



Faculty of Engineering

**Synthesis and Characterization of Activated Carbon from Dabai
(*Canarium odontophyllum*) Nutshell for Removal of Water Pollutants**

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Synthesis and Characterization of Activated Carbon from Dabai (*Canarium
odontophyllum*) Nutshell for Removal of Water Pollutants

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DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. Except where due acknowledgements have been made, the work is that of the author alone. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

A handwritten signature in black ink, consisting of a large loop followed by a series of smaller, connected strokes, ending in a horizontal line.

Signature

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ABSTRACT

This research is conducted to explore the potential of utilizing dabai nutshell as the precursor for the purpose of synthesizing biochar and activated carbon (AC) for the purpose of removing water pollutants. Dabai nutshell is commonly thrown away as waste instead of being utilized for industrial purpose. Previous studies on chemical activation of the biomass do not meet the required properties of the AC, and do not include the optimization of carbonization temperature. The potential of the AC from dabai nutshell for removal of heavy metal ions are not explored in prior studies. Inert gases and complex equipment set up to provide oxygen-less atmosphere for the synthesis of AC are not available in rural areas, thus further studies are required to determine the alternatives for the inert gas. This research aimed to synthesise the AC from Dabai nutshell using chemical activation and carbonization (both processes are without inert gas flow) and characterize it using several analytical techniques. This work also studies on the effect of different chemical activating agents with different concentration on the synthesis of AC, to optimize the carbonization temperature and to apply the AC on removal of selected water pollutants. The dabai nutshell underwent physical treatment to clean, dry and reduce its size down to 1 mm. The biomass then carbonized under different atmosphere, and at different temperature, in order to perform optimization study for the process's temperature. The resulting biochar is then activated using sodium hydroxide (NaOH), potassium chloride (KCl) or hydrochloric acid (HCl). The synthesized AC were then characterize using several analytical methods and applied on removal of dye methylene blue and heavy metal ions (zinc, chromium, and lead). The results showed that the biochar is dominated by carbon and oxygen, and the percentage yield and ash content of the biochar are more than 26% and less than 4.00%, respectively. The nitrogen

adsorption isotherm of the biochar is similar to Type I of IUPAC classification, and biochar is observed to have the surface area more than 370 m²/g. The optimization of the carbonization temperature on synthesizing biochar that met the set criteria concluded that 721.469 °C is the optimum temperature. The biochar derived without inert gas flow during carbonization have comparable properties with the biochar derived under nitrogen and argon gas flow. AC derived through chemical activation using NaOH have comparable BET surface properties with commercial AC, with micropores properties, BET surface area of more than 328 m²/g, and total pore volume of more than 0.194 m³/g. The nitrogen adsorption isotherms are similar to Type II isotherm of the IUPAC categorization across all replicates. AC replicates derived through HCl and KCl activation are dominated with carbon and oxygen and have ash content less than 3%. All AC replicates however are having low MB adsorption uptake, lower than the standard (60-120 mg/g), and the kinetic study of MB adsorption reveals that the most suited model to describe the MB adsorption on the AC replicates are pseudo-second-order model and Elovich kinetic model. All AC replicates have more than 35% removal of heavy metal ions with initial concentration of 30 ppm. These findings conclude that dabai nutshell are suitable to be utilized as precursor for AC, with carbonization and chemical activation are performed on the precursor without the use of inert gas flow. The resulting AC also performed excellent adsorption to reduce the concentration of heavy metal ions.

Keywords: Dabai nutshell, chemical activation, activated carbon, adsorption, carbonization temperature, optimization, dye methylene blue, heavy metal ions.

Sintesis dan Perawatan Karbon Diaktifkan daripada Kulit Kacang Dabai (Canarium odontophyllum) untuk Penyingkiran Bahan Pencemaran Air

ABSTRAK

Kajian ini dilaksanakan bagi mengenali potensi penggunaan kulit kacang dabai sebagai bahan asas penghasilan bio-arang dan karbon teraktif (AC) untuk tujuan penyingkiran bahan pencemar air. Kulit kacang dabai sering dibuang dan tidak dimanfaatkan untuk tujuan industri. Kajian terdahulu ke atas pengaktifan kimia pada biojisim berkenaan tidak menepati ciri AC, dan tidak merangkumi pengoptimuman suhu pengkarbonan. Kajian terdahulu juga tidak mengenali potensi AC daripada kulit kacang dabai untuk penyingkiran ion logam berat. Gas lengai dan kelengkapan peralatan yang kompleks bagi menghasilkan keadaan tanpa oksigen untuk penghasilan karbon teraktif juga tiada di kawasan pedalaman, maka kajian selanjutnya diperlukan untuk menemui alternatif kepada gas lengai. Kajian ini bertujuan untuk menghasilkan AC daripada kulit kacang Dabai melalui pengaktifan kimia dan pengkarbonan (kedua-dua proses dilaksanakan tanpa aliran gas lengai) dan mencirikan AC berkenaan melalui beberapa kaedah analitikal. Kajian ini juga akan meneliti kesan penggunaan agen pengaktifan kimia yang berbeza, dengan kepekatan yang berbeza ke atas penghasilan AC, mengoptimumkan suhu pengkarbonan dan menggunakan AC berkenaan dalam penyingkiran bahan pencemar air yang terpilih. Kulit kacang dabai terlebih dahulu melalui rawatan fizikal, dengan membersihkan, mengering dan mengurangkan saiz sehingga 1 mm. Biojisim berkenaan kemudian dikarbonkan di bawah keadaan atmosfera yang berbeza, dan suhu yang berbeza bagi melaksanakan kajian pengoptimuman ke atas suhu proses berkenaan. Bio-arang yang telah dihasilkan kemudiannya diaktifkan menggunakan natrium hidroksida (NaOH), kalium klorida (KCl) atau asid hidroklorik (HCl). AC yang telah dihasilkan kemudiannya dicirikan

melalui beberapa kaedah analitikal dan digunakan untuk penyingkiran pewarna metilena biru dan ion logam berat. Keputusan dari kajian ini menunjukkan bahawa bio-arang yang terhasil didominasi oleh karbon dan oksigen, dan peratusan hasil dan kandungan abu pada bio-arang masing-masing adalah 26% dan kurang daripada 4.00%. Isoterm penjerapan nitrogen bagi bio-arang ini adalah serupa dengan Jenis I dalam klasifikasi IUPAC, dan bio-arang diperhatikan mempunyai luas permukaan melebihi $370 \text{ m}^2/\text{g}$. Pengoptimuman untuk suhu pengkarbonan yang menepati kriteria yang telah ditetapkan menyimpulkan bahawa 721.469°C ialah suhu optimum untuk proses berkenaan. Bio-arang yang dihasilkan tanpa menggunakan aliran gas lengai mempunyai ciri-ciri yang setanding dengan bio-arang yang dihasilkan menggunakan aliran gas nitrogen dan argon. AC yang dihasilkan melalui pengaktifan kimia menggunakan NaOH adalah setanding dengan AC komersial, dengan mempunyai ciri-ciri mikropori, luas permukaan BET melebihi $328 \text{ m}^2/\text{g}$ dan jumlah isi padu pori melebihi $0.193 \text{ m}^3/\text{g}$. Isoterm penjerapan nitrogen bagi kesemua replika AC berkenaan adalah serupa dengan Jenis II dalam klasifikasi IUPAC. Replika AC yang dihasilkan melalui pengaktifan HCl dan KCl didominasi oleh karbon dan oksigen, dan mempunyai kandungan abu kurang daripada 3%. Namun, kesemua replika AC mempunyai penjerapan MB yang rendah, lebih rendah daripada standard ($60\text{-}120 \text{ mg/g}$) dan kajian kinetik terhadap penjerapan MB mendapati model yang paling sesuai menjelaskan penjerapan MB ke atas kesemua replika AC adalah model pseudo-urutan-kedua dan model kinetik Elovich. Kesemua replika AC telah mengurangkan sekurang-kurangnya 35% daripada kepekatan asal (30 ppm) ion logam berat. Dapatan ini menyimpulkan bahawa kulit kacang dabai sesuai digunakan sebagai bahan asas untuk AC, dengan pengkarbonan dan pengaktifan kimia dilakukan pada bahan asas tanpa menggunakan aliran gas lengai. AC yang terhasil

juga melakukan penjerapan yang sangat baik untuk mengurangi kepekatan ion logam berat.

Kata kunci: Kulit kacang dabai, pengaktifan kimia, karbon teraktif, penjerapan, suhu karbonisasi, pengoptimuman, pewarna biru methylene, ion logam berat

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LIST OF ABBREVIATIONS

AC	Activated Carbon
ASTM	American Society for Testing and Materials
BET	Brunauer-Emmett-Teller
COD	Chemical Oxygen Demand
EDX or EDS	Energy Dispersive Xray Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
HCl-AC	AC derived though hydrochloric acid, HCl activation
ID	Intra-particle diffusion kinetic model
IUPAC	International Union of Pure and Applied Chemistry
KCl-AC	AC derived though potassium chloride, KCl activation
MB	Methylene Blue
NaOH-AC	AC derived though sodium hydroxide, NaOH activation
PFO	Pseudo-first-order adsorption kinetic model
PSO	Pseudo-second-order adsorption kinetic model
SEM	Scanning Electron Microscope

LIST OF NOMENCLATURE

H_3PO_4	Phosphoric acid
HCl	Hydrochloric acid
KCl	Potassium Chloride
KOH	Potassium hydroxide
NaOH	Sodium Hydroxide

CHAPTER 1

INTRODUCTION

1.1 Study Background

Responsibility towards curing Mother Earth from pollution is one of the major concerns worldwide. Reducing the various pollutants through numerous methods are necessary for each nation on this planet, which induce countless efforts to explore all resources and procedures available. Current development in the combat against water pollution includes the physical treatment such as sedimentation and filtration, and chemical treatments such flocculation, coagulation, adsorption, and ion exchange methods (Saravanan et al., 2021). For adsorption, one of the common methods being deployed is the utilization of highly porous activated carbon.

Ukanwa et al. (2019) stated that activated carbon (AC) is a carbonaceous material produced by thermal or thermochemical processes from coal or biomass. ACs are distinguished by their well-developed pore morphology, extraordinary surface area, electron-conducting amphoteric tendencies, and high adsorptive capacity (Pezoti et al., 2016). The activated carbon has a variety of uses in the treatment of wastewater, including the removal of metal ions and dye from aqueous solutions as well as the sterilization of drinking water. (Ioannidou & Zabaniotou, 2007).

Conventionally, AC is developed using coal, wood and coconut shells as described by Crini et al. (2019). Non-conventional AC are synthesized from solid biomass waste containing high percentage of carbon, and industrial byproducts such as sewage sludges and waste tires. Utilization of solid biomass such as date stones, palm kernel husks, nutshells and

palm fruit bunch is studied thoroughly to determine the suitability of the raw materials as the precursor in AC production (Crini et al., 2019).

One of the most underutilized lignocellulosic wastes in Borneo is Dabai (*Canarium odontophyllum*). The dabai fruit, leaves, and stem (in terms of extract), is proven by various studies to have pharmaceutical advantages, ranging from potential diabetic medication to cancer treatment (Fredalina Basri, 2015; Hamzah et al., 2022). According to Kasron et al. (2020), in 2018, Dabai had the greatest crop area and led overall indigenous fruit production in Malaysia, accounting for 29% of land area and 15% of production. However, it is different for the nutshell of the fruit, where this material is usually thrown away after its flesh being consumed, and very little research is made on the nutshell in order to determine its value. Dabai nutshell, for instance, has a lot of undiscovered value since it could potentially be used as a precursor in the production of activated carbon. Some folks like to boil and dry the nutshell before eating the nut within. The nutshell is very hard, where it requires nutcrackers to open it, and heavy-duty grinder to further crush it into powders. The biomass also took long time to be decomposed naturally. By looking at the possibility of using the Dabai nutshell as raw material for the synthesise of AC, it could open up fresh opportunities for using Dabai for commerce., instead of just being thrown away as waste. Additionally, this will result in a significant increase in the number of available positions for labour. Furthermore, the expansion of Dabai tree plantation areas would bring value to the state economy, particularly through the use of Dabai by-products as a precursor to the production of activated carbon. These advantages will increase the value of agricultural goods and enable a broader range of low-cost solutions to water pollution (Ioannidou & Zabaniotou, 2007).

The further studies on the carbonization parameters such as the carbonization temperature and atmosphere conditions during the process of thermal decomposition of the dabai nutshell are important to determine the optimum conditions for the manufacturing process. Among various parameters, pyrolysis temperature has the most significant effect on the quality of the resulting adsorbent (Huang et al., 2014). Chemical activation of the precursor also affected by various factors, such as type of activating agents and its concentration, which will determine the further development of porous surface on the adsorbent.

Previous studies on the synthesis of AC from dabai nutshell were conducted by Vicinisvarri et al. (2014) and James et al. (2022). Vicinisvarri et al. (2014) treated the precursor with phosphoric acid (H_3PO_4), and activated the precursor at 700 °C. The resulting AC is tested for methylene blue adsorption. James et al. (2022) activated the precursor with potassium hydroxide (KOH) at 400 °C, and the resulting AC is further milled into nano-size. In both studies, the dabai nutshell is only activated using one chemical activating agent, and the properties of dabai char is not determined. The ACs are also not being evaluated on the performance upon adsorption of heavy metal ions.

