approximation to estimate thermo-kinetic parameters[188]. However, the result also indicates that the data was not randomly distributed in the model. It can be interpreted that some information was not captured in the model[189].

Looking closer to the data distribution, **Figure 19(f)** shows that the residual between dataset and the model was not randomly distributed. Indication that a linear model has a high accuracy is when the upper layer residual data and under layer residual data is distributed randomly in the model[190]. When there are still some patterns shown in the residual data, it can be interpreted that the dataset cannot be estimated accurately using linear model. Even though the model is not highly accurate it gives information for the possibility reaction that can be used as approximation in the nonlinear regression method[191].

Figure 19(e) shows the normal probability plot for linear regression. It shows the normal probability plot pattern in left-skewed dataset. It means that the dataset showed a non-linear pattern, and the dataset was not normally distributed. Assumption of normally distributed data is needed for linear regression to get unbiased standard error for best fit parameter. However, in the large sample size data, not normally distributed data does not have significant impact on the result of linear regression[192]. Because of this reason, linear regression was not sufficient and nonlinear regression was needed to reconfirm pattern on the dataset of thermal decomposition of *CP*.

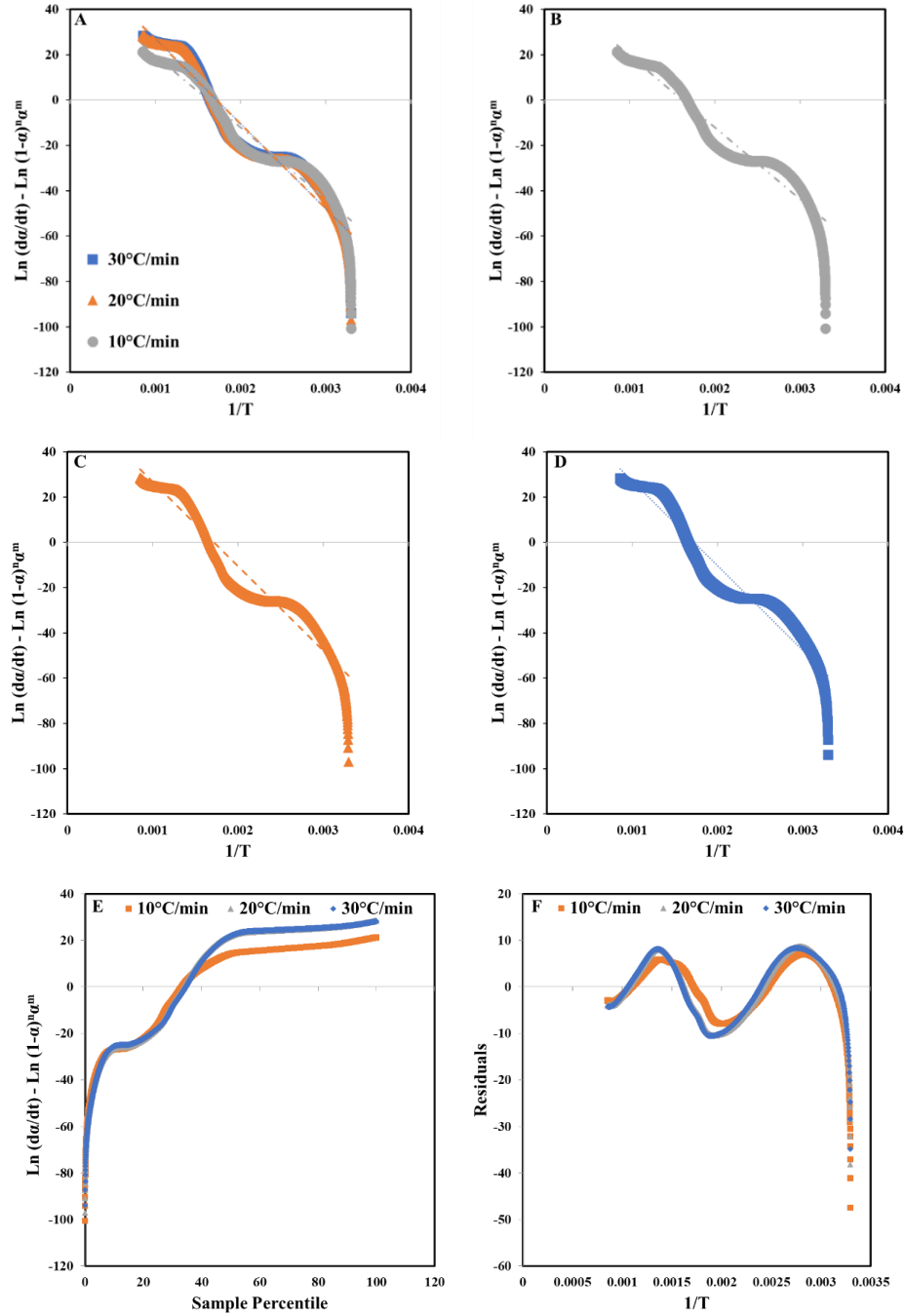


Figure 19 Result of Linear Regression Method: a)Linear Regression plot for different β , b)Linear regression plot for 10°C/min, c)Linear regression plot for 20°C/min, d)Linear regression plot for 30°C/min, e) Normal probability plot for Linear Regression, and f) Residual plot for Linear Regression

Table 7 Analysis of Variance (ANOVA) Linear Regression Model

Heating Rates (β)	E_{α}	Ln cA	R^2
10	262.8	51.1	0.95
20	310.7	64.33	0.94
30	311.5	64.56	0.94
<i>Average</i>	295	60	0.95
<i>Std. Error</i>	16.11	4.45	0

5.3.3 Non-Linear Regression Method

Nonlinear regression model can be used when linear regression model cannot capture all of information in the data and generate considerable error in the estimation. Even though nonlinear model in usual cases gives better approximation than linear model, but nonlinear model needs initial guess of parameter and initial guess of reaction model[193]. Regarding the reaction model for nonlinear regression, there are two options that can be used, first is the utilization of common reaction model in literature and second is the utilization of flexible single step reaction model (ePT) proposed by Burnham et al. 2015 [194]. In this study, the second option was chosen because of its flexibility to use in different reaction case.

Figure 20 shows the result of the nonlinear regression method. **Figure 20(a)** shows the simultaneously non-linear regression model without setting the activation energy value to be fixed. It shows that the model was almost perfectly fitted with the experimental data. It indicated that the reaction model and the best fit parameter satisfied and captured almost all information in the

experimental data. From the **Figure 20(a)**, activation energy (E_a) and pre-exponential Arrhenius constant ($\ln A$) were 124.92 ± 2.74 kJ/mol and 23.38 ± 4.63 , respectively. This result was much lower than the result from iso-conversional method and linear regression method. It was possibly because the assumption of normal distribution that was used in the linear regression and iso-conversional model that made the standard error became much smaller than the actual result. To check how well the activation energy obtained from previous method, fixed activation energy parameter was applied in the nonlinear regression. The parameters taken from Friedman model, KAS model, and FWO model were chosen to represent the parameters resulted from another method because its range of activation energy value was already covering the result obtained from the other methods.

Figure 20(b), 20(c) and 20(d) shows the result of non-linear regression using selected iso-conversional model activation energy (E_a). From those figures, it can be interpreted that activation energy (E_a) from iso-conversional analysis had a good approximation, but it had limitation in the assumption that the dataset should be normally distributed. It made the standard error from the result in the iso-conversional analysis was lower than the actual standard error. The result of residual standard error (RSE) from non-linear regression model was 0.02 while residual standard error from FM-NLM was 0.11, FWO-NLM was 0.088, and KAS-NLM was 0.091. From this result of residual standard error, it was also concluded that non-linear regression model demonstrated the most accurate approximation for thermo-kinetic parameters of thermal decomposition of CP [195,196]. However, it is worth noting that even though the iso-conversional model gave higher residual standard error (RSE) than non-linear regression model, it gave straightforward result

without requirement of initial guess and reaction model selection. It also showed reasonably low residual standard error (RSE) in terms of approximation result of thermo-kinetic parameters.

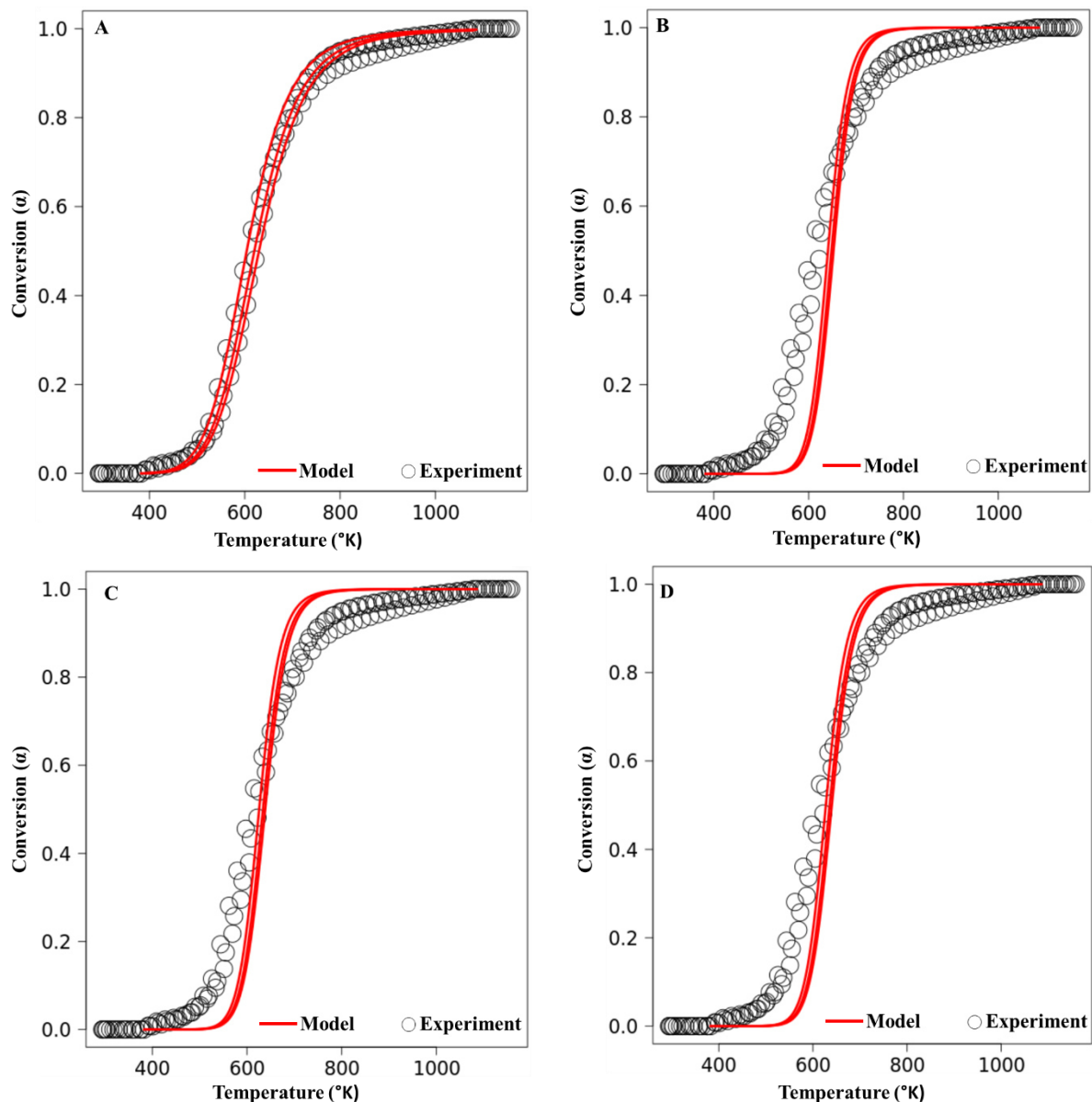


Figure 20 Result of Simultaneous Non-Linear Regression: a) Non-Linear Regression for different heating rate, b) Non-linear regression of Activation energy from Friedman, c) Non-linear regression of Activation energy from FWO, and d) Non-linear regression of Activation energy from KAS.

5.4 Thermodynamics Analysis

Thermodynamics analysis was employed in this study to observe an overall picture of thermal decomposition process of *CP*. In this study, the result of iso-conversional model was used to observe the effect of temperature and conversion on thermodynamics parameters such as enthalpy (ΔH), Gibbs free energy (ΔG) and change of entropy (ΔS). **Figure 21** shows the result of thermodynamic analysis for different iso-conversional models and different heating rates. **Figure 21(a)** shows the effect of conversion to enthalpy and change of entropy. It shows that both enthalpy and change of entropy increased along with the increase of conversion. Similar to the discussion in the previous section, because of Friedman model generally over-estimated activation energy and pre-exponential Arrhenius constant ($\ln A$), the approximation of enthalpy and change of entropy between 20-60% conversion was higher than the other models. It also shows that beside Friedman model, all other iso-conversional models generated almost identical enthalpy (ΔH) and change of entropy (ΔS) on all conversion. **Figure 21(b)** shows the effect of temperature on enthalpy (ΔH) and change of entropy (ΔS). It shows that both enthalpy (ΔH) and change of entropy (ΔS) increased along with the increase of temperature. It was to be expected because conversion and temperature had positive correlation between each other that made the effect of conversion similar to the effect of temperature to enthalpy (ΔH) and change of entropy (ΔS). Interestingly, there was also a clear effect of different heating rates on enthalpy (ΔH) and change of entropy (ΔS). It shows that at the same temperature, the enthalpy (ΔH), and the change of entropy (ΔS) of higher heating rate was lower than 10°K/min. It can be stated that with the increase of heating rate, the energy needed for thermal decomposition decreased and the degree of irreversibility also decreased. It is because high enthalpy (ΔH) indicates that the process is highly endothermal[197] and high change of entropy (ΔS) indicates that the process is highly irreversible[198].

Figure 21(c) shows the effect of conversion into Gibbs free energy (ΔG) for different iso-conversional models. It clearly showed the limitations of Friedman model that there was no consumption of activation energy curve under 23% conversion, and it made the reaction seemed directly spontaneous. In reality, some of energy is needed to start the spontaneous reaction[199,200], which is called activation energy. For other iso-conversional models, the result of Gibbs free energy (ΔG) from FWO was slightly lower than Starink and KAS before the spontaneous reaction occurs, and *vice versa* the FWO was slightly higher than Starink and KAS after the Gibbs free energy (ΔG) started to be in negative value or its reaction began to be spontaneous. It confirmed the result of activation energy from FWO which was slightly lower than KAS and Starink. However, the difference between FWO, Starink and KAS was very small and nearly negligible. Gibbs free energy (ΔG) curve indicated that the reaction occurred in the exergonic condition, where there was positive flow of energy from the system to the surroundings during thermal decomposition process[201,202].

Figure 21(d) shows the effect of temperature on Gibbs free energy (ΔG) for different heating rates. Similar to the effect of conversion, from Gibbs free energy (ΔG) curve it can be interpreted that the reaction occurred in the exergonic condition and spontaneously after 555°K. There was an effect of heating rates to Gibbs free energy (ΔG) result, that was, at lower heating rates the spontaneous reaction was occurring faster than at higher heating rates. While 20°K/min and 30°K/min needed 565°K and 570°K to start the spontaneous reaction, 10°K/min only needed 555°K to start spontaneous reaction. However, after 573°K the Gibbs free energy (ΔG) of 10°K/min started to be shifting higher than 20°K/min and 30°K/min. It was indicated that when devolatilization of hemicellulose was almost finished and devolatilization of cellulose was starting,

the stability of reaction at higher heating rates was better than 10°K/min. It is deduced from **Figure 21(d)** that once the temperature reached 573°K, the Gibbs free energy (ΔG) that was resulted from the heating rate of 20°K/min and 30°K/min at the same temperature was lower than 10°K/min[203].

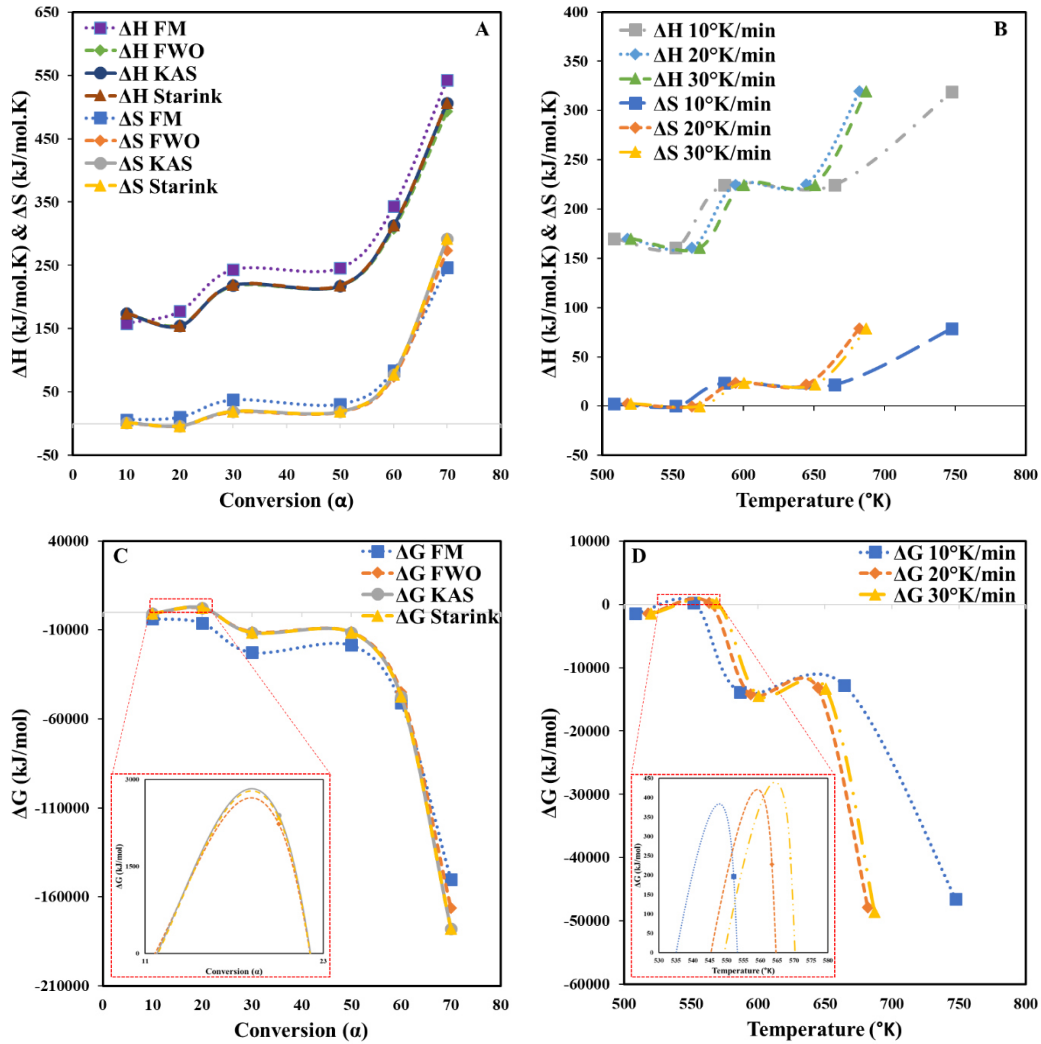


Figure 21 Result of Thermodynamic Analysis: a) ΔH & ΔS vs α for Different Model, b) ΔH & ΔS vs α for Different Heating Rates, c) ΔG vs α for Different Model, and d) ΔG vs α for Different Heating Rates