To further investigate the properties and potential of dabai-driven AC, this study includes the investigation on the carbonization parameters that influenced the properties of char derived from dabai nutshell, and its optimization. The study also stepped into the investigation of the impact of different type of chemical activating agents at different concentrations, other than phosphoric acid and potassium hydroxide.

This study aimed to develop activated carbon (AC) from Dabai nutshell using carbonization and chemical activation, which can be utilized for removal of water pollutants. This study also includes the optimization of the carbonization temperature, and the research

on the potential synthesis of activated carbon without using any inert gas flow during both carbonization and chemical activation. The resulting AC is further characterized to determine its properties and suitability and evaluated for its performance for removal of water pollutants.

1.2 Problem Statement

Dabai nutshell is commonly described as biomass waste as it is not consumable (Vicinisvarri et al., 2014). The biomass is also very hard to be crushed and requires a long time to decay naturally. Dabai itself is very unique resource, but its nutshell is a biomass waste with huge potential. Only few research are made to study its properties and further utilized it as potential adsorbent. Previous studies as mentioned in Section 1.1, did not include the further potential of dabai-driven AC on heavy metal ions adsorption and treatment on wastewater. Thus, intense research should be executed to utilize the biomass waste into adsorbents and its application on wastewater treatment, and other potential usage, instead of just disposing it directly.

Chemical activating agents commonly used for the synthesis of AC are chloride salts, base, and acid, with the activating agents acts distinctly with distinct raw materials. The activating agents used and its concentration influences porosity in the AC, where the higher porosity will increase the effectiveness of the activated carbon (Ademiluyi & David-West, 2012; Ukanwa et al., 2019). There is no study conducted to determine the performance of the activated carbon from dabai nutshell for the reduction of heavy metal ions concentration. Thus, the effect of different chemical activating agents and its concentrations on the properties of the activated carbon are needed to be determined.

The biochar would have varied percentage of yield, ash content, BET surface area and total pore volume based on the temperature of the pyrolysis process (Daud et al., 2001;

Katesa et al., 2013). The optimum pyrolysis temperature is needed to be determined for obtained biochar from dabai nutshell with high percentage of yield, BET surface area and total pore volume and low ash content.

Inert atmosphere for the synthesis of activated carbon (carbonization and chemical activation) requires inert gas flow, which is not available in rural areas and requires complex experimental setup (Ahiduzzaman & Sadrul Islam, 2016). Thus, further investigation towards the potential of producing the adsorbent from dabai nutshell through oxygen-less atmosphere without nitrogen or argon gas flow is needed to be performed.

1.3 Research Gap

Very few research is made on the potential of Dabai nutshell in terms of industrial potential, specifically as precursor for activated carbon, for any purposes. A study that was made on the mentioned biomass only specifies on the characterization of the produced activated carbon, with one chemical agent and one application is made, which is on dye methylene blue adsorption (Vicinisvarri et al., 2014). The other study conducted by James et al. (2022), succeeded to develop nano-sized AC through KOH activation and ball milling, but at the lowest carbonization temperature, which is 400 °C. However, the study deduced that the surface area of the AC and nano-sized AC are very low, which is 5.093 and 25.779 m²/g respectively.

The temperature setting for the pyrolysis of dabai nutshell that can induce high percentage of yield and low ash content has not been studied on the precursor. In this work, optimization is performed to determine the temperature setting suitable to reach the desired properties of char.

The impact of using different chemical activating agent for chemical activation of the precursor has not yet been clarified, thus induce difficulties to conclude which of those chemicals induce better porous structure on the adsorbent surface. This study includes the comparison between different chemical activating agents at different concentrations and activation temperatures for the synthesis of the adsorbent.

The common practice of carbonization and chemical activation require the flow of inert gases such as nitrogen and argon to flush out oxygen gas, to reduce potential of combustion and complete, direct conversion of the precursor into ash. The mentioned gases are not available in rural areas and requires complex machinery setup (Ahiduzzaman & Sadrul Islam, 2016), thus a method of synthesising the activated carbon without those gases are needed to be studied.

Characterization of the char and activated carbon is yet to be performed, which leads to less understanding on the properties and capabilities of the adsorbents. This research provides further characterization of the char and activated carbon in terms of yield, ash content, elemental mass percentages, surface properties, functional groups and more. there is no research that determine the removal performance of heavy metal ions for the AC derived from Dabai nutshell. The current study also performed the evaluation for the removal of few selected water pollutants.

1.4 Hypothesis

The hypothesis of this research is dabai nutshell can be utilized as precursor of AC by deriving it through heat and chemical treatment, without any inert gas flow. Better morphological and physical properties of Dabai AC can be achieved by activating it using NaOH, HCl and KCl as chemical activating agent. The highest percentage of yield, lowest

ash content, with large surface area and high total pore volume of the Dabai nutshell biochar can be achieved by optimizing the carbonization temperature. Performance of the Dabai AC replicates on removal of water pollutants can be evaluated through assessment of adsorption capacity of the adsorbent on reducing methylene blue and heavy metal ions concentrations.

1.5 Aim and Objectives

- a) To synthesise biochar and activated carbon from Dabai nutshell through carbonization and chemical activation (both processes are without inert gas flow) and characterize it using several analytical techniques.
- b) To study the effect of different chemical activating agents with different concentration on the properties of activated carbon (AC)
- c) To optimise pyrolysis temperature of the precursor (Dabai nutshell)
- d) To evaluate the adsorption uptake of AC for removal of water pollutants.

1.6 Scope of Research

The scope of this research is converting biomass waste to wealth; potential industrial material, by synthesizing biochar and value added-activated carbon from dabai nutshell, which is obtained from Dabai trees grown in Sibu, Sarawak. This plant grows wildy along the rivers in the state and being planted in field for commercial purposes. The dabai nutshell itself are commonly discharge as waste. For chemical activation, the chemical activating agents utilized are sodium hydroxide (NaOH), potassium chloride (KCl) and hydrochloric acid (HCl). The carbonization study is performed to determine the optimum temperature for the process and to compare the properties of biochars derived using three different carbonization atmospheres; nitrogen gas, argon gas and no inert gas flow. The water

pollutants selected for the performance of AC are dye methylene blue and heavy metal ions solutions (Zinc, Chromium and Lead).

CHAPTER 2

LITERATURE REVIEW

Overview

This chapter provides the literature review related to the current research, which is the activated carbon derived from Dabai nutshell. The chapter describes the morphology of the plant, advantages and studies performed on different parts of the plant. This chapter also includes review on activated carbon, describing on adsorption, activation methods, precursor, and earlier study on the activated carbon derived from dabai nutshell. Another topic discussed in this chapter is water pollution and available treatment. Graphical structure of this chapter is as shown in Figure 2.1.

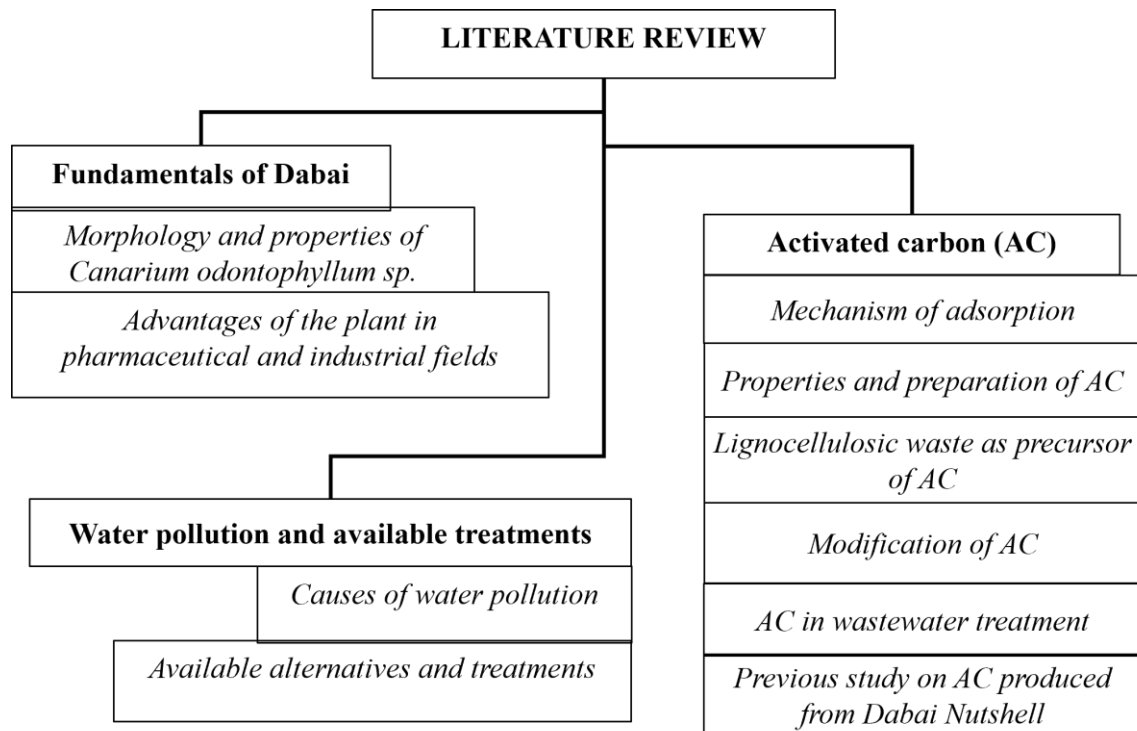


Figure 2.1: Graphical understanding for the literature review.

2.1 Fundamentals of Dabai

Sarawak's indigenous seasonal fruit, *Canarium Odontophyllum* sp, is commonly called as Dabai (Kadir et al., 2018). This fruit can only be found on the island of Borneo, it is abundant in east Malaysia's tropical woods, especially in the Sarawak regions of Sibuan and Kapit (Abdul Aziz et al., 2022; James et al., 2022). It is also known as Sarawak Olive because of its physical look, texture, and flavour, which are similar to olives. Dabai offers a wide range of types, including Jampa, Sibuan, and others, all of which are high in quality (Chai et al., 2010). Dabai is a seasonal product that is available from November to January each year (Prasad et al., 2010). The market price is USD 2.9–5.1 kg⁻¹ and it can only be purchased in Sarawak and Sabah's local markets because the fruit has a short shelf life of only 3 days at 27°C (Ding & Tee, 2011).

To consume this hard fruit, soak it in warm water for five to ten minutes to soften it (Prasad et al., 2011) before lightly dipping it in salt, sugar, and soy sauce. The fruits can also be softened by soaking them in hot water (about 50°C) for 10 to 20 minutes before eating (Ding and Tee, 2011). To consume this hard fruit, soak it in warm water for five to ten minutes to soften it (Prasad et al., 2011) before lightly dipping it in salt, sugar, and soy sauce. The fruits can also be softened by soaking them in hot water (about 50°C) for 10 to 20 minutes before eating (Ding & Tee, 2011).

2.1.1 Properties of Dabai

The following section provides the information on the characteristics of the proposed precursor for the synthesis of activated carbon.

2.1.1.1 Morphology of Dabai

Canarium odontophyllum plants are androdioecious, according to Brooke and Yuon, (1980) which means the trees are either male or hermaphrodite in terms of reproductive

system. According to the experts, only hermaphrodite trees yield dabai fruit (Brooke & Yuon, 1980). Farmers' technique of planting trees using Dabai seed may result in the development of male plants. Only after the trees have blossomed for 8 to 10 years can the male sex of the trees be established (Brooke & Yuon, 1980). According to Fern and Morris (2019), this mid-canopy tree can reach a height of 36 meters. The bole may be up to 18 metres long, branch-free, with an 86 cm breadth and buttresses at the base (Fern & Morris, 2019).

2.1.1.2 Morphology of Dabai fruit

Chua et al. (2015) studied the physical properties of Dabai fruits from six distinct genotypes, namely Besar, Biasa, Jernah, Bujur, Seluang, and Bulat. The dabai fruits were purchased in marketplaces in Sarawak's Sibu and Kuching. Size (length, breadth, pulp thickness) and form (sphericity index and aspect ratio) were the physical parameters investigated by the researchers, as indicated in Table 2.1. In Table 2.2, the fruit fraction mass of the examined genotypes is also listed.

Table 2.1: Six dabai fruit genotypes (n = 10) were measured for length, breadth, and pulp thickness, as well as form (sphericity index and aspect ratio) (Chua et al., 2015)

Genotypes	Fruit length (cm)	Fruit width (cm)	Pulp thickness (cm)	Sphericity index (%)	Aspect ratio (%)
Besar	3.60 ± 0.15b	2.58 ± 0.22a	0.43 ± 0.07a	42.91 ± 2.88b	71.57 ± 5.82b
Biasa	3.07 ± 0.23c	2.10 ± 0.17c	0.35 ± 0.05b	42.46 ± 1.68b	68.44 ± 3.88bc
Jernah	3.00 ± 0.11c	1.94 ± 0.08d	0.28 ± 0.03c	39.17 ± 1.49c	63.77 ± 4.60cd

Table 2.1 Continued

Bujur	3.98 ± 0.20a	2.40 ± 0.13b	0.36 ± 0.03b	37.73 ± 0.95c	60.38 ± 3.55d
Seluang	2.90 ± 0.07c	1.94 ± 0.10d	0.22 ± 0.03c	36.97 ± 1.46c	66.89 ± 3.09c
Bulat	3.01 ± 0.14c	2.63 ± 0.15a	0.43 ± 0.03a	49.94 ± 0.90a	87.42 ± 3.75a
Means in the same column with the same letter are not significantly different ($p>0.05$)					

Table 2.2: Fruit mass fraction in six typical genotypes of dabai fruits (Chua et al., 2015).