Table 8 Summary of Residual Standard Error (RSE) and R-Squared (R^2) for different method

Kinetics Parameters	Ea (kJ/Mol)			Ln A (1/min)			R ²	RSE
Friedman	318.11	±	56.46	61.01	±	8.55	0.93	-
Flynn-Wall-Ozawa	277.48	±	45.14	55.12	±	9.05	0.86	-
Kissinger-Akahira-Sunose	281.51	±	47.05	55.92	±	9.43	0.89	-
Starink	281.70	±	47.03	55.96	±	9.43	0.89	-
Linear Model	295.00	±	16.11	60.00	±	4.45	0.95	-
Non-Linear Model	124.92	±	2.74	23.38	±	4.63	-	0.02

5.5 Effect of Sodium Bicarbonate on Thermal Characterization

Figure 22(a) illustrates the comparison of the thermal decomposition of *Chlorella pyrenoidosa* (CP) with and without addition of Sodium bicarbonate. It is shown from DTG curve that the carbonization process with sodium bicarbonate was faster compared to the one without sodium bicarbonate. This information is beneficial to determine the minimum temperature to produce biochar. Another consideration is that the melting point of sodium carbonate around 851°C that possibly reduce amount of sodium salt in the sample [204]. It is recommended to not produce biochar above 850°C to maximize the effectiveness of sodium bicarbonate. Therefore, in the whole modification process of biochar there are no losses of sodium bicarbonate. Another consideration is that at higher temperatures, the energy consumption is much higher, and it will increase the

production cost of biochar. However, to achieve high surface area, high temperature is needed. Reduction of production cost can be obtained by using a part of pyrolytic gas and bio-oil for energy production. Hence, the economic feasibility of activated carbon on a large scale will be increased.

Figure 22(b) illustrates the result of N₂ adsorption-desorption for biochar with and without sodium bicarbonate. It shows that the biochar without sodium bicarbonate behaved like non-porous material with BET specific surface area 0.063 m²/g. While the biochar with sodium bicarbonate generated a very high BET specific surface area with 1282 m²/g. This result shows the potential of increase on the value of biochar from pyrolysis process that usually has lower value than biochar from torrefaction. High specific surface area potentially increases the performance of physical adsorption for either heavy metal adsorption or CO₂ adsorption [179].

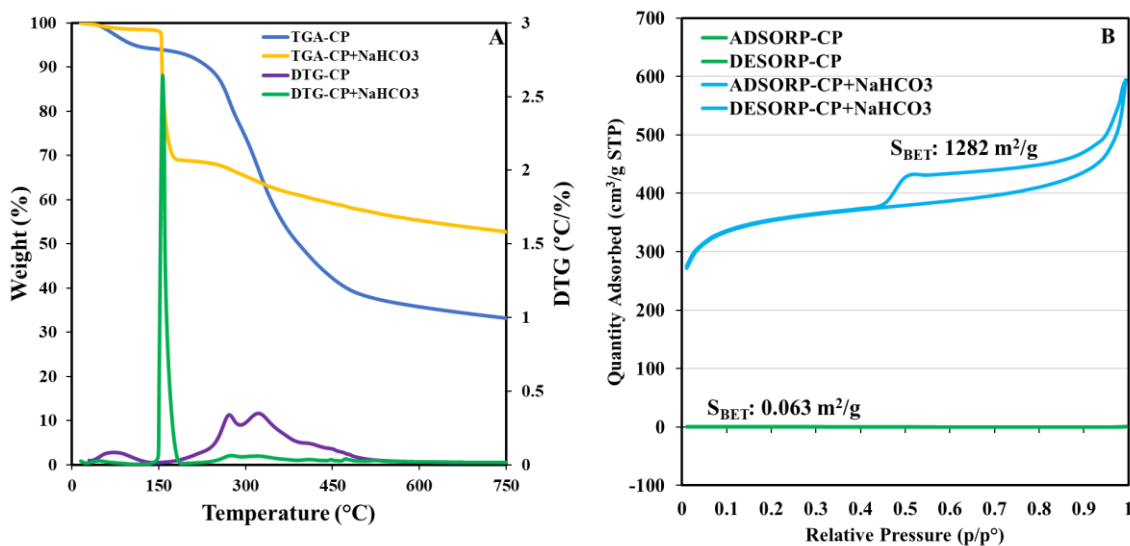


Figure 22 Effect of addition Sodium bicarbonate on (a) thermal characteristics behavior and (b) physical characteristics behavior.

CHAPTER 6

CHARACTERISTICS OF ACTIVATED CARBON FROM *CHLORELLA PYREONOIDOSA*

6.1 Yield Analysis of Activated Carbon

Figure 23 illustrates the impact of temperature on the yield of modified biochar (activated carbon) for different treatment. The graph depicts a decreasing trend in yield as temperatures rise, aligning with the expectations that higher temperatures during pyrolysis lead to increased solid decomposition [205]. Consequently, this results in a diminished yield of activated carbon. The observed yield range of 13 to 25% is consistent with literature findings, indicating that the fast pyrolysis process typically yields between 10 and 30% [206]. Compared to the one with no treatment and acid treatment, the yield of the one with activating agent was lower. It was possibly because the effect of sodium bicarbonate increased pore and surface area, then ultimately reduced the weight of activated carbon. The decomposition stage of sodium bicarbonate released carbon dioxide. It was ultimately producing crater-like surface in the material that was reflected in the increase of specific surface area. The significant impact of temperature on thermal degradation served as a key factor influencing the yield of activated carbon. Furthermore, the limited effect of sodium bicarbonate salt, an activator, on yield is attributed to its role in promoting the consumption of carbon as a reactant, leading to the production of carbon dioxide and hydrogen gases [207].

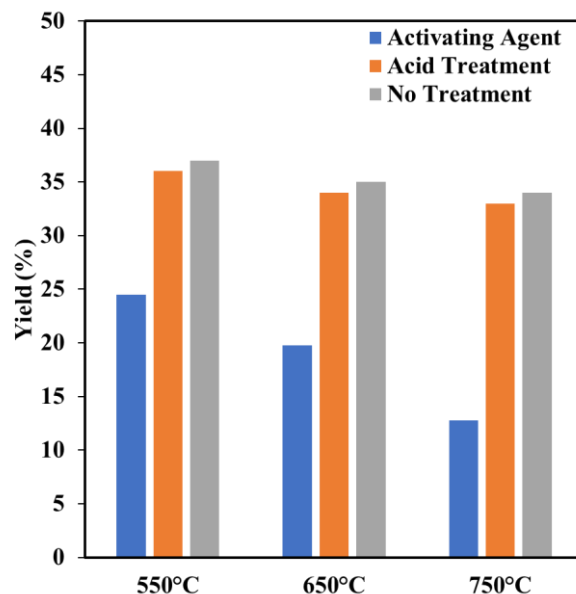


Figure 23 Yield of activated carbon for different temperature and treatment.

6.2 X-ray Diffraction (XRD) Analysis

An X-ray diffraction (XRD) analysis was required to determine the presence of carbon after pyrolysis. The purpose of XRD analysis was to identify the type of carbon produced by the modified biochar (activated carbon) pyrolysis process. It was significant because different kinds of carbon have distinct purposes. The more amorphous the carbon, the better it is for the adsorption process [208] while the more crystalline carbon (such as carbon nanotube), the more suitable it is for catalytic support application. [209]. Carbon typically exhibits a peak around 24° in XRD results [210]. **Figure 24** shows that the XRD data for the activated carbon were visually represented, with a large peak at 24.3° . This outcome was consistent with the expected production of carbon in the sample, indicating amorphous carbon properties due to the broadness of the peak [211]. Amorphous carbon, distinguished by its reactivity, is generally more reactive than crystalline

carbon [212]. Our study further categorizes amorphous carbon into soft and hard carbon based on interplanar spacing and grain size, using the Scherer equation [213].

Table 9 Summary of the activated carbon characterization for XRD and BET Analysis

<i>Temperature ($^{\circ}\text{C}$)</i>	<i>550</i>	<i>650</i>	<i>750</i>
<i>d-spacing, $\text{\AA}$</i>	37.97	35.92	36.75
<i>Average grain size, $\text{\AA}$</i>	4.91	9.12	11.53
<i>S_{Micropore}, m^2/g</i>	39.44	260.3	871.1
<i>S_{External}, m^2/g</i>	24.81	87.69	411.14
<i>S_{BET} m^2/g</i>	64.25	347.99	1282.24
<i>Average pore width, mm</i>	6.11	3.39	2.90
<i>Micropore volume, cm^3/g</i>	0.16	0.21	0.49

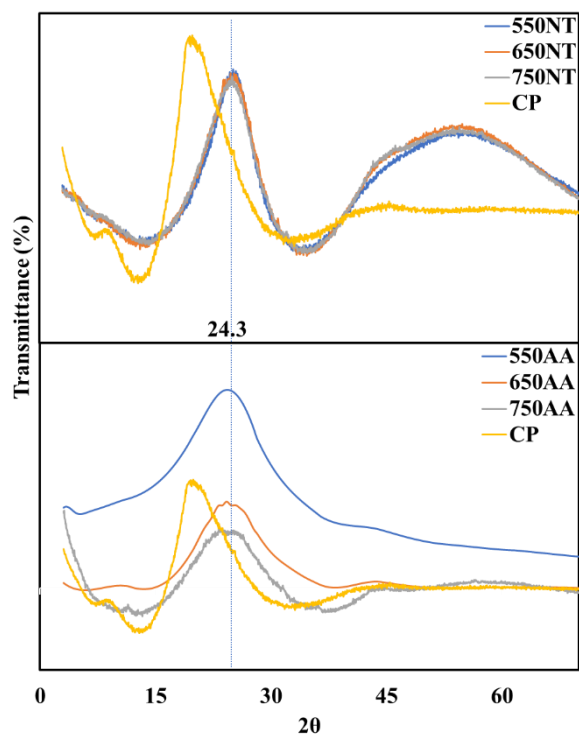


Figure 24 Result of XRD analysis for different treatment and different pyrolysis temperature.

The calculated results, presented in **Table 9**, highlighted a significantly larger interplanar spacing than the typical particle size, classifying the activated carbon as soft carbon, specifically amorphous carbon [214]. The implications of interplanar spacing and average grain size for wastewater treatment applications have been explored in various studies. For instance, Chimdessa and Ejeta's experiment demonstrated that an average grain size of 40 nm led to the adsorption of 99% of cadmium in synthetic wastewater [215]. Extrapolating from this insight, enhanced performance in heavy metal removal is anticipated with a smaller average grain size. **Figure 24** provides additional insights, with the additional of Sodium bicarbonate in the pyrolysis process, the activated carbon showed a trend of decreased peak intensity as temperature increased. This trend signifies an increase in porosity within the transformed carbon, evident in the decrease in 002 peak intensity [216].

6.3 Fourier Transform Infrared (FTIR) Spectrophotometry Analysis

Having confirmed the presence of carbon through X-ray diffraction (XRD) analysis, the subsequent investigation focuses on elucidating the specific functional groups present on the surface of the activated carbon. These distinctive functional groups played a pivotal role in various reactions, including ion exchange and complexation reactions, thereby influencing the adsorption potential of the activated carbon. This study systematically explored the impact of temperature, acid treatment, and sodium bicarbonate activation on these functional groups. Understanding these functional groups is paramount, as they contribute significantly to various reactions affecting adsorption potential. **Figure 25** illustrates the Fourier Transform Infrared (FTIR) spectrophotometry analysis—a key analytical technique employed to identify and characterize the functional groups on the surface of the activated carbon of *Chlorella pyrenoidosa*. FTIR spectroscopy measures the absorption of infrared radiation by distinct functional groups within the

sample. Each functional group exhibited absorption at unique wavelengths, allowing researchers to discern specific chemical bonds and molecular structures [217,218]. For activated carbon, this analysis sheds light on how temperature, acid treatment, and sodium bicarbonate activation influence the distribution of functional groups. The spectral information obtained from FTIR is crucial for understanding the chemical composition of the activated carbon, particularly its suitability for adsorption applications, such as wastewater treatment. **Figure 25** comprises spectral charts or diagrams depicting characteristic absorption peaks associated with different functional groups, providing a visual representation of the chemical changes induced by the modification process.

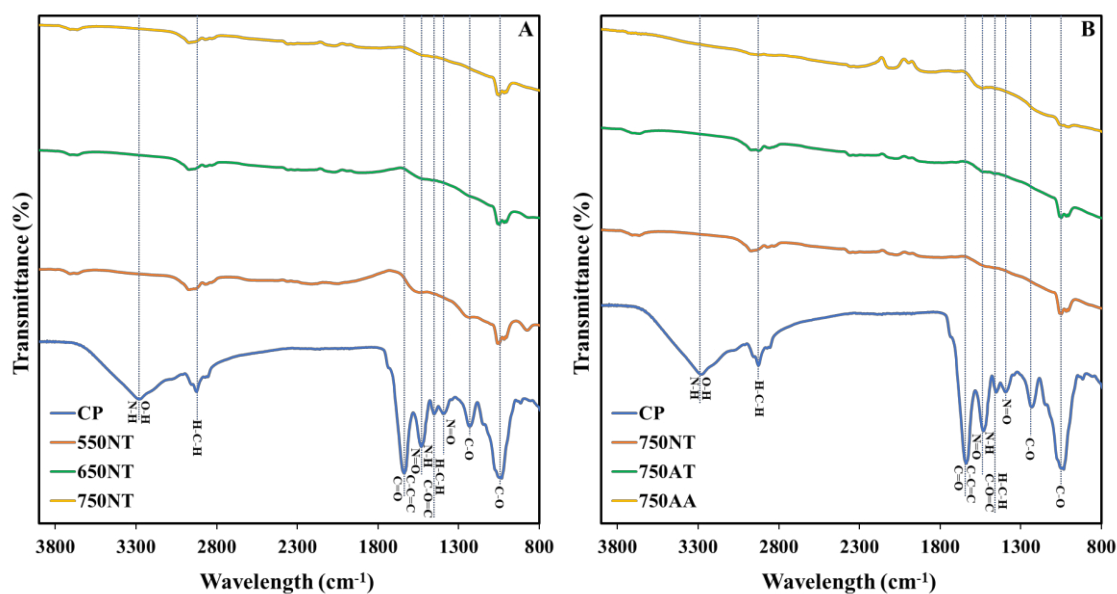


Figure 25 Result of FTIR analysis for different treatment and different pyrolysis temperature.

This study meticulously explored how temperature, acid treatment (AT), and the sodium bicarbonate(AA) activator influenced the composition of functional groups. The FTIR analysis revealed that elevated temperatures can lead to the destruction of several functional groups. Post-

pyrolysis, only five functional groups (Alkanes, Amines, Nitrous, Esters, and Ethers) remain out of the initial nine identified through Fourier Transform Infrared (FTIR) analysis. Interestingly, acid treatment exhibited minimal impact on the functional groups. However, with the addition of the sodium bicarbonate activator, only four of the original five functional groups persisted. Notably, at 750°C and in the presence of sodium bicarbonate, the alkanes functional group was no longer detected. This observation aligns with the expected result, given that sodium bicarbonate promotes the addition reaction of organic chains, resulting in the generation of additional gaseous hydrogen and carbon dioxide. From the remaining functional groups that were detected from FTIR analysis, it is important to be noted that there is an existence of nitrogen functional groups. Previous research showed that nitrogen functional group increase the affinity with heavy metal and increase hydrophilicity of activated carbon with water[219].

The absence of the alkanes functional group suggests its consumption during the reaction with sodium bicarbonate, rendering it undetectable through FTIR analysis. Despite this reduction in functional groups, studies indicate that the process of generating carbon dioxide and hydrogen gas can alter the physical structure of activated carbon by inducing the formation of bubbles. This phenomenon, despite the consumption of one functional group, enhances the porosity and creates a more porous and crater-like structure. Such alterations in the physical structure have the potential to increase the specific surface area, a characteristic that will be further explored through isotherm adsorption-desorption analysis using the BET model.

6.4 Isotherm Adsorption and Desorption Analysis

To ascertain the specific surface area and pore distribution of the activated carbon, a crucial study involving isotherm adsorption-desorption was conducted. This study plots the amount of absorbed and desorbed nitrogen against relative pressure ($\frac{p}{p_0}$), providing valuable insights into the precise surface area and pore distribution. The Brunauer–Emmett–Teller (BET) model, a widely accepted model for estimating surface area, was employed for analysis. **Figure 26(a)** and **Figure 26(b)** presents a comprehensive overview of the outcomes across various treatments and temperatures, unequivocally demonstrating that the addition of the sodium bicarbonate activator significantly enhanced the specific surface area of the activated carbon.

Furthermore, the BET model confirmed that the initial hypothesis derived from the XRD study, indicating that elevating the temperature enhances the porosity of the activated carbon, consequently increasing the specific surface area. This observation aligns with existing literature that establishes a positive correlation between temperature and the surface area of activated carbon [220]. Acid treatment was also found to positively impact the BET specific surface area of biochar even without modification. The rise in BET specific surface area with acid treatment was attributed to the cleaning of external pores that may have closed during the restructuring process at high temperatures. This allows nitrogen gas to penetrate internal pores, resulting in an increased BET specific surface area. This interpretation finds support in the work of Liou and Wu, who explain that acid treatment effectively cleans metal impurities and residual activating agents from the biochar [221]. With both Sodium bicarbonate (activator) addition and acid treatment, the activated carbon achieves its maximum specific surface area (1282.24 m²/g) at 750 °C. This surface area comprised 411.14 m²/g of external surface area and 871.1 m²/g of micropore surface area. The

Figure 26(b) visually captures the comparative outcomes of different treatments and temperatures, providing a clear illustration of the substantial impact of sodium bicarbonate activator and temperature on the specific surface area of the activated carbon.