Dabai genotype	Total fruit mass (g)	Total seed mass (g)	Skin mass (g)	Pulp mass (g)	Kernel mass (g)	Total edible portion (%)
Besar	15.33 ± 1.63a	5.84 ± 0.41a	1.45 ± 0.32a (9.46%)	8.04 ± 1.28a (52.45%)	1.33 ± 0.14a (8.68%)	70.59a
Biasa	10.23 ± 2.07b	3.83 ± 0.80c	0.78 ± 0.25a (7.62%)	5.62 ± 1.18b (59.94%)	0.94 ± 0.23b (9.19%)	71.75a
Jernah	7.41 ± 0.68c	2.83 ± 0.28d	1.21 ± 0.20a (16.33%)	3.36 ± 0.29c (45.34%)	0.48 ± 0.04d (6.48%)	68.15b
Bujur	15.28 ± 2.16a	6.48 ± 1.02a	1.10 ± 0.19a (7.20%)	7.71 ± 1.20a (50.46%)	1.08 ± 0.10b (7.07%)	64.73c
Seluang	7.60 ± 0.53c	350 ± 0.25cd	0.85 ± 0.10a (11.18%)	3.25 ± 0.33c (42.76%)	0.69 ± 0.08c (9.08%)	63.02c
Bulat	13.31 ± 1.10a	4.78 ± 0.34b	1.11 ± 0.32a (8.34%)	7.42 ± 1.13a (55.75%)	0.96 ± 0.14b (7.21%)	71.30a
Means in the same column with the same letter are not significantly different ($p>0.05$)						

2.1.1.3 Morphology of Floral Structure

The male bloom of the dabai tree is unisexual and unfinished (Ting et al., 2017). The calyx, corolla, and androecium are the three whorls present. The calyx, which is green in colour and has three sepals, is found near the bottom of the receptacle. The inside of the

sepals houses the corolla, which consists of three white petals with a crimson mark on the tips. Figure 2.2 depicts the overall shape of a dabai tree's male bloom.

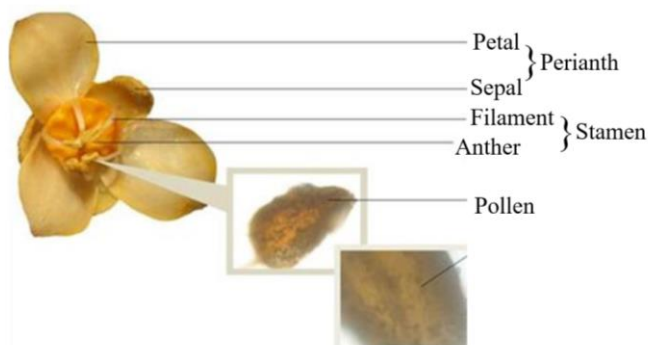


Figure 2.2: Male flower morphology of dabai trees in general (Ting et al., 2017).

2.3.3.4 Structure of Dabai Nutshell

The potential of dabai nutshell as a precursor of activated carbon, which was activated via chemical activation (phosphoric acid) for methylene blue dye adsorption, was investigated (Vicinisvarri et al., 2014). Before being synthesized into activated carbon, the nutshell was investigated using Fourier Transform Infrared (FTIR) spectroscopy, Scanning Electron Microscope (SEM), and Energy Dispersive X-ray (EDX).

A cross section of a Dabai nutshell is shown in Figure 2.3. The nutshell's surface was discovered to be dense and flat. There were no fractures or pores, which were typical of lignocellulosic materials. The EDX spectrum of Dabai nutshell is shown in Figure 2.4. Carbon and oxygen predominate in the spectrum, with potassium and calcium showing just a little presence.



Figure 2.3: A cross section of Dabai nutshell

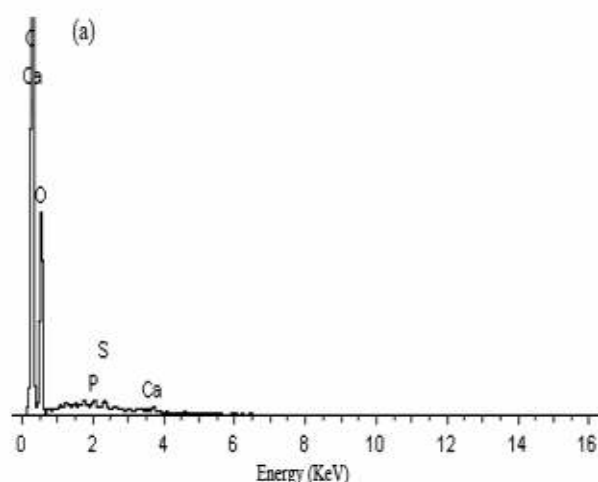


Figure 2.4: EDX spectrum of Dabai nutshell (Vicinivarri et al., 2014)

2.1.1.5 Dabai Phytochemical Characteristics

Several investigations were carried out to evaluate the chemical characteristics of the Dabai fruit, which comprises the peel, pulp, and seed. Azrina et al. (2010) identified the high phenolic content of Dabai in a study on the antioxidant effects of methanolic extract of Dabai fruit. The peel of the dabai fruit had the greatest proportion of total phenolics, with 387.5 ± 33.23 mg GAE/100 g, while the pulp had 267.0 ± 4.24 mg GAE/100 g and the kernel had 51.0 ± 0.01 mg GAE/100 g, where GAE stands for gallic acid equivalents (Azrina et al., 2010).

2.1.2 Advantages of Dabai Nutshell

There haven't been much research on the potential uses of dabai nutshell. Basri et al., (2014) investigated the nutshell extract's potential as an antibacterial agent. The underused material's ethyl acetate extract included flavonoid and tannin, while the nutshell's acetone extract contained terpenoid and tannin, according to phytochemical screening. The presence of compounds suggested that the nutshell acetone extract had the potential to be a new source of antibacterial agent, which may be employed as a phytotherapeutic therapy for illnesses caused by *A. baumannii* and *P. mirabilis*. (Basri et al., 2014).

Vicinisvarri et al. (2014) derived activated carbon (AC) from dried, powdered dabai nutshell and used phosphoric acid as a chemical activator. They tested the AC's adsorption capacity using the colour methylene blue. The AC activated with 60 percent phosphoric acid exhibited a high degree of methylene blue adsorption, indicating the potential of dabai nutshell as an AC precursor (Vicinisvarri et al., 2014).

Another study conducted by James et al. (2022) to synthesis novel nano-carbon mixture as an adsorbent from dabai nutshell. The research concluded that the adsorbent mixture synthesized with potassium hydroxide (KOH), titanium dioxide and montmorillonite (MMT) clay. This study showed that activated carbon from Dabai has excellent potential for treating wastewater. Both the non-activated and AC samples displayed an uneven, granular, and porous morphology (James et al., 2022). These two studies will be further explained in Sub-section 2.2.8.

2.2 Activated Carbon (AC)

According to Rodríguez-Reinoso and Sepúlveda-Escribano (2001) activated carbon is an amorphous solid made primarily of carbon that has unique adsorbent characteristics due to its high internal surface area and pore volume. Ganjoo et al. (2023) stated that it contains a broad range of pores, from visible fissures and fractures to molecular diameters. Due to its large surface area, AC are widely used for a number of applications, such as purging water and air of pollutants (Ganjoo et al., 2023). Mariana et al. (2021) mentioned that scientists are paying close attention to activated carbon because it can reduce heavy metals concentration. Activated carbons have been produced from carbon-rich source materials using a variety of methods (Mariana et al., 2021).

Carbonization (pyrolysis in an inert environment) followed by activation (heat treatment with an oxidizing agent) or simultaneous carbonization and activation with a dehydrating chemical are the common practices to synthesize AC from carbon-rich source materials. Rodriguez-Reinoso and Silvestre-Albero (2016) stated that the porosity of the carbon increased as a result of the physical or chemical treatment compared to its predecessor (char), resulting in a high interior surface area (Rodriguez-Reinoso and Silvestre-Albero, 2016)

Rodriguez-Reinoso and Silvestre-Albero (2016) also stated that the removal of contaminants from gases and liquids via adsorption is the most common use of activated carbon. By primarily physical forces of the Van der Waals type, the surface of activated carbon can bind molecules from the liquid or gas phases, resulting in a greater concentration of the adsorbate at the interface than in the bulk fluid. There is also the potential of chemisorption, which is generated by higher valence forces on the carbon surface's so-called active sites. The effectiveness of activated carbon will thus be determined by the amount of accessible surface area for physical adsorption and the availability of active sites for chemisorption (Rodriguez-Reinoso & Silvestre-Albero, 2016).

These materials are utilized in a variety of applications, including gas adsorption, separation and storage, wastewater, and drinking water treatment, and as a catalyst for chemical processes, due to the mentioned characteristics of AC that improve the effectiveness of adsorption of the AC (Contescu et al., 2018). The hydrophobic and non-polar characteristics of carbon-based adsorbents make them ideal for phenol removal in wastewater (Abussaud et al., 2016). Aside from its large surface area, AC is also widely used as an energy storage material due to its stability, high polarizability, amphoteric character, high accessibility, and economic and environmental benefits (Indayaningsih et al., 2016).

This section provides the knowledge on activated carbon prior to its utilization for adsorption.

2.2.1 Mechanism of Adsorption

Kecili and Hussain (2018) defined adsorption as a surface-based exothermic process in which molecules of a liquid or gaseous substance aggregate on the surface of an adsorbent. Adsorbate is the term for the accumulated molecules. Desorption, on the other hand, is the process of releasing the adsorbate from the adsorbent. Physical adsorption (also known as physisorption), chemical sorption (also known as chemisorption), and electrochemical enhanced adsorption (also known as electrosorption) are the three types of adsorptions (Foo & Hameed, 2009; Kecili & Hussain, 2018).

According to Kecili and Hussain (2018), The interactions between molecules and the surface separate the two processes. In physisorption, weak forces such as Van der Waals forces and electrostatic interactions are involved. Strong chemical connections, such as covalent bonds, are generated between the adsorbent surface and the adsorbate in chemisorption. Physisorption is quicker than chemisorption in terms of the pace of the process. Chemisorption produces a monomolecular layer (also known as monolayer), but physisorption produces a multilayer due to a higher adsorption rate than chemisorption. Electrosorption on the other hand, defined by Foo and Hameed (2009) and Han et al. (2006) as an adsorption phenomenon on the surface of charged electrodes caused by current or polarization potential. This process occurred charged ions are pushed to migrate towards the oppositely charged electrodes when an external electrostatic field is applied to the surface of electrodes submerged in an aqueous electrolyte solution, allowing charge separation across the interface to occur (Li et al., 2008). As a result, powerful electrical double layers formed near surfaces with high conductivity and surface area (Oren, 2008). The charge on the

electrode is compensated for ionic countercharges at the electrolyte side of the interface when the electrical field is removed, which can be accomplished by contact adsorption of ions (Bán et al., 1998) or an accumulation of counter ions in the outer Helmholtz plane and diffuse (Gouy–Chapman) layer.

2.2.1.1 Adsorption Isotherms

The curve of the quantity of adsorbate to the adsorbent surface as a function of partial pressure, or concentration of adsorbed molecules at a given temperature, is known as an adsorption isotherm (Limousin et al., 2007). There are six types of adsorption isotherms, according to the IUPAC categorization of gas adsorption on the surface of solid adsorbents, and the isotherm types are shown in Figure 2.5 (Donohue & Aranovich, 1998). According to Kecili and Hussain, (2018), there are six different forms of adsorption isotherms.

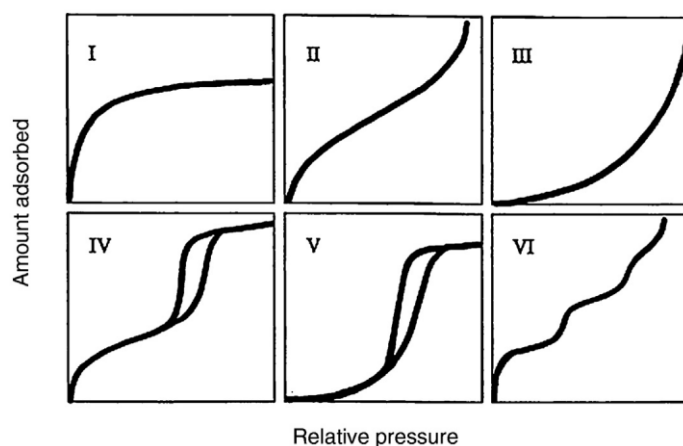


Figure 2.5: 6 types of isotherms of adsorption (Donohue & Aranovich, 1998).

Table 2.3: A brief review of the types of adsorption isotherms (Kecili & Hussain, 2018).

Types of adsorption isotherms	Brief review
Type I	Describes the adsorption of gas molecules to an adsorbent with micropores (for example, activated carbon) and the production of adsorbate monolayers on the adsorbent.

Table 2.3 Continued

Type II	Describes the adsorption of gas molecules onto an adsorbent with macropores, the absence of a saturation point (as in Type I), and the development of a multilayer of adsorbate after the monolayer has covered the adsorbent's surface.
Type III	Refers to multilayer adsorption with low-energy weak interactions between the adsorbate and the adsorbent.
Type IV and Type V	Refer to multilayer adsorption involving capillary condensation on mesoporous adsorbents.
Type VI	Explains the gradual development of multilayer of adsorbate on the surface of adsorbent with no holes.

Various adsorption isotherms models, such as Langmuir, Temkin, Dubinin-Radushkevich, Freundlich, and Harkins-Jura, were used to obtain detailed information on the interaction between the surfaces of the adsorbents and the adsorbate. The isotherms are explained in the subsections that follow (Kecili & Hussain, 2018).

1. *Langmuir Isotherm*

Irving Langmuir proposed this model in 1932. The Langmuir isotherm model is based on the following assumptions:

- (i) Adsorption occurs at specific binding sites that are localized on the surface of the adsorbent,
- (ii) All adsorption sites on the surface of the adsorbent are identical,
- (iii) A monolayer of adsorbate covers the surface of the adsorbent, and
- (iv) There is no interaction of the adsorbate with the surface.

The model equation is expressed as,

$$\frac{C_e}{q_m} = \frac{1}{K_L q_{\max}} + \frac{C_e}{q_{\max}} \quad \text{Equation 2.1}$$

Where,

C_e (mg L⁻¹) : The equilibrium concentration of the molecules

q_m (mg g⁻¹) : The quantity of adsorbed molecules on the surface of the adsorbent at any time

q_{max} (mg g⁻¹) : The maximum adsorption capacity

K_L (L mg⁻¹) : Langmuir constant.

2. *Freundlich Isotherm*

The model depicts the development of multilayers and the adsorbate's heterogeneous adsorption onto the adsorbent surface, where the model equation is as follows;

$$\log q_m = \log K_F + \frac{1}{n} \log C_e \quad \text{Equation 2.2}$$

Where,

K_F (mg g⁻¹) : The Freundlich exponent, which is proportional to the adsorbent's adsorption capacity towards the adsorbate. Its value greater than 1 implies a favourable adsorption of the adsorbate onto the adsorbent surface.

n : Freundlich constant which is proportional to the degree of surface heterogeneity and defines the distribution of adsorbed molecules on the adsorbent surface. Larger value of n suggests a higher intensity of adsorption.

3. *Temkin Isotherm*

In 1940, Temkin and Pyzhev proposed an adsorption isotherm, which relates adsorption heat with the adsorbate layer. The model equation may be written as follows:

$$q_e = \left(\left(\frac{RT}{b_T} \right) \right) \ln(AC_e) \quad \text{Equation 2.3}$$

Where,

T (K)	: Temperature
R	: Ideal gas constant, 8.314 Jmol ⁻¹ K ⁻¹
b_T (J mol ⁻¹)	: The Temkin constant, which depends on adsorption heat
A (L mg ⁻¹)	: The equilibrium adsorption constant, related to the maximum adsorption energy.

4. Dubinin–Radushkevich Model

This model depicts the adsorption of molecules into adsorbent micropores when molecular adsorption does not occur on the adsorbent's surface. Instead, the action takes place within the adsorbent's micropores. This model is commonly used to describe the adsorption of subcritical vapour in adsorbent micropores. The following are the equations associated with this model:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad \text{Equation 2.4}$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad \text{Equation 2.5}$$

Where,

q_e (mg g ⁻¹)	: The number of molecules adsorbed per mass of adsorbent
q_m (mg g ⁻¹)	: Adsorption capacity
β (mol ² J ⁻²)	: The activity coefficient, which represents the adsorption energy
ε	: Polanyi potential.

5. Harkins–Jura Isotherm

This model is used to describe multilayer adsorption onto heterogeneous pore distribution adsorbent surfaces. The model equation is written as follows:

$$\left(\frac{1}{q_e^2}\right) = \left(\frac{B_{HJ}}{A_{HJ}}\right) - \left(\frac{1}{A_{HJ}}\right) \log C_e \quad \text{Equation 2.6}$$

Where, B_{HJ} and A_{HJ} are Harkins-Jura constants determined by plotting $\left(\frac{1}{q_e^2}\right)$ versus $\log C_e$.

2.2.1.2 Thermodynamic and Kinetic of Adsorption

According to Kecili and Hussain (2018) thermodynamics of adsorption determines how temperature affects the adsorption process. The thermodynamics of the adsorption process are described using the following relationships (Batoool et al., 2018);

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \text{Equation 2.7}$$

$$\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad \text{Equation 2.8}$$

$$\Delta G = -RT \ln K_c \quad \text{Equation 2.9}$$

Where,

ΔG : Change in Gibbs free energy of the reaction

ΔH : Enthalpy change

ΔS : Entropy change

K_c : Equilibrium constant

The constant is calculated using the equation below (Batoool et al., 2018);

$$K_c = \frac{C_e}{1 - C_e} \quad \text{Equation 2.10}$$

Where C_e is the sorbent concentration at equilibrium.

The spontaneity of the adsorption process is determined by the ΔG^0 value. If the ΔG^0 value is negative, adsorption occurs spontaneously. ΔH^0 determines whether or not the adsorption process is endothermic (if ΔH^0 is positive) (Kecili & Hussain, 2018).

The pseudo-first-order model, pseudo-second-order model, intraparticle diffusion model and Elovich kinetic model are the most commonly used models for studying adsorption kinetics. The followings are explanation of the kinetic models (Chakrapani et al., 2010; Kecili & Hussain, 2018).

1. Pseudo-First-Order Model

Kecili and Hussain (2018) stated that, Lagergren developed a pseudo-first-order model based on the following assumptions:

- (i) Adsorption occurs only at specific binding sites located around the adsorbent surface,
- (ii) Formation of a monolayer on the adsorbent surface has no effect on the adsorption energy, the rate of the adsorption process is governed by a first-order equation, and there are no interactions between the adsorbents.

The model's exponential equation is written as follows:

$$Q_t = Q_e(1 - e^{-k_1 t}) \quad \text{Equation 2.11}$$

Where,

Q_t : the quantity of adsorbate after a certain amount of time

t (minutes) : Time

Q_e : The amount of adsorbate at equilibrium

k_1 is : The rate constant

The logarithmic form of the equation can be expressed as, and the linear form of the equation can be expressed as,

$$\ln(Q_e - Q_t) = \ln(Q_e) - k_1 t \quad \text{Equation 2.12}$$

2. *Pseudo-Second-Order Model*

This model is essentially identical to the pseudo-first-order model in terms of assumptions.

The rate of the model is the difference. The equations for the model are as follows:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \left(\frac{1}{Q_e}\right) t \quad \text{Equation 2.13}$$

This equation is rearranged to obtain the non-linear expression, as follows;

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad \text{Equation 2.14}$$

Where, rate constant for this model is represented by k_2 .

3. *Intraparticle Diffusion Model*

Weber and Morris created this model, which is mostly used to represent the adsorption process where the rate-limiting phase is the diffusion of the adsorbate to the porous adsorbent. The model equation is as follows (Chakrapani et al., 2010);

$$q_t = k_{id}t^{1/2} + C \quad \text{Equation 2.15}$$

Where,

- C : The boundary layer thickness
- $q_t (\text{mg g}^{-1})$: The amount of adsorbent at a certain amount of time
- t (minutes) : Time
- $k_{id} (\text{mg g}^{-1} \text{min}^{-0.5})$: The rate constant of the intraparticle diffusion.

4. *Elovich Kinetic Model*

Elovich kinetic model is commonly utilized to study the kinetics of chemical adsorption. The linearized equation of the model is as shown in Equation 14 (Bello et al., 2021). According to Murugesh et al. (2016), the equation is shown to be acceptable for sorption systems with energetically heterogeneous adsorbing surfaces, although it does not suggest any definite adsorbent-adsorbate mechanism.

$$q_t = \frac{1}{\beta} \ln \alpha \beta + \frac{1}{\beta} \ln t \quad \text{Equation 2.16}$$

In this equation, α is the initial adsorption rate (mg/g min) and β is desorption constant (g/mg). By plotting q_t against $\ln t$, the linear relationship can be represented to determine the value of α and β , which is from its slope and intercept.

2.2.2 Porosity of Activated Carbon

The porosity of activated carbon is one of the material's most distinguishing characteristics, since it provides the foundation of the material's large surface area. According to Achaw (2012) the porosity of activated carbon is primarily determined by three factors:

- (i) The precursor material's internal cellular structure,
- (ii) The condition setting during the synthesis of activated carbon, and
- (iii) The precursor's composition.

Achaw (2012) stated that the overall pore volume, pore size distribution, characteristics of specific pore size regimes, and the carbon's surface chemistry all affect the AC's adsorption effectiveness. The categorization of the pore size regime into micropores, mesopores, and macropores was based on the varied behaviour of molecules within the pore size regime (Achaw, 2012).

Micropores have a size width of less than 2 nm, according to the International Union of Pure and Applied Chemistry (IUPAC) nomenclature (Sing, 1982), and tiny pores constitute the bulk of the surface involved with adsorption. Mesopores, on the other hand, have a size range of 2 nm to 50 nm, which is critical for adsorption of bigger molecules. Macropores, on the other hand, are larger than 50 nm. This size regime creates pathways inside the AC structure, as well as access to the micropores and mesopores, and is mostly found on the AC's exterior surface (Sing, 1982).

Ilomuanya et al. (2017) studied the impact of circumstances establishing for carbon activation on the dimensions of pores on the AC. The study is performed with physical activation and varied concentrations of chemical activation agents, Micropores volume ranges from 0.232 cm³/g to 0.578 cm³/g, while total pore volume ranges from 0.795 cm³/g

to $1.577 \text{ cm}^3/\text{g}$, according to the surface area acquired from the research. Physical activation produces microporous structure, whereas chemical activation of the adsorbent produces macroporous structure (Ilomuanya et al., 2017).

Another study looked at the influence of activation agents, as well as their ratio for impregnation, on AC porosity, which is conducted by Okhovat et al. (2012). Dark coal was utilized as a precursor, and it was activated using zinc chloride, ZnCl_2 , and potassium hydroxide, KOH, in proportions of 50, 75, 100, and 200 percent impregnation. The pore volume grew as the impregnation ratio rose in each set of chemical activators. Microporous structure was seen in AC produced from ZnCl_2 with low chemical ratios (up to 100%), whereas mesopores predominated in AC with higher ratios. Micropores predominated in KOH-activated carbon as the chemical ratio rose. In general, ZnCl_2 -AC has a greater adsorption capacity than KOH-AC (Okhovat et al., 2012).

2.2.3 Synthesis of AC

Figure 2.6 generally describes the process to synthesis activated carbon. The precursors required several preparation procedures before going into activation or carbonization step (Koehlert, 2017). The main processes are carbonization, activation (of several types) and thermal treatments (Tadda et al., 2016). Those steps were then followed by post treatment to make sure the produced adsorbent met the requirements for its specific purposes (Rodriguez-Reinoso & Silvestre-Albero, 2016). The carbonization of the precursor without the presence of oxygen, and the activation of the carbonized product are the two key stages in the production of activated carbon (Oubagaranadin & Murthy, 2012). The steps can be swapped out based on the type of activation. The activation might be done chemically, physically, or mechanochemically. Further explanation is provided by the following subsections.

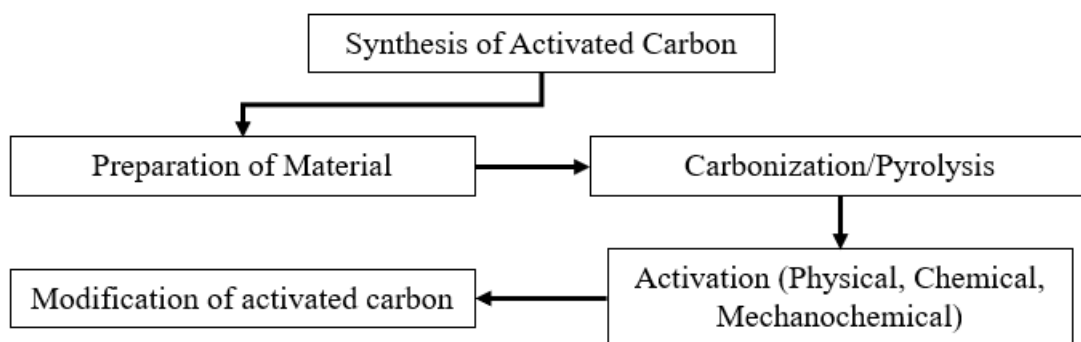


Figure 2.6: General step for the synthesis of activated carbon.