In the BET model, the quantity of nitrogen undergoing adsorption and desorption was conventionally plotted against relative pressure. **Figure 26(c)** provides a visual representation of the hysteresis loop shape observed at various temperatures with the addition of an activator. The distinctive form of the hysteresis loop offers insights into the pore structure of the activated carbon (AC). Specifically, the estimated pore shape derived from the hysteresis loop at 750°C indicated a slit-shaped or plate-like pore structure, as indicated in the literature [222]. Notably, only the temperature result at 750°C revealed the intersection of the absorb and desorb lines, implying complete desorption of all nitrogen trapped within the activated carbon at this temperature. **Figure 26(d)** provides a visual representation of the hysteresis loop shape observed at various temperatures without the addition of Sodium Bicarbonate (activator). From all hysteresis loop, it could be concluded that without activating agent, biochar had very small specific surface area and the amount of N₂ that adsorb and desorb in it was very limited. It was also difficult to recognize the pore type in the biochar without activating agent because of its shape that is unusual compared to mesoporous material.

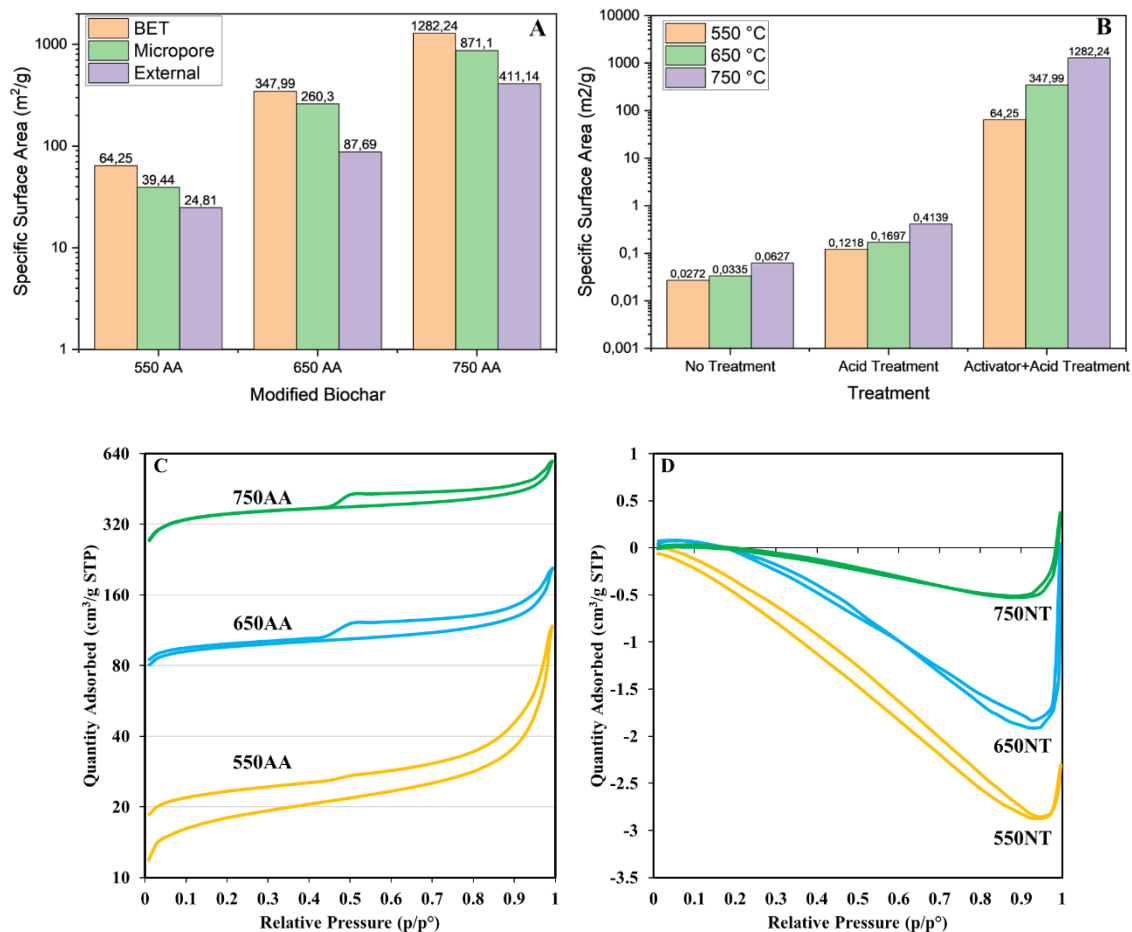


Figure 26 N₂ adsorption-desorption isotherm analysis result: (a) Comparison of BET surface area AC at different temperature (b) Comparison of BET surface area AC at different treatment (c) Different hysteresis loop shapes of AC with activating agent (AA) and (d) Different hysteresis loop shapes of AC without activating agent (NT).

Contrastingly, the hysteresis loop's shape was absent at 550°C, suggesting properties akin to non-porous materials. This absence was attributed to the immediate desorption of nitrogen absorbed in the surface, while the nitrogen absorbed in the pore remained trapped. For the temperature of 650°C, the hysteresis loop shape resembled that of 750°C, although the desorb and adsorb lines did not intersect. This is indicative of a reasonably large specific surface area at 650°C compared

to 550°C, yet some nitrogen was still trapped in the activated carbon at this temperature. **Figure 27** further reveals that the quantity of nitrogen undergoing adsorption and desorption at 750°C was significantly higher than at 650°C and 550°C. The graphical representation effectively illustrates the temperature-dependent variations in nitrogen adsorption and desorption behavior, providing valuable insights into the porous nature of the activated carbon at different temperatures.

Figure 27(a) provides valuable insights into how the analysis of isotherm adsorption-desorption can be employed to deduce the average pore width and pore distribution within the activated carbon. The graphic clearly illustrates the alteration in pore size distribution as the temperature increases. Notably, the pore diameter distribution was predominantly centered around 3.89 nm. The distinctive variations in derivative pore values were a direct consequence of temperature differences, with higher temperatures corresponding to elevated derivative pore volumes.

The derivative of pore volume essentially indicated the location within the material where nitrogen gas desorbs when the relative pressure is low. In the context of the results, it can be inferred that, irrespective of the specific temperature, gaseous nitrogen could access the internal structure of the activated carbon through pores with a diameter of 3.89 nm. Even in the case of the sample at 550°C, which exhibited a lower pore volume, the presence of accessible pores at 3.89 nm is evident. This observation implied that the material falls under the category of mesoporous materials, characterized by pores within the range of 2-50 nm. The graphical representation in **Figure 27(a)** effectively communicates the temperature-dependent variations in pore size distribution, providing critical insights into the mesoporous nature of the activated carbon.

Figure 27(b) illustrates that as the temperature increases, there was a simultaneous rise in pore volume while the average pore width experiences a decrease. This phenomenon was likely

attributed to alterations in the pore structure, leading to a reduction in the average pore width at higher temperatures. A similar trend was observed in the research conducted by Dilokekunakul et al. in 2020, which establishes a correlation between temperature and pore width, although the precise reasons for pore width fluctuation remain inconclusive [223].

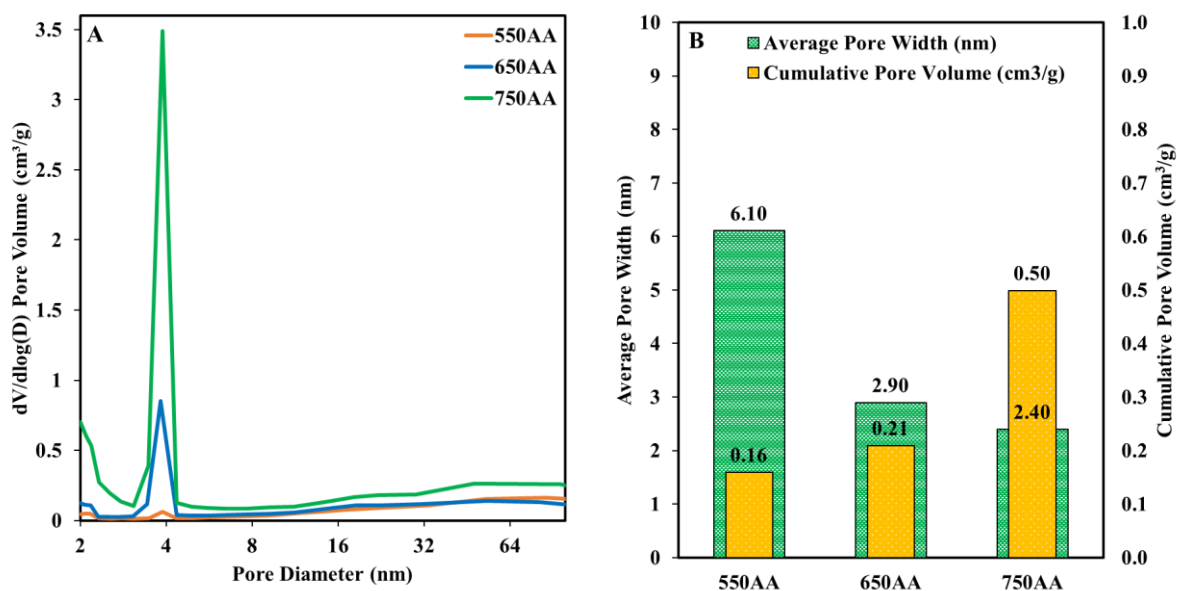


Figure 27 (a) Pore size distribution and (b) average pore width plot of activated carbon at different temperatures.

In the context of heavy metal adsorption, the impact of pore volume and average pore width was not markedly higher than that of specific surface area. This was because the size of heavy metal particles was generally larger than the pore width, resulting in the deposition of heavy metals primarily on the surface of the adsorbent material. Contrastingly, for applications such as gaseous adsorption, higher pore volume and pore width had a more significant effect than specific surface area. This was because gaseous adsorption tended to be challenging to deposit on the surface of the adsorbent material and was likely to be released when the relative pressure was low. These

findings suggest that, for heavy metal adsorption, higher temperatures are advantageous in producing adsorbent materials due to the resultant increase in specific surface area. The figure effectively communicates the temperature-dependent variations in both pore volume and average pore width, providing valuable insights into the optimization of adsorbent materials for specific applications.

CHAPTER 7

PERFORMANCE TEST OF ACTIVATED CARBON FOR LEAD REMOVAL APPLICATION

7.1 Scanning Electron Microscope (SEM) Analysis

To substantiate the conversion process from *Chlorella pyrenoidosa* to activated carbon through the fast pyrolysis method and validate the performance test, visual confirmation was crucial, and this was achieved through Scanning Electron Microscope (SEM) imaging. The SEM images in **Figure 28(a)** and **Figure 28(b)** vividly depict alterations in the structure of both the raw material and the activated carbon product. The surface of the activated carbon exhibited numerous pores, indicating a restructuring of the material that results in the formation of crater-like surfaces. This observation aligns with the earlier hypothesis, affirming the positive impact of temperature and sodium bicarbonate on increasing the specific surface area through the generation of gaseous mechanisms.

Figure 28(c) and **Figure 28(d)** present distinct images of fresh activated carbon and used activated carbon. Notably, even at an initial concentration of 100 mg/L, several active sites on the biochar surface were already occupied by lead particles. Despite this, the SEM results revealed no significant difference between the fresh and used activated carbon, signifying the stability of the activated carbon during the adsorption process. This SEM outcome is consistent with a study by Zhao et al. in 2022, which utilized Zinc Ferrite nanoparticles (ZF-NPS) and found no substantial difference in SEM results between fresh and used ZF-NPS. The SEM images provide visual

evidence supporting the transformation process and the stability of the activated carbon during the adsorption of lead particles. The figures effectively convey changes in material structure and the presence of active sites, reinforcing the credibility of the conversion process and its applicability in adsorption applications.

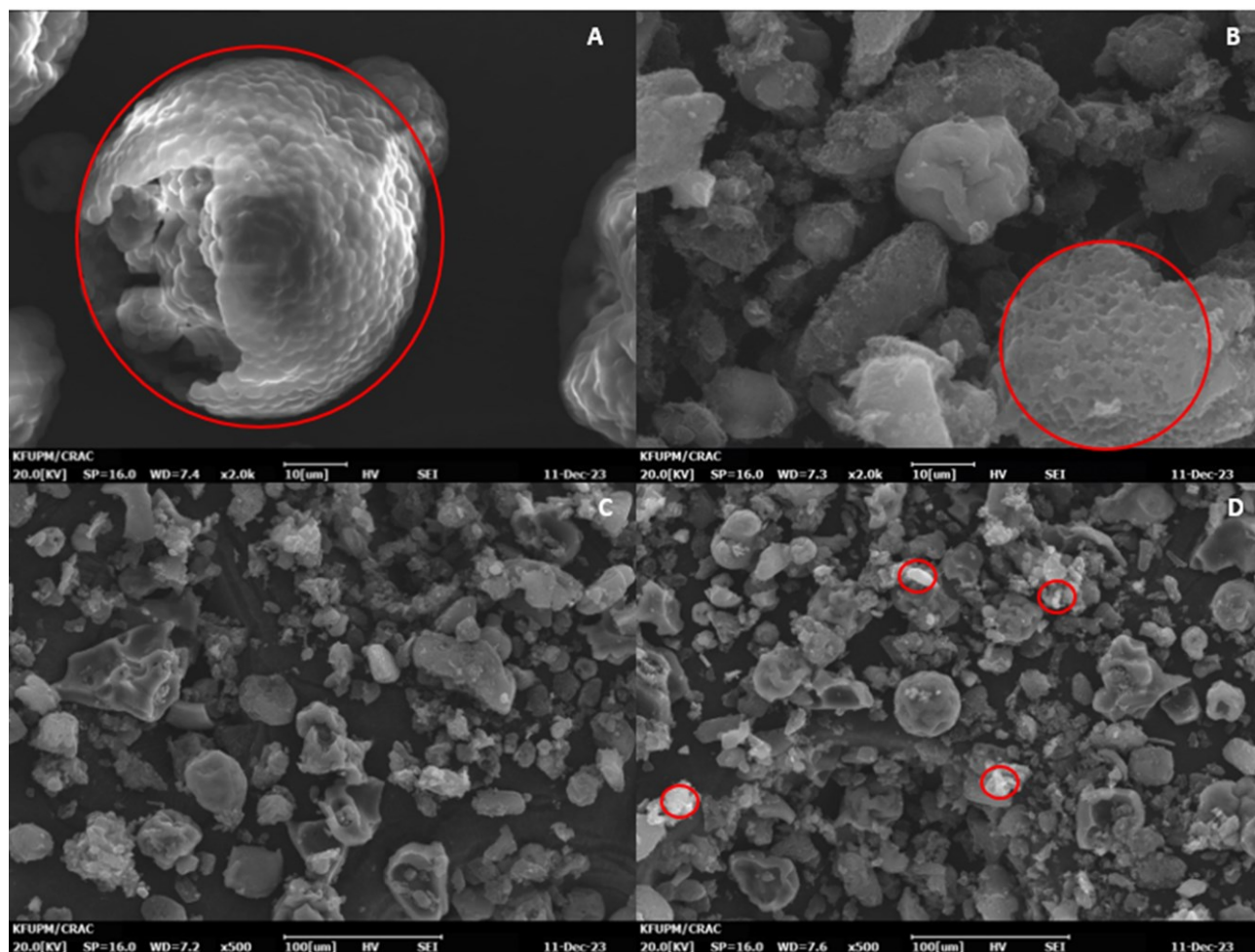


Figure 28 Scanning Electron Microscopy (SEM) images of the samples: a) Raw *Chlorella pyrenoidosa*, b) Activated carbon at 750°C, c) Activated carbon before adsorption, and d) Activated carbon after adsorption.

7.2 Performance Test of Activated carbon

Following various characterizations, it was imperative to subject the activated carbon derived from *Chlorella pyrenoidosa* to performance testing for lead synthetic wastewater treatment applications. The adsorption isotherm section of the test employs the Langmuir, Freundlich, Dubinin-Radushkevich and Elovich Models, chosen for their widespread application in evaluating the performance of adsorbent materials. The Langmuir model assumes an adsorption process occurs at specific homogenous sites in the surface of adsorbent. The Langmuir equation is then utilized in this evaluation [224]:

$$q_e = q_{max} K_L \frac{C_e}{1 + K_L C_e}$$

where C_e is equilibrium concentration, q_e is equilibrium adsorption capacity, q_{max} is maximum adsorbent capacity and K_L is Langmuir adsorption constant. From Langmuir adsorption constant, dimensionless separation factor (R_L) can be estimated to evaluate the favorability of adsorbent material. The expression of separation factor is [225]:

$$R_L = \frac{1}{1 + K_L C_0}$$

From the separation factor (R_L), favorability adsorption can be divided into 4 classifications: irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) and unfavorable ($R_L > 1$). Irreversible means that K_L is too large that makes $R_L \approx 0$. In this case, the binding between adsorbate and adsorbent is very strong that makes it difficult to desorb again, so that it called irreversible. While favorable means that the adsorbent material is suitable for the application and K_L value is relatively high for adsorption process. Linear means that adsorption process only

depends on the initial concentration and the amount of adsorbent material while $K_L \approx 0$. Lastly, unfavorable means that the adsorbent material is not suitable for the adsorption process. It is possible only when the K_L is negative (–) and $-1 < K_L C_0 < 0$. In this case, concentration of adsorbate increases instead of decreases. And instead of adsorption, the material is promoting desorption process.

Freundlich model assumes the adsorption process occurs in the heterogeneous surface and in the multilayer adsorption with interaction between adsorbed molecules. Freundlich Model can be defined by the following equation [224] :

$$q_e = K_F C_e^{h_f}$$

where K_F is Freundlich adsorption constant and h_f is heterogeneity factor of the model. The heterogeneity factor in the Freundlich Model indicates the heterogeneity between active sites in the surface of adsorbent. Generally, heterogeneity factor value is between 0 and 1. A higher h_f value indicates that the active site in the adsorbent material tends to be homogenous and a lower h_f value indicates that the active site in the adsorbent material tends to be heterogeneous.

The Elovich Model adopted the adsorption phenomena described by Langmuir. The Elovich model assumes that the rate of adsorption decreases exponentially with the increase of ratio between maximum adsorption capacity and equilibrium adsorption. Elovich model can be defined by the following equation [226]:

$$q_e = q_{max} K_E C_e^{\frac{q_e}{q_m}}$$

where K_E is Elovich adsorption constant, and q_{max} is maximum adsorption capacity.

Dubinin-Raduskovich Model assumes that adsorption process occurs with considering adsorbent size is comparable with micropore size and adsorption equilibrium relation between adsorbate and adsorbent is independent with temperature. Dubinin-Radukovich model can be defined by the following equation [227] :

$$q_e = q_{max} K_{DR} e^{RT \ln(1 + \frac{1}{C_e})}$$

where K_{DR} is Dubinin-Raduskovich adsorption constant, and q_{max} is maximum adsorption capacity.