2.2.3.1 Carbonization/Pyrolysis

Carbonization or also commonly named as pyrolysis, eliminates, or reduces non-carbon components like hydrogen and oxygen, resulting in a carbon skeleton (also known as char) with an initial pore structure (Nor et al. 2013; Rodríguez-Reinoso & Sepúlveda-Escribano, 2001). Basu (2018) stated that this process, together with torrefaction are the three stages in biomass thermal breakdown. The average temperature range for carbonization was between 400 and 850 °C (Oubagaranadin & Murthy, 2012). This process is performed in inert condition (Marsh & Rodríguez-Reinoso, 2006a), to prevent combustion of the biomass due to the presence of oxygen.

According to Chowdhury et al. (2013) and Reza et al. (2020), there are 4 stages for carbonization, as shown in Figure 2.7. During the pre-carbonization stage, some pyroligneous acid such as methanol and acetic acid is produced, and small amount of non-condensable gases, such as carbon monoxide and carbon dioxide. Those substances are removed from the precursors in the third stage to synthesis charcoal. Further reduction of the volatile component occurs in stage 4 (Chowdhury et al., 2013; Reza et al., 2020).

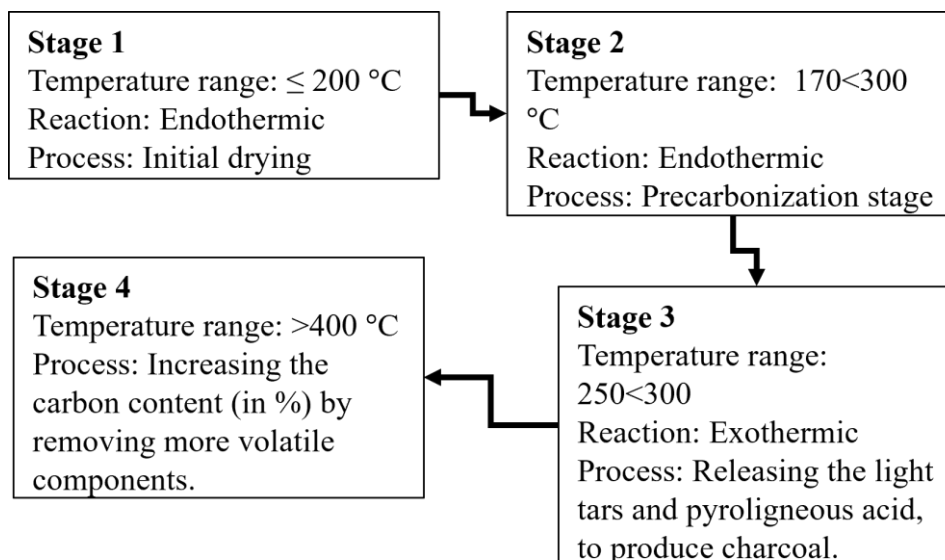


Figure 2.7: Stages of carbonization (Chowdhury et al., 2013; Reza et al., 2020).

Ioannidou and Zabaniotou, (2007) and Yahya et al. (2018) stated that basically, greater carbonization temperatures reduce the yield of activated carbon synthesis. In terms of activated carbon compositions, raising the carbonization temperature reduces moisture and volatile matter content while increasing ash and fixed carbon content (Ioannidou & Zabaniotou, 2007; Yahya et al., 2018).

Katesa et al. (2013) studied the effect of temperature on carbonization of coconut shell, for the synthesis of activated carbon. The temperature range investigated in this study is 250-750 °C, 2 hours under 100 cm³/min of the nitrogen flow. The study resulted that increasing temperature reduces the char yield and porosity properties such as pore volume, surface area and mean pore size (Katesa et al., 2013).

Similar impact is shown in a study on pyrolysis of used tire (Zabaniotou & Stavropoulos, 2003), where the char yield is reduced as the pyrolysis temperature is increased. Better surface area development is also can be observed as the pyrolysis temperature is increased. Different impacts were resulted on the impact of carbonization temperature, for the synthesis of activated carbon from polyurethane foam (Hayashi et al.,

2005). This study concluded that better surface area properties are developed as the carbonization temperature is increased. Thus, further in this study, the impact of temperature increase during carbonization will be studied on the performance of the activated carbon synthesized from dabai nutshell.

Indayaningsih et al. (2017) stated that the carbonization process carried out in an inert gas environment or without air or oxygen. In the process of pyrolysis to obtain carbon, nitrogen (N₂) or argon (Ar) gases are typically utilized which results in the breakdown of material without oxidation (Indayaningsih et al., 2017).

A study is conducted by Gomez-Delgado et al. (2022) on synthesizing microporous AC from *Prosopis Ruscifolia* sawdust. The investigation showed that the resulting ACs' chemical and textural properties, and thus, their potential to adsorb CO₂, were not significantly impacted by the carbonization environment. Because of the lower operating temperature required, using air instead of N₂ during the carbonization stage of the activation process may be an intriguing alternative that can minimize energy consumption and running expenses without noticeably compromising the performance of ACs.(Gomez-Delgado et al., 2022).

2.2.3.2 Physical Activation

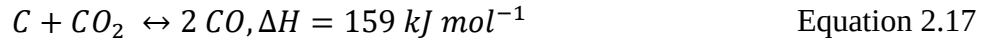
Physical activation (also known as thermal activation) was characterized as a two-step process that included;

- (i) Carbonization or pyrolysis, in which the precursor (carbonaceous material) was carbonized, and
- (ii) Activation, in which the resultant char was activated at a higher temperature.

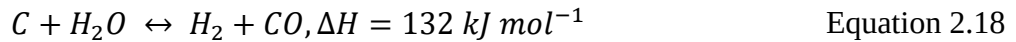
The second heat treatment is necessary to remove the tar that has clogged the pores and to improve the sample's porosity (Rodríguez-Reinoso & Sepúlveda-Escribano, 2001).

During the activation, oxidizing gases such as steam, air, carbon dioxide (CO₂), or a combination of these gases were employed. The activation temperature ranged from 600 to 900 degrees Celsius (Oubagaranadin & Murthy, 2012).

The following is the chemical equation for CO₂ activation (Menéndez-Díaz & Martín-Gullón, 2006);



Another activation method is steam pyrolysis/activation, in which the precursors are heated under a stream of pure steam at temperatures ranging from 500°C to 700°C, or under steam at higher temperatures (700-800°C). The following is the chemical equation for steam activation (Menéndez-Díaz & Martín-Gullón, 2006),



The porosity generated by these two oxidizing agents differs when compared to CO₂ and steam activation, which aids in determining which of these two should be utilized depending on the application. The holes in activated carbon generated from CO₂ activation are smaller than those in activated carbon derived from steam activation. Thus, CO₂-activated carbon is better for gas-phase adsorption because of its smaller pores, but steam-activated carbon is better for liquid-phase adsorption because of its larger micropores, which aid in adsorbate diffusion into the adsorbent (Menéndez-Díaz & Martín-Gullón, 2006).

2.2.3.3 Chemical Activation

Chemical activation, on the other hand, was described as a two-step process that took place at the same time. The precursor was combined with chemical activators that served as dehydration agents and oxidants before being carbonized. The temperature of carbonization was determined by the chemical activating agent employed, which included zinc chloride, phosphoric acid, and alkaline hydroxides (Menéndez-Díaz & Martín-Gullón, 2006).

Chemical activation is a process of treating the precursor with a dehydrating agent (also known as chemical activating agents) at temperatures ranging from 400 to 1000 °C, followed by extensive washing to bleach the compounds (Rodríguez-Reinoso & Sepúlveda-Escribano, 2001). According to Lee and Ahmad Zaini, (2016), the dehydrating agent's aim is to prevent tar formation during pyrolytic breakdown and enhance carbon output. The following Table 2.4 describes several research made on chemical activation for the production of activated carbon.

Table 2.4: Several studies on chemical activation method for synthesis of activated carbon.

Precursor	Chemical activating agent		Description	References
Coffee residue	Phosphoric acid, H ₃ PO ₄	Acid	Coffee residue is washed and dried for 24 hours and activated with H₃PO₄ at different concentration for 18 hours. The characterization is performed using phenol adsorption. With a correction factor $R^2 > 0.92$, the adsorption is compatible with Langmuir and Freundlich models.	(Lamine et al., 2014)
Waste tyre	Hydrogen peroxide, H ₂ O ₂	Weak acid	- The precursor is pyrolyzed at 900°C in electric tubular furnace before being impregnated with H₂O₂ at 200 °C for 2 hours. - Tyre-based activated carbon has shown promise in removing Cd (II) and Pb(II) from wastewater and surface water samples.	(Dimpe et al., 2017)

Table 2.4 Continued.

Low density polyethylene (LDPE), generally known as plastic waste	Acetone, CH_3COCH_3	Ketone	- The plastic waste (used in the form of plastic bags cuts) is heated at 415 °C for 135 minutes (for clear plastic bags) and 120 minutes (for black plastic bags). Activation using ketone and KOH with variation of concentration. - The study resulted the success of the synthesis of AC, with developed pores were visible under SEM observations, and the EDX observations indicates high presence of carbon mass percentage, which is up to 96.62%.	(Yuliusman et al., 2019)
	Potassium hydroxide, KOH	Base		
Dry bamboo	Sulphuric acid, H_2SO_4	Acid	- The dry bamboo is treated with H_2SO_4 or KOH and then underwent the microwave activation at different power (100 and 300 W). The sample is further carbonized at different temperature (400 and 800 °C). - The AC is successfully synthesised, with highest BET surface area is achieved (1162.73 m^2/g) with total pore value 0.7237 cm^3/g, using KOH activation at carbonization temperature of 800 °C and microwave power of 300W.	(Zawawi et al., 2017)
	Potassium hydroxide, KOH	Base		

Chemical activation provides an advantage over the physical approach, in which the creation of activated carbon is a combined process requiring low temperature and therefore

aiding the synthesis of superior porous carbon structure. The following Table 2.5 provides the comparison on chemical activation performed by several different types of chemical activating agent.

This recent study is conducted also to investigate the impact of concentration and temperature factor on the development of better activated carbon from dabai nutshell, and provide comparison based on several parameters and properties, on selected activating agents, which are potassium chloride, KCl, sodium hydroxide, NaOH, and hydrochloric acid, HCl.

Table 2.5: Comparison on chemical activation performed by several different types of chemical activating agent.

Properties/ Parameters	Salts Treatment	Base/Alkaline Treatment	Acidic Treatment
Description	When metal chloride salts are impregnated into biomass, hydrolysis reactions occurred, owing to intermolecular exchange and molecular migration, resulting in structural changes due to weight loss and the release of volatiles (Ukanwa et al., 2019).	For activation of lignocellulosic waste, alkaline may promote glucose breakdown and carbohydrate branching. They react with lignin, ether bonds, and hydroxyl groups when solvated, thus inducing delignification, which is crucial for the manufacture of AC (Ukanwa et al., 2019).	Acid hydrolysis induce delignification of lignocellulosic biomass, by breaking down the cellulose and hemicellulose's polymeric bonds (Ukanwa et al., 2019).
Impregnation step	Performed before carbonization (Hayashi et al., 2000; Marsh & Rodríguez-Reinoso, 2006b; Liu & Huang, 2016)	Two step chemical activation; activation is performed after carbonization (Deliyanni, 2019; Tseng, 2006).	• Performed before carbonization for phosphoric acid (Marsh & Rodríguez-Reinoso, 2006b) • For stronger acid (HCl, HNO₃), activation is performed after carbonization (Allwar et al., 2017; Budi et al., 2016; Grycova et al., 2018; Hanum et al. 2017)

Table 2.5 Continue

Concentration/ Impregnation ratio factor	- Higher microporosity is developed at lower impregnation ratio (<0.5, weight of ZnCl₂/weight of precursor) (Marsh & Rodríguez-Reinoso, 2006b). - Excessive amount may lead to destruction of microporous structure and induce development of mesopores and macropores (Dolas et al., 2011).	Higher impregnation ratios resulted better formation of pores, as well as an increase in surface area and pore volume (Foo & Hameed, 2012; Heidarinejad et al., 2020).	- Higher impregnation ratio induce better microporous and mesoporous structure. (Örkün et al., 2012; Ukanwa et al., 2019) - However further increase on the ratio will develop more mesopores than micropores (Marsh & Rodríguez-Reinoso, 2006b).
Temperature factor	- Higher temperature resulted lower yield (Lee & Ahmad Zaini, 2016). - Higher temperature induce better microporosity (Lee & Ahmad Zaini, 2016).	Higher temperature (ranging from 500 to 800 °C) induce high surface area and microporous structure (Hayashi et al., 2000).	Carbonization temperature more than 450 °C can reduce the N ₂ adsorption volume, which is may due to shrinking of the pores. (Örkün et al., 2012).
Examples of activating agents	ZnCl ₂ , NaCl, MgCl ₂ , FeCl ₃ , K ₂ CO ₃ (Lee & Ahmad Zaini, 2016; Marsh & Rodríguez-Reinoso, 2006b; Mohanty et al., 2006)	NaOH, KOH (Deliyanni, 2019; Hayashi et al., 2000; Heidarinejad et al., 2020)	H ₃ PO ₄ , H ₂ SO ₄ , HNO ₃ , HCl (Marsh & Rodríguez-Reinoso, 2006b; Ukanwa et al., 2019)

2.2.3.4 Mechanochemical Activation

Another technique of precursor activation is mechanochemical activation, which involves ball milling of an impregnated precursor, which have been impregnated with chemical activating agents (Tzvetkov et al., 2016). Ball milling has been shown to be successful in the production of ceramic powders and nanomaterials, the conduct of organic processes without the need of solvents, and the degradation of waste materials. Simple, easy scale-up, the capacity to create metastable phases, mild/short reaction conditions, environmental friendliness, and low cost are all mentioned as advantages of the approach over standard solvent-based procedures (Tzvetkov et al., 2016).