Figure 29(b) shows the relation between $\frac{C_e}{q_e}$ and adsorbate equilibrium concentration (C_e) for different model. The line represents the regression result of corresponding model, and the plotted yellow dot represents the experiment result. Using the non-linear regression method, the best fit parameter for different models is obtained. For Langmuir model, Maximum adsorbent capacity (q_{max}) and Langmuir Constant (K_L) from the model were 159.071 ± 23.4008 mg lead/g Adsorbent and 0.6531 ± 0.2372 , respectively. Evaluation of this model resulted in r squared (R^2) value of 0.95527 with Residual Standard Error (RSE) 6.583 which was a good approximation. For different initial concentration of isotherm adsorption experiment, all of it resulted very small value of separation factor ($R_L \approx 0$), it was indicated that the adsorption of lead using our activated carbon can be classified as irreversible with its characteristics of strong bond between adsorbate and adsorbent.

For Freundlich model, Heterogeneity factor (h_f) and Freundlich Constant (K_F) from the model were 0.467 ± 0.06394 and 63.0659 ± 3.97602 , respectively. Based on heterogeneity factor obtained from the model, it can be interpreted that active sites in the activated carbon tend to be

heterogeneous and the adsorption process is mainly dominated by physical adsorption. Evaluation of this model resulted in r^2 value of 0.97992 with RSE 5.143 which is a good approximation.

For Elovich model, Maximum adsorbent capacity (q_{max}) and Elovich Constant (K_E) from the model were 95.1506 ± 37.4786 mg lead/g Adsorbent and 1.1352 ± 0.9103 , respectively. Evaluation of this model resulted in r^2 value of 0.92058 with Residual Standard Error (RSE) of 12.82 which is a good approximation.

For Dubinin-Radushkevich model, Maximum adsorbent capacity (q_{max}) and Dubinin-Radushkevich Constant (K_{DR}) from the model were 113.452 ± 8.725 mg lead /g Adsorbent and 0.16 ± 0.0467 , respectively. Evaluation of this model resulted in r^2 value of 0.90228 with Residual Standard Error (RSE) of 9.815 which is a good approximation.

From different models, the highest R^2 (0.97992) and the lowest RSE (5.143) were obtained by Freundlich model. It shows that the adsorption process occurs in multilayer and heterogeneous active sites. To estimate maximum adsorption capacity, Langmuir model showed the highest R^2 (0.95527) and the lowest RSE (6.583). It showed that the actual q_{max} was estimated more accurately with Langmuir Models which was 159.071 ± 23.4008 mg/g.

Adsorption kinetic models are usually used to determine kinetic parameters in the adsorption process. Badawi *et al.*, 2017 showed that pseudo-second-order kinetic model has a high suitability to describe the adsorption process of lead. Pseudo-second-order kinetic model is described by the following equation:

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{t}{q_e}$$

Where q_t (mg/g) is concentration of adsorbate at the t (min) time and k_2 (g/mg min) is pseudo-second-order kinetic rate constant. From pseudo-second-order kinetic model, nature of bonds between adsorbate and adsorbent can be interpreted. As comparison, pseudo-first-order kinetic model will also be used in this kinetic study. Pseudo-first-order kinetic model is described by the following equation[228]:

$$q_t = q_e(1 - e^{(-k_1 t)})$$

Figure 29(a) shows the relationship between $\frac{t}{q_t}$ and time (t). The green line represents the pseudo-first-order kinetics model, The purple line represents the pseudo-second-order kinetics model and plotted orange dot represents the experiment result. Using regression method, the best fit parameter of pseudo-second-order kinetic parameter for lead adsorption can be estimated. Pseudo-second-order kinetic rate constant (k_2) from the model was 0.00931 ± 0.00222 g/mg.min and Pseudo-first-order kinetic rate constant (k_1) from the model was 0.24465 ± 0.04726 min⁻¹. Evaluation of this model resulted in r squared (R^2) value of 0.99902 and RSE of 0.00665 for pseudo-second-order kinetic model and r squared (R^2) value of 0.9981 and RSE of 4.035 for pseudo-first-order kinetic model. This result shows that adsorption of lead heavy metal using activated carbon was explained better using pseudo-second order kinetic model. Wang and Guo reported that some activated carbon, also has high value of R^2 which mean the kinetic adsorption is better modeled with pseudo-second-order kinetic model. Wang and Guo also estimated that activated carbon that has high value of R^2 in pseudo-second-order kinetic model has abundant active site which increase the performance of adsorption process. This is also reconfirming the result of Langmuir isotherm

adsorption that resulted in the irreversible adsorption process because of its abundance active site [229].

For better understanding of adsorption process, thermodynamics analysis was needed[230]. Enthalpy (ΔH), change of entropy (ΔS) and Gibbs free energy (ΔG) can be estimated from adsorption result in different temperatures. Van't Hoff Equation that is employed for estimating thermodynamics parameters is as follows [231]:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

$$\Delta G = \Delta H - T\Delta S$$

$$K_d = \frac{q_e}{C_e}$$

Where K_d is thermodynamics equilibrium constant of adsorption. From slope and intercept of plot between $\ln K_d$ and $\frac{1}{T}$, enthalpy (ΔH) and entropy (ΔS) can be estimated. Hence, Gibbs free energy (ΔG) for different temperatures can be determined.

Figure 29(c) illustrates the relationship between Gibbs free energy(ΔG) and $\ln K_d$ with temperature. It showed that the adsorption process was occurring in the endothermic condition. The increase in temperature increased the quantity of lead heavy metal that was absorbed by activated carbon. It was to be expected because at higher temperature, the frequency of movement of lead heavy metal molecule increased, and the interaction with activated carbon would also increase. The other information that can be interpreted from **Figure 29(c)** is that the increase of temperature went along the decrease of Gibbs free energy. It indicates that higher temperatures

made the adsorption process occur more spontaneously. From the plot between $\ln K_d$ and $\frac{1}{T}$ in the **Figure 29(c)**, the result of enthalpy and change of entropy were 82.95 kJ/mol and 290.8 J/mol. K, respectively. Model evaluation resulted in the R-squared (R^2) of 0.9968 which indicated a high accuracy of the model.

Figure 29(d) illustrates the relationship between pH with zeta potential and q_e . It showed that the adsorption performance increased along with the increase of pH. It is possibly because at high pH, the adsorbent was more favorable on the adsorption of cation than in the lower pH. It is understood that Lead in the wastewater solution is in the cation form, so if the adsorbent is more favorable with cation in the higher pH, more Lead will be adsorbed into activated carbon. It is also supported by the result of Zeta potential analysis in **Figure 29(d)** that, the surface discharge of activated carbon in the high pH tended to be negative. It increased the electrostatic attraction of Lead cation with surface of activated carbon and resulted in more Lead adsorbed in the activated carbon through this mechanism. From zeta potential analysis the pH_{pzc} (pH at the point of zero charge) was around 3.1, it means that at pH that was higher than 3.1 the adsorbent would be favorable to adsorb cation and vice versa [232].

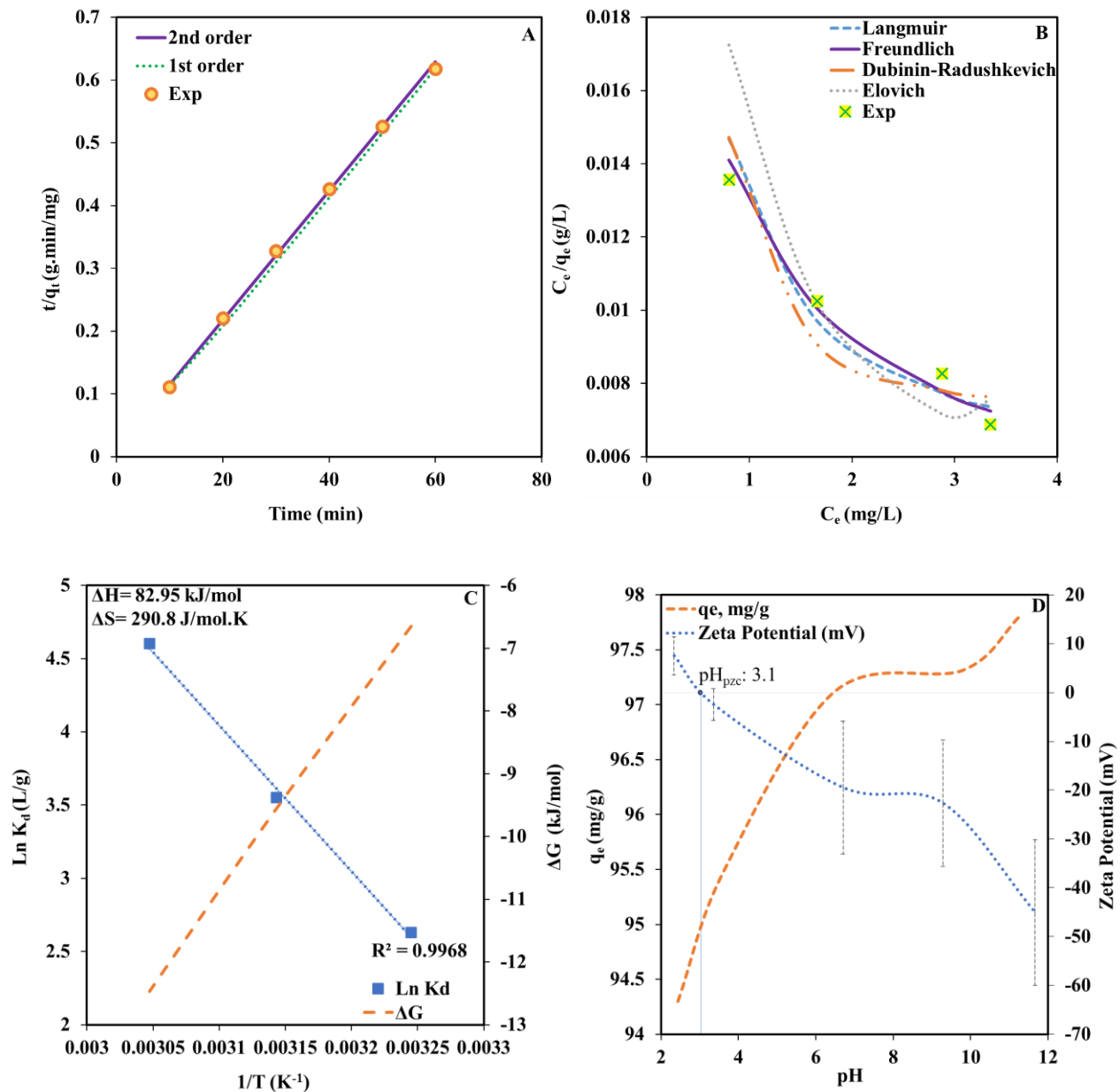


Figure 29 Performance test result: (a) Kinetic model, (b) Isotherm adsorption model, (c) Thermodynamic Adsorption curve and (d) Effect of pH on adsorption capacity and zeta Potential.