Chen et al. (2012) conducted on a study to synthesis activated carbon, using sugarcane bagasse through mechanochemical activation. The activating agent used is 20% phosphoric acid, where the precursor is impregnated with the acid for 2 hours, and the ratio of acid to the precursor is 2.0. The mechanical part of the activation is performed using high-energy ball milling at 400 rpm, with 5:1 mass ratio of ball to the precursor). The impregnated, milled precursor is then placed under heat treatment in a furnace at 400 °C. The produced activated carbon achieved iodine number, the methylene blue adsorption value and specific surface areas of 889.37 mg/g, 177 mg/g, and 1254.52 m²/g, respectively (Chen et al., 2012).

A study is conducted by Fatriansyah et al. (2018) to synthesis activated carbon from coconut shell charcoal through novel dry mechanochemical activation. The charcoal is activated using KOH, with the mixing ratio is 1:1. The following step is ball-milling using planetary ball mill at 200 rpm, for 4 hours. The resulting adsorbent is tested against hydrogen gas, H₂. The Langmuir and Dubini-Asthakov adsorption isotherm models were used to determine adsorption parameters, and they were found to be in good agreement for Type II adsorption as referred to IUPAC classification. It was also discovered that activated carbon's

adsorption capability was ideal for hydrogen storage, as evidenced by its ability to absorb hydrogen (Fatriansyah et al., 2018).

2.2.4 Utilization of Lignocellulosic Material/Biomass as Precursor for AC

Rodriguez-Reinoso and Silvestre-Albero, (2016) stated that the selection of the precursor is based mainly on the following criteria:

- (i) The possibility of yielding a good-quality activated carbon;
- (ii) Low content in inorganic matter;
- (iii) Availability and cost;
- (iv) Low degradation upon storing; and
- (v) Ease of activation (calcined coke is a difficult material while wood char is easily activated).

Plants' cell walls contain lignocellulosic elements such as cellulose, hemicellulose (carbohydrates), and lignin (aromatic polymer) (Ballesteros et al., 2018). Through covalent and hydrogen interactions, the carbohydrates are firmly linked to the aromatic polymer, resulting in a complex and strong structure. Proteins, lipids, pectin, and ashes are among the other components contained in these materials, although in less amounts.

According to Nor et al. (2013), lignin is the primary component of lignocellulosic materials that may be used in the adsorption process. It is stated that, after cellulose, lignin-based bio-waste is the most abundant renewable carbon resource on Earth, with an estimated annual output of 40-50 million tons. Because lignocellulosic materials have a high carbon content, they are a good starting point for the production of activated carbon (Nor et al., 2013). The following Table 2.6 are a few examples of activated carbon made from lignocellulosic biomass.

Table 2.6: Examples of lignocellulosic material/biomass utilized as adsorbent material.

Lignocellulosic material/biomass	Description	References
Horse chestnut shell	The biomass is activated using potassium carbonate through mechanochemical treatment. Resultant AC have total pore volume of 1.01 cm ³ /g and a maximum BET surface area of 1040 m ² /g. The adsorption capacity of the AC for malachite green oxalate (MGO) is value of 250 mg/g of AC.	(Tzvetkov et al., 2016)
Pistachio shells	The biomass is carbonized, physically activated using steam and further ball-milled to be nano-sized activated carbon. The BET surface area of the adsorbent is 1196 m ² /g.	(Nazem et al., 2020)
Banana stem	Banana stem is impregnated with phosphoric acid and pyrolyzed at 400 °C. The resulting AC has the surface area of 837.453 m ² /g.	(Misran et al., 2022)
Grass	Grass waste is activated using phosphoric acid and pyrolyzed at 700 °C for 90 minutes. The synthesized AC have methylene blue (MB) number of 241 mg/g.	(Jawad et al., 2020)
Dragon fruit peel	Dragon fruit peel is ground into powder and mixed with KOH. The mixture is thermally treated in tubular furnace for 60 minutes at 700 °C. The BET surface area of the resulting AC is 756.3 m ² /g and the maximum MB adsorption of the AC is 195.2 mg/g.	(Jawad et al., 2021)

2.2.5 Forms of Activated Carbon

The size and shape of the carbon particles were used to classify the different types of activated carbon (Carabineiro et al., 2012). Figure 2.8 depicts several types of activated carbon. Powdered activated carbon, with a carbon particle size of less than 0.1 mm, is

commonly utilized in liquid applications. Granular activated carbon particles with diameters ranging from 0.5 to 5 mm have uneven morphologies. Activated carbon pellets and extrudates have a width of 1-5 mm and a length of 5-10 mm. For liquid and gas phase applications, both powdered and non-powdered activated carbon can be utilized.

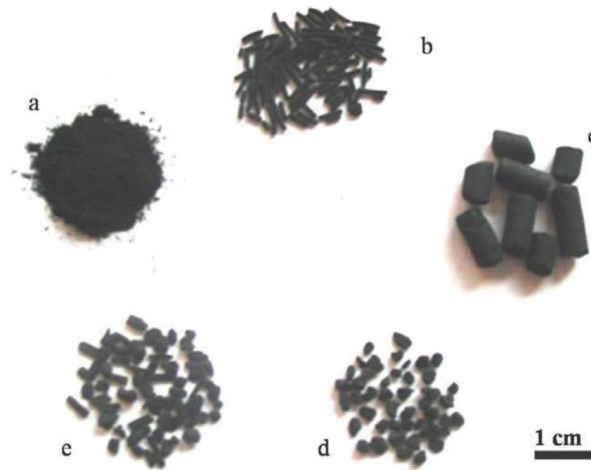


Figure 2.8: (a) Powdered AC, (b) pellets of AC, (c) extruded AC, while (d) and (e) is granular AC (Carabineiro et al., 2012).

2.2.6 AC in Wastewater Treatment

The use of activated carbon for wastewater treatment has been studied in a number of ways. The AC is potential to adsorb a variety of wastewater pollutants because to its non-polar adsorbent characteristics, large specific surface area, and many micropores. In terms of wastewater treatment, the researchers proposed increasing the microbiological characteristics of activated carbon and using microwave radiation into the production of the AC (Jiang et al. 2019). Table 2.7 shows a list of organics that can be adsorbed onto activated carbon and those that cannot (Çeçen, 2011). Table 2.8 shows the Malaysian standard for powdered activated carbon for use of potable water supply, as described by Department of Standards Malaysia, (2005). The standard is prepared for the manufactures for the terms of production, packaging, transporting, and testing requirement. Hanum et al. (2017) described

the Indonesian standard for activated carbon, as shown in Table 2.9 that should be achieved to produce suitable activated carbon for the purpose of adsorption in wastewater treatment.

Table 2.7: Organics susceptible and not susceptible for adsorption onto AC (Çeçen, 2011).

Organics susceptible for adsorption onto AC	Organics not susceptible for adsorption onto AC
Pesticides, herbicides, flavoring solvents, poly-nuclear flavorings, chlorinated aromas, phenolics, chlorinated solvents, high-molecular weight (HMW) aliphatics and flavoring acids, hydrocarbonate amines and fine aromatical amines (aromatic amines), fuelles, esters, ethers, alcoholics.	Compounds with low molecular weight (LMW) and high polarity, such as LMW amines, nitrosamines, glycols, and certain ethers.

Table 2.8: Malaysian standard for powdered activated carbon for the use of potable water supply (Department of Standards Malaysia, 2005)

Parameter	Requirement	
A Specific requirement	Limit	
Iodine number, mg/g product	900 min.	
B Impurity		
Water soluble matter, % w/w	3.0 max.	
Moisture, % w/w	5 max.	
Ash, % w/w	10 max.	
Zinc, % w/w	0.002 max	
C Physical requirement		
Pass through 150 µm sieve, % w/w	95 min.	
D Water-extractable toxic substance	Limit	
	mg/kg of product, max	mg/g of product
Arsenic, As	50	0.05
Cadmium, Cd	5	0.005

Table 2.8 Continued

Nickel, Ni	50	0.05
Lead, Pb	50	0.05
Chromium, Cr	50	0.05
Mercury, Hg	1	0.001
Selenium, Se	10	0.01
Antimony, Sb	10	0.01
Cyanide, CN	50	0.05
Polycyclic aromatic hydrocarbons	0.2	0.0002

Table 2.9: Indonesian standard for activated carbon (Hanum et al., 2017).

Analysis	Quality Requirements	
	Particle	Powder
Volatile matter 950 °C, %	Maximum: 15	Maximum: 25
Moisture content, %	Max. 4.5	Maximum: 15
Ash content, %	Maximum: 2.5	Maximum: 10
Parts that are not carbonized	0	0
Iodine Number, mg/g	Minimum: 750	Minimum: 750
Pure activated carbon, %	Minimum: 80	Minimum: 65
Benzene adsorption capacity, %	Minimum: 25	-
Methylene blue Number, mg/g	Minimum: 60	Minimum: 120
Bulk specific gravity, g/ml	0.45 – 0.55	0.3 – 0.35
Escaped mesh 325, %	-	Minimum: 90
Distance, %	90	-
Violence, %	80	-

2.2.6.1 Utilization Of GAC In Wastewater Treatment

Granular AC (GAC) is now utilized in the tertiary treatment of household and industrial wastewater as an adsorptive material (Rodríguez et al., 2015). The material is utilized for the adsorption of organic molecules associated with waste discharged from

biological treatment. GAC filters were employed in Europe to dechlorinate water in the 1930s and 1940s, but the method did not utilize adsorption since the removal of chlorine is solely dependent on a catalytic reaction happening on the surface of AC. However, due to the development of further chlorine compounds on the filters, these treatments were halted (Çeçen, 2011).

Altmann et al. (2016) performed a pilot study on the use of GAC adsorption and deep-bed filtration with coagulation as a single advanced treatment step for the simultaneous removal of organic micropollutants (OMP) and phosphorus from secondary effluent. This study is conducted at a domestic wastewater treatment plant, located at Muenchehofe, which is a municipality located in Germany, for a duration of 10 months. Two identical filter columns, each with a diameter of 0.15 m and a height of 4 m, make up the pilot plant. The first filter is a dual-media downflow filter, consisting of GAC and quartz sand, whereas the second filter employs just GAC as a filter material and the influent is supplied upstream. The pilot study concluded that both filters are able to reduce the concentration of total suspended solid (TSS) and total phosphorus (TP) to 1 mg/L and 0.1 mg/L respectively, which are the goals of wastewater treatment (Altmann et al., 2016).

Dash et al. (2009) investigated the efficacy of activated carbons in batch reactors under laboratory settings for the removal of zinc and iron metal cyanide complexes as well as sodium cyanide from effluents. Sodium cyanide (NaCN), zinc cyanide (ZnCN) and iron cyanide (Fe (CN) solutions were prepared to test the adsorption capability of commercial GAC. The study concluded GAC managed to perform removal of ZnCN and FeCN up to more than 80% and 65% for removal of NaCN (Dash et al., 2009).

2.2.6.2 Utilization of PAC in Wastewater Treatment

Powdered AC (PAC) is widely used as the final step in several wastewater treatment procedures, particularly after biological treatment, when PAC adsorption removes refractory organics and, to a lesser degree, inorganic contaminants (Çeçen, 2011). In a study conducted by Kristiana et al. (2011), PAC is added into the enhanced coagulation treatment in a water treatment plant in Australia in order to remove natural organic matter, which is a precursor for disinfection by-products. The addition of PAC resulted an improvement of 70% on the removal of natural organic matter, thus leading to reduction of formation of disinfection by-products, up to 80-95% (Kristiana et al., 2011).

Gai and Kim (2008) performed research on improvement of submerged flat sheet membrane for water treatment using PAC. The membrane system used in this study is a combination of PAC and microfiltration (PAC-MF), and tested against synthetic water, which is a mixture of raw water, polypeptone, yeast extract, glucose, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$. The research concluded that PAC increased continuous filtering duration by preventing membrane fouling caused mostly by organic compounds, served as a buffer against excessive organic loading due to its adsorbing capacity, and offered an excellent home for bacteria that may contribute to organic material biodegradation (Gai & Kim, 2008).

In an earlier study, Kim et al. (2007) carried out bench-scale tests for a microfiltration system with powdered activated carbon, utilizing river water as a feed water at a water treatment facility. The microfiltration system consist of a filtration tank, with a membrane module and the PAC is set at the bottom of the tank. The raw water used for this study was obtained from Tama River, which is in Tokyo, Japan. In terms of treatment effectiveness, larger PAC doses resulted in higher effluent quality, where the organic elimination was increased by more than 80% when a high concentration of PAC (40 g/L) was used. Similar

outcomes are witnessed as higher dose of PAC (40 g/L) reduced the turbidity of the influent up to 98%. As a result, it is predicted that microfiltration systems combined with a high PAC dose can be used to treat severely polluted raw fluids for advanced water treatment (Kim et al., 2007).

2.2.7 Earlier Research on Dabai Nutshell as An Adsorbent

As mentioned in sub-section 2.1.2.3, the possibility of Dabai nutshell as a precursor for the production of AC has been investigated by Vicinisvarri et al. (2014). The nutshell is separated from its nut by crashing it using hammer, follows with cleaning it, using distilled water repeatedly. After being dried under sunlight until fully dried, the clean nutshell is grinded and sieved to get the size range of 2-3 mm. Phosphoric acid (H_3PO_4) was used to chemically activate the lignocellulosic material at varied concentrations of 20, 40, 60, and 80% by weight (the resulting AC was noted as AC-20, AC-40, AC-60, and AC-80). The mixture is dried overnight in an oven at 110 °C. The treated material of each concentration area carbonized for 2 hours at 700 °C in a horizontal tube furnace with a nitrogen gas flow rate of 200 cm³/min.

For FTIR analysis, the peak intensity of the AC spectra showed a substantial reduction, which might be attributable to a large loss of functional groups during the carbonization process. The majority of ACs had a faint band on their spectra, approximately 1000-1200 cm⁻¹, indicating C-O stretching. The AC-60 exhibited a large BET surface of 1024 m²/g and a Langmuir surface area of 1343 m²/g, according to BET surface analysis. This AC also produced a total pore volume of 0.48 cm³/g. The Langmuir isotherm model best represented equilibrium data, with the highest monolayer adsorption of the dye methylene blue by AC-60 was 333.33 mg/g in the adsorption test (Vicinisvarri et al., 2014).

James et al. (2022) conducted a study to synthesis nano carbon mixture using dabai nutshell. The adsorbent is made by activating the dabai nutshell using potassium hydroxide (KOH) and ball-milled for 30 hours until it reached 50 to 120 nm. The activated carbon is further mixed it with titanium dioxide and montmorillonite (MMT) clay. The resulting nano carbon mixture's surface has significant adsorbent characteristics because to the presence of functional groups such hydroxyl, phenolic, amide, and carbonyl. The obtained FTIR spectra showed that the activated carbon sample included carboxylic chemicals, which enhanced its adsorption capabilities. BET surface area for KOH activated carbon from the same study and the nano-carbon mixture are $5.09 \text{ m}^2/\text{g}$ and $25.779 \text{ m}^2/\text{g}$ (James et al., 2022).

2.3 Water Pollutants and Available Treatment

Schwarzenbach et al. (2010) stated that more than a third of the worlds' population are facing the disaster of lacking safe, clean drinking water, due to lack of proper sanitation and treatment. Afroz et al. (2014) mentioned that when little or large volumes of materials (pollutants) are introduced into a body of water, it causes pollution. Further present threats appeared nowadays, which causing pollution towards the clean water consumption are the presence of pathogens and chemical toxic materials. Regarding the chemical water pollutants, Schwarzenbach et al. (2010) categorized it into two; small quantity of macropollutants, which present at the level of milligram per litre of water, and nutrients, which includes nitrogen, phosphoric-containing material and natural organic constituents (Schwarzenbach et al., 2010).

2.3.1 Causes of Water Pollution

According to Afroz and Rahman (2017), there are two types of water contamination sources: point sources and non-point sources. Pipelines and pipes are examples of point

sources with discharges that enter a body of water at a specific spot. Industries, sewage treatment plants, and animal farms are all examples of point sources. According to Afroz et al. (2014), In 2008 at Malaysia, sewage treatment plants (54.1%), industrial businesses (387.7%), animal farms (4.48%), and agro-based enterprises (2.78 %) were among the point sources for water pollution. Non-point sources are produced from diffuse sources, such as agricultural operations and surface runoff, which have no instances of particular release locations (Afroz & Rahman, 2017).

Afroz et al. (2014) also stated that the quality of run-off within a watershed is usually altered due to urbanization, which has an impact on the water quality of receiving waterways. Rainfall washes pollutants collected on land surfaces into storm water systems in metropolitan areas. Wastewater from residential, commercial, and industrial sectors has a terrible odour, especially when waste is present, degrades storm water quality, and pollutes the existing river system (Afroz et al., 2014). The authors listed several causes of the water pollution, as shown in Figure 2.9. Meanwhile, Aulakh et al. (2009) mentioned that the most major anthropogenic cause responsible for ground-water contamination in Punjab and the rest of India is urban and industrial wastewater.

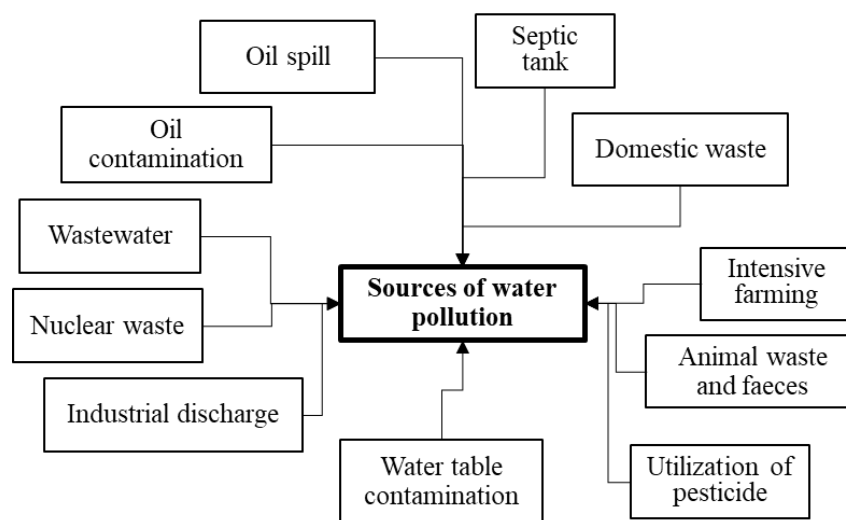


Figure 2.9: Several sources of water pollution (Afroz et al., 2014)

2.3.2 Dye and Heavy Metal Ions as Water Pollutants and Contaminants

Ali et al. (2022), Almroth et al. (2021) and Al-Tohamy et al. (2022) describes that textile companies produce a lot of highly coloured wastewater with a variety of persistent contaminants in it. This wastewater is a major environmental polluter that also has an impact on human health. Al-Tohamy et al. (2022) stated that some textile manufacturers release their wastewater into bodies of water without treating it, which poses major ecotoxicological risks as well as toxic impacts on living things. Other textile factories treat their wastewater to break down the free azo dyes released into the environment. Textile colours are released with wastewater as effluent because they don't adhere strongly to fabric. Figure 2.10 shows various types of dyes and its applications (Al-Tohamy et al., 2022).

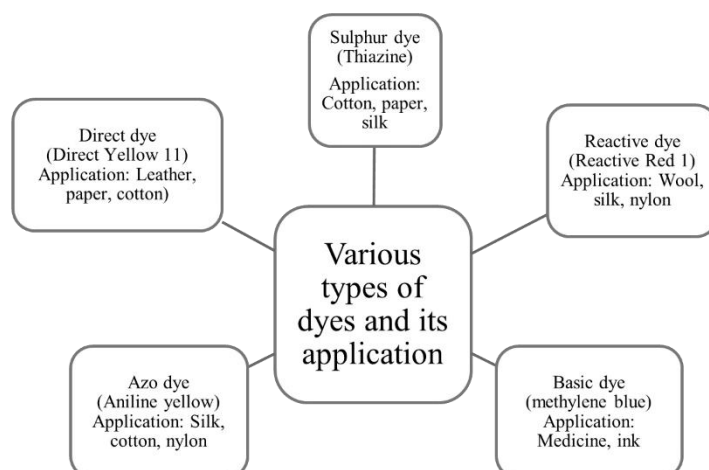


Figure 2.10: Several types of dyes and its applications (Al-Tohamy et al., 2022)

Focusing on dye methylene blue, Al-Tohamy et al. (2022) stated that the basic dye generates potentially cancer-causing aromatic amines like benzidine and methylene and is a commonly used cationic dye in a range of textile industries. According to Haq et al. (2018), The primary metabolite of methylene blue, azure B, is a cationic dye that may intercalate with DNA and duplex RNA's helical structures. Ali et al. (2022) stated that following dye

exposure, methylene blue suppresses the synthesis of chlorophyll, which lowers the growth and photosynthetic rate of the green pigments.

Adriano, (2001) stated that a rise in the flow of metallic compounds into the aquatic and terrestrial environments has been an inevitable consequence of the massive expansion in the use of heavy metal ions during the past few decades. Gautam et al. (2016) describes that Geological weathering and erosion industrial processing of ores and metals, use of metals and their compounds, leaching of metals from garbage and solid waste dumps, landfill waste, manure from cattle and poultry, animal and human discharge, urban runoff, and reuse of drainage water and sewage effluent are the main causes of heavy metal contamination in the environment. Briffa et al. (2020) provided a list of various heavy metals with densities more than 5 g/cm^3 that are increasingly common in our daily lives, as shown in Figure 2.11. Heavy metals can enter the body through four routes: ingestion of unsafe food, inhalation from the environment, drinking contaminated water, and skin contact in farm, pharmaceutical, production, residential, and industrial regions. Metals are not biodegradable and are unable to be broken down. Metal ions can be detoxified by concealing the active element within a protein or depositing them in intracellular granules in an insoluble form for excretion or long-term storage. (Briffa et al., 2020).

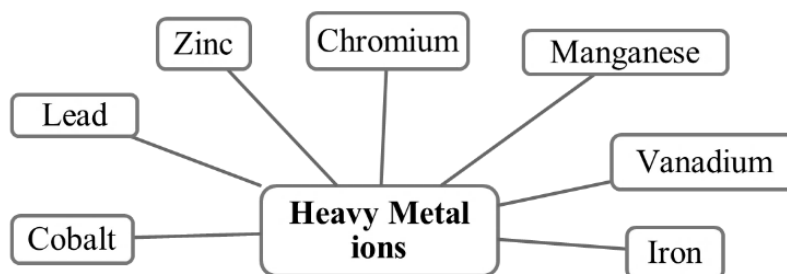


Figure 2.11: Several heavy metal ions (Briffa et al., 2020).

2.3.3 Available Alternatives and Treatments for Water Pollution

Reza et al. (2020) listed several water treatment alternatives as follows: filtration, aerobic and anaerobic digestion, oxidation, magnetic separation, reverse osmosis, adsorption, and flocculation. Each method are briefly described in Table 2.10.

Table 2.10: Several methods towards water treatments

Methods	Brief description	Reference
Filtration	Filtration is the process of separating non-settling materials from water and wastewater by passing them through a porous media.	(Farzaneh & Mokshapathy, 2018)
Advanced oxidation process (AOP)	The oxidation mechanisms that result in the production of hydroxyl radicals ($\text{OH}^\cdot$) or sulphate radicals ($\text{SO}_4^\cdot$) in sufficient quantities to purify water.	(Deng & Zhao, 2015)
Reverse osmosis (RO)	RO is a membrane-based method used to either clean water or extract soluble solids (known as dewatering) such as ions from a given solution. It is a diffusion-controlled method in which permeant mass transfer occurs via a dense membrane via a regulated solution-diffusion mechanism.	(Trishitman et al., 2019)
Adsorption	Adsorption refers to the sticking of chemicals from gases or liquids to the interface of two phases, primarily solids. Adsorption is utilised in water and used in purification to remove dissolved pollutants. The most popular method for adsorbing organic compounds is to use activated carbon.	(Pillai, 2020)
Coagulation and Flocculation	Coagulation and flocculation occur in stages, allowing particle collision and floc development. The coagulation/flocculation process's primary goal is to remove turbidity from water.	(Prakash et al., 2014)

According to Q. Han et al. (2020) in terms of treating dye wastewater, numerous physical, chemical, and biological techniques have been employed. The most popular are the physical techniques, which include physical adsorption, the extraction procedure, and filtration via membranes (Q. Han et al., 2020). Cherifi et al. (2013) stated that due to AC having high surface area per unit mass and a high adsorption capacity for colours, numerous studies have demonstrated that it is an efficient adsorbent for organic molecules, particularly dye methylene blue. The adsorbent dosage, granularity, pH, temperature, and initial methylene blue concentration all had an impact on the AC's adsorption capability on reducing concentration of dye methylene blue (Cherifi et al., 2013).

Bolisetty et al. (2019) stated that the adsorption has emerged as a popular, practical, and affordable heavy metal removal technique. The advantages of using adsorption for removal of heavy metal ions are high removal performance, reversible characteristic that permits adsorbent renewal, and adaptability in terms of both design and use (Bolisetty et al., 2019). According to Aziz et al. (2023), with many benefits, biochar-based adsorption has been shown to be an efficient eco-remediation technique for lowering heavy metal contamination in soil and water. Due to its large specific surface area and pore volume, numerous functional groups, versatility in raw material synthesis, and environmental friendliness, chemically enhanced biochar has been extensively researched and is regarded as an effective adsorbent. Many factors, including the amount of biochar used, the temperature and pH of the water, the kind of heavy metals, the properties of the biochar, the initial concentration, and the presence of other cations in the water, affect how well heavy metals are adsorbed by biochar (Aziz et al., 2023).