7.3 Technical and Economical Comparison with Commercial Activated Carbon

Result of characterization and performance test of activated carbon is needed to be compared to the data of another activated carbon [233] and commercial activated carbon from the literature [234] to observe technical feasibility. The result of the comparison is shown in **Table 10** below. From **Table 10**, it can be interpreted that activated carbon was proven to surpass all the value of characterization and performance except kinetic adsorption for Lead from the literature. Modification methods in this study had been proven to increase the value and performance of residue from energy extraction via pyrolysis process. In the aspect of technical feasibility, activated carbon produced from *Chlorella pyrenoidosa* satisfied the characteristics and performance especially for lead heavy metal applications.

In term of economic feasibility, the normal biochar product cost is estimated to be 0.3\$/kg [235], meanwhile the commercial activated carbon price is around 2.75 \$/kg [236]. Cost of raw material is 0.42 \$/kg for *Chlorella pyrenoidosa* [237] and 0.3 \$/kg for Sodium Bicarbonate [238]. From the calculation of economic potential, it was around 1.13 \$/kg. This information gives a hint that in the aspect of both economic and technical, modification of biochar gave a notable added value and at the same time increases the performance of biochar. This will ultimately bring positive impact, especially on environment, because the cultivation, energy extraction, and pyrolysis residue of *Chlorella pyrenoidosa* is able to generate energy and bio-remediation at the same time.

Table 10 Comparison characteristics and performance of activated carbon with commercial activated carbon

Parameter	Commercial Activated Carbon	Magnetic Biochar (White tea)	Activated carbon (<i>C. Pyrenoidosa</i>)
BET Specific Surface Area, m²/g	1241	-	1282
Pore Volume, cm ³ /g	0.445	-	0.49
Average pore width, nm	2.781	-	2.9
Lead Maximum Adsorption Capacity, mg/g			
Langmuir	42.5	74.6	159
Dubinin-Raduskovich	23.9	77	113.45
Kinetic Adsorption for lead			
Pseudo-1 st -order, min ⁻¹	0.00069	11.9	0.24465
Pseudo-2 nd -order, g.mg ⁻¹ .min ⁻¹	0.01	0.442	0.00931
Literature	[234]	[233]	This Study

CHAPTER 8

CONCLUSION AND RECOMMENDATIONS

8.1 Potential of *Chlorella pyrenoidosa* Based on Its Characterizations

Detailed potential investigation has been done in this study. The result of XRD analysis and FTIR analysis showed the potential of CP biomass as adsorbent material with its amorphous character and its abundant functional group in the surface. The result of physicochemical analysis showed that the CP had relatively high heating value and from Van Krevelen diagram it showed that it had high potential to be converted into another compound that has high energy density.

The analysis of thermo-kinetic parameter for thermal decomposition of microalgae was explained clearly in this study. Different approximation methods for kinetics parameters can be summarized in Table 7. It clearly showed that the non-linear regression method was much better for approximation of thermo-kinetic parameters with comparison of model fitting using several activation energies of other model. To get a highly accurate non-linear model, suitable reaction model and reasonable initial guess is an important aspect to consider. The linear model can be useful for estimating reaction model for non-linear regression. The Iso-conversional method was still proven to be a good approximation for estimating thermo-kinetics parameter because of its straightforward calculation. A highly accurate iso-conversional model was considerably favorable to estimate thermo-kinetic parameter. Because non-linear models required reaction model and initial guess. Moreover, the time needed for regression was also relatively much longer than model-free method or iso-conversional model.

Thermodynamics analysis showed that thermal decomposition of CP was highly endothermic and exergonic. The increase of conversion and temperature increased the enthalpy (ΔH) and change of entropy (ΔS). Spontaneous reaction started after 23% of conversion, with Friedman model showing its limitation in the Gibbs free energy plot. Gibbs free energy (ΔG) plot showed that at initial stage, the heating rate of 10°K/min could initiate a spontaneous reaction on lower temperature. However, compared to 10°K/min, high heating rates were indicated to have a higher stability reaction when cellulose starts devolatilization process. Modification of iso-conversional model and linking its thermo-kinetics study with thermodynamics analysis is an interesting topic to explore for another biomass. Detail interpretation will provide a complete picture of the thermal decomposition process.

From thermogravimetric analysis of CP with and without sodium bicarbonate, it shows that addition of sodium bicarbonate had positive impact on the increase of its specific surface area. This result showed the potential of CP biomass with sodium bicarbonate treatment to produce biochar that is comparable with activated carbon. Further study on CP biomass and the effect of carbonate salt needs to be studied in the larger scale such as pyrolysis process with higher capacity tubular furnace for adsorption application.

8.2 High Performance Activated Carbon from *Chlorella pyrenoidosa*

This study offers a comprehensive analysis of the influence of temperature and the sodium bicarbonate activator in the synthesis of activated carbon derived from *Chlorella pyrenoidosa*. Elevated temperatures contribute to increased porosity and, consequently, a larger surface area. However, the sodium bicarbonate activator exhibits a more pronounced effect on the specific surface area due to its bubble-expansion mechanism, creating additional pore and crater-like

regions on the activated carbon surface. Utilizing acid treatment and the sodium bicarbonate activator, the highest specific surface area ($1282.82 \text{ m}^2/\text{g}$) was achieved at 750°C , comprising $871.1 \text{ m}^2/\text{g}$ of micropore surface area and $411.14 \text{ m}^2/\text{g}$ of external surface area, as determined through isotherm adsorption-desorption analysis.

Pore analysis indicated that as the temperature increases, pores become smaller, resulting in an average pore size of 7.943 nm and a total micropore volume of $0.486 \text{ cm}^3/\text{g}$ for activated carbon at 750°C with activator and acid treatment. The hysteresis loop shape suggested a slit-shaped or plate-like pore structure for the activated carbon. According to XRD analysis, the produced activated carbon fell into the category of amorphous soft carbon and mesoporous material.

The FTIR analysis revealed a substantial reduction in functional groups on the surface of activated carbon due to increased temperature. Notably, the alkanes functional group disappeared from the surface with the addition of the sodium bicarbonate activator. In the performance test of Langmuir, Freundlich, and kinetic isotherm lead adsorption, various kinetic parameters are estimated. According to the Langmuir model, the maximum adsorption capacity of activated carbon (q_{max}) was estimated at $159.071 \pm 23.4008 \text{ mg lead/g Adsorbent}$, indicating an irreversible adsorption process with a strong bond between adsorbate and adsorbent. The Freundlich model suggested a medium heterogeneous active site on the surface, with a heterogeneity factor (h_f) of 0.4671 ± 0.06394 . The kinetic study demonstrated a high R^2 value for the pseudo-second-order kinetic model with rate of lead adsorption of $0.00931 \pm 0.00222 \text{ g/mg.min}$, implying the presence of abundant active sites on the surface. In addition to these findings, this study advocates for the exploration of various microalgae species as feedstock for creating diverse materials and applications, aligning with a broader initiative for microalgal diversification and bioremediation.

Thermodynamics analysis showed that the increase of temperature was favorable for the adsorption of lead. The adsorption process was shown as endothermic process with enthalpy and change of entropy were 82.95 kJ/mol and 290.8 J/mol. K, respectively. The comparison of activated carbon with commercial activated carbon and magnetic biochar showed satisfying results with activated carbon produced from *Chlorella pyrenoidosa* almost surpassed all parameters in the literature for both characteristics and performance for lead adsorption applications.

8.3 Recommendations

From this study a lot of area of research can be pursued for future work:

- Functionalization of activated carbon from *Chlorella pyrenoidosa* for further application will be beneficial because it has a high surface area. Addition of carboxyl and hydroxyl functional group will enhance the performance of activated carbon both for adsorption either for wastewater applications or carbon sequestration applications.
- Investigation of other by products such as bio-oil and non-condensable gas will be beneficial for increasing economic potential of production process activated carbon from *Chlorella pyrenoidosa*.
- Investigating other microalgae and other carbonate salt activators will be beneficial for other promising raw materials to produce activated carbon with high surface area. utilization of waste such as eggshell that has more than 90% of calcium carbonate will be contributing on the topic of circular economy and activated carbon.
- Investigation for adsorb-desorb behavior will be beneficial for higher scale application. Technoeconomic analysis also needs to be investigated to increase the potential of implementation in both technical feasibility and economic feasibility.

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