2.4 Conclusion

According to previous studies, Dabai nutshell has the potential to be a precursor of activated carbon. More study is needed to investigate the possibilities of increasing the activated carbon's adsorptive capacity by using a more efficient activation technique, as well as to identify novel chemical activating agents and other synthesis factors on wastewater. The findings might strengthen the lignocellulosic materials' relevance and appropriateness for commercially successful wastewater treatment.

CHAPTER 3

MATERIALS AND METHODS

Overview

This chapter provides the methodology for the synthesis of activated carbon (AC) from dabai nutshell. The synthesis of AC includes the pyrolysis of the precursor and chemical activation of precursor with different impregnation concentration. This chapter also describes the optimization of carbonization parameter (temperature) and the impregnation concentration, characterization, adsorption study and application of the AC in wastewater treatment.

3.1 Research Variables

The research variables for this study are as mentioned in Table 3.1. The variables are based on the aim and objectives of this study.

Table 3.1: Research variables for the synthesis of AC from dabai nutshell.

Process/ Condition	Manipulated variables	Responding variables	Constant variables
Carbonization	• Temperature range (400-800 °C) • Atmosphere condition	• Char yield (percentage) • Ash content • Elemental mass and atomic percentage • BET surface area • Total pore volume • FTIR analysis	• Mass of precursor • Duration of carbonization

Table 3.1. Continued

Chemical activation	• Type of chemical activating agents (Salt, base, and acid) • Impregnation concentration (in %-mass to volume)	• Ash content • Elemental mass percentage • BET surface area. • Total pore volume • FTIR analysis	• Mass of precursor • Activation temperature (700 °C) • Duration of chemical activation
Adsorption study	• Type of AC (Salt, base, and acid); with optimized impregnation concentration	• Adsorption of dye methylene blue • Adsorption of heavy metal ions	• Dose of AC for each solution • Duration of adsorption

3.1.1 Materials

The materials for this study are listed as follows.

Table 3.2 Materials and its specifications

Materials	Specifications
Synthesis of Biochar and AC	
Dabai fruit (20 kg)	-
Chemical activating agent	- Potassium chloride, KCl powder; 99.9%, manufactured by Laboratoriumdiscounter - Hydrochloric acid, HCl, aqueous, 36.5-38%, manufactured by JT Baker - Sodium hydroxide, NaOH, pellets, $\geq 98\%$
Distilled water	-
Deionized water	-

Table 3.2 Continued

Adsorption Study		
Dye	methylene blue	Methylene blue hydrate (powder), $\geq 97\%$, manufactured by Sigma-Aldrich
Heavy metal ion solutions		Zinc, lead and chromium, aqueous, 1000 mg/L, manufactured by Merck.

3.1.2 Apparatus

The apparatus used for this study are listed as follows.

Table 3.3 Apparatus and its specifications

Apparatus	Specification
General Use	
Beakers	100 ml, 250 ml, 1000 ml
Weighing balance	-
Measuring cylinder	50 ml and 100 ml
Incubator oven	-
Spatula; small and large	-
Synthesis of biochar and AC	
Crucibles with lid	-
Table vice	-
Sieve; 1.00 mm	-
Heavy duty mixer grinder	-
Hot plate with stirrer function	-
Furnaces;	- High temperature muffle furnace, KSL-1700X-A4, Max. 9.5KW, 7000 KW average at 5°C/min - LT Furnace TL 150-1200
Reusable clay	-

Table 3.3 Continued

Characterization	
Scanning electron microscope (SEM) with electron dispersive X-ray (EDX) function.	Hitachi TM4000 Plus Tabletop Microscope
Fourier transform infrared (FTIR) analysis machine.	Shimadzu IRAffinity-1 Fourier Transform Infrared Spectrophotometer
Brunauer-Emmett-Teller (BET) surface analysis machine	Quantachrome Autosorb iQ-MP, Automated Gas Sorption Analyzer
Adsorption Study	
Ultraviolet-visible (UV-Vis) spectrophotometry	Shimadzu UV-1800 UV Spectrophotometer
Atomic absorption spectroscopy (AAS)	Shimadzu AA-7000 Atomic Absorption Spectrophotometer

3.2 Synthesis of Activated Carbon

The experimental procedure for the synthesis of activated carbon from dabai nutshell is described as in Figure 3.1.

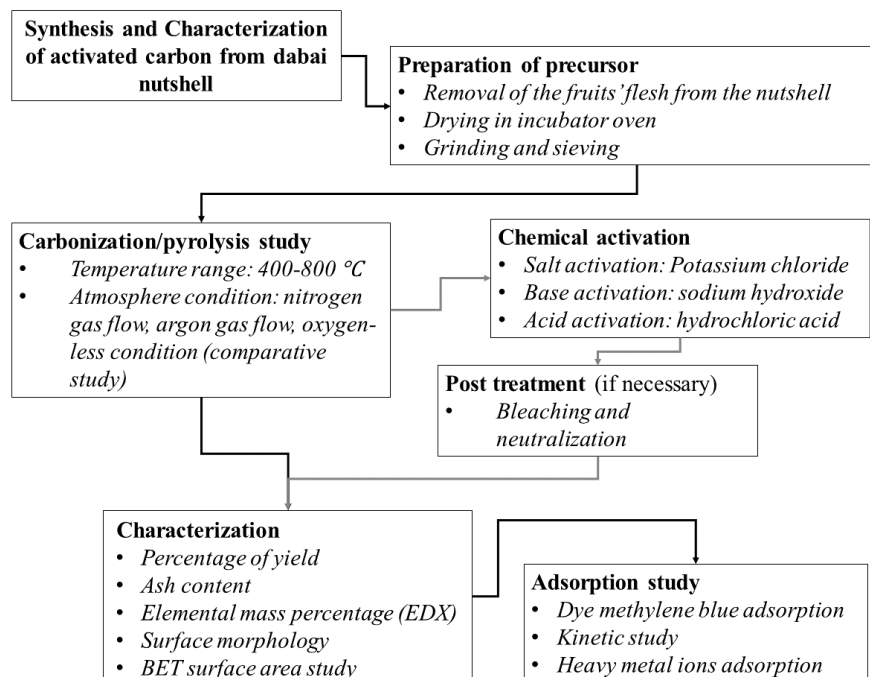


Figure 3.1: Experimental procedure for the synthesis of activated carbon from dabai nutshell.

3.2.1 Preparation of Precursor

Dabai fruits is soaked in warm water (approximately 50 °C) to soften the hard flesh for about 20 minutes, for better removal of the flesh (Ding & Tee, 2011). Next, the nutshells is dried using a drying oven, with average temperature of 45 °C, for 4 hours. Figure 3.2 shows the dabai nutshell, with its flesh removed. As the drying is completed, the nutshells are crushed using table vice to separate the nuts from its shell. Heavy-duty mixer grinder is used to reduce the size of the shells, and the resulting fined shells is sieved to the size of 1 mm.



Figure 3.2: Dabai nutshell (uncracked)



Figure 3.3: Reducing the size of dabai nutshell using heavy duty grinder.

3.2.2 Study on Carbonization Parameter

The carbonization parameter study includes the carbonization temperature and the carbonization atmosphere. Carbonization temperature is considered to be the most important process parameters for the synthesis of AC, where this parameter affects the yield percentage, amount of volatile matter and the surface properties of the adsorbent, which is crucial for the adsorption process (Açıkyıldız et al., 2014). The study on carbonization atmosphere is conducted to determine the effect of using nitrogen and argon gas flow during

carbonization, and the potential of not using any inert gas during the process, on the properties of resulting dabai char.

LT furnace is used for the study of effect of carbonization temperature, and an addition of high temperature muffle furnace for the study of the atmosphere condition during the carbonization process. For the LT furnace, it is a different approach from common practice for carbonization where inert gas flow is provided into the furnace to avoid combustion and more production of ash. For this particular equipment, the precursor is placed in a closed crucible, covered in aluminium wrap, and reusable clay is placed on and around the lid to avoid and reduce the presence of oxygen/air.

3.3.2.1 Carbonization Temperature

Study on the impact of carbonization temperature of dabai nutshell to synthesis activated carbon is performed by utilizing LT furnace (as shown in Figure 3.3). Figure 3.4 depicted the machine's temperature setting. The heating process was held at the furnace's minimum working temperature (200 °C) for 15 minutes before being escalated to the specified maximum temperatures (400, 500, 600, 700, and 800 °C) according to safety precautions. The carbonization was carried out for 2 hours at maximum temperatures. After that, a desiccator was used to chill the bio-carbon to room temperature.



Figure 3.4: LT Furnace (conventional furnace)

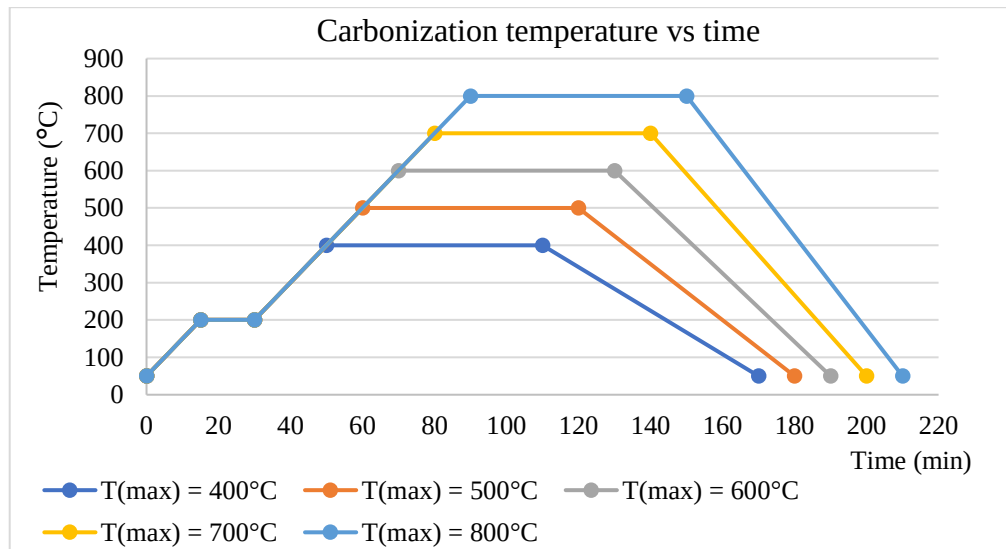


Figure 3.5: Carbonization temperature graph vs time

3.2.2.2 Atmosphere Condition

The study on the impact of atmosphere condition on the carbonization is performed by varying the atmosphere in a high temperature muffle furnace as shown in Figure 3.5; inert gas flow ((a) argon and (b) nitrogen gas) and (c) limiting the presence of oxygen in the LT furnace. The temperature is fixed at 700 °C.



Figure 3.6: High temperature muffle furnace, KSL-1700X

3.2.3 Chemical Activation of Dabai Biochar

Chemical activation is performed with different chemical types to compare the AC produced based on the variation of the chemical activating agents and its concentration, as shown in Figure 3.6. The carbonization (for KCl) and activation temperature (HCl and NaOH) are fixed at optimized temperature of carbonization, using LT furnace due to economic and availability of the equipment in the current facility. The impregnation concentration is set within the range of 1% to 13% (mass of chemical activating agent/100 mL), with 3 replicates for each concentration. Selection of the chemicals for each type are as justified as follows. 0.05 g of all impregnated samples are then kept for observation (EDX observation), and the remaining are used for carbonization/activation. The concentration of the chemical activating agent used is fixed to mass of chemical activating agent (g): volume (ml), where 1 g/100 ml is 1% concentration.

- KCl for salt activation, for salt activation as the salt is less harmful towards aquatic life and environment (Lee & Ahmad Zaini, 2016)
- NaOH for alkaline activation, because sodium hydroxide is less expensive, more ecologically friendly, and less hazardous than potassium hydroxide (Heidarinejad et al., 2020).
- Selection of HCl for acidic activation is to investigate more on the dehydrating effect of the acid on the char.



Figure 3.7: Chemical activation of biochar using chemical activating agents, performed in fume hood.

2.3.1.1 KCl Activation

The salt-based activation of the precursor is performed using KCl in powder form. The impregnation method is modified from research conducted by Mohanty et al. (2006) and Şahin et al. (2015), with the impregnation ratio 1:10 (precursor mass: volume of solution) (Rufford et al., 2010), but performing the impregnation after carbonization of the

dabai nutshell as performed by Pan et al. (2019). Determined amounts of KCl (in g) were added to a 100 ml distilled water to obtain KCl aqueous solutions of certain concentrations (1%, 4%, 7%, 10% and 13%). The prepared KCl solutions are mixed with 10g of dabai nutshell, using magnetic stirrer and hot plate to raise the temperature. The mixing process is done for 1 hour at 50 °C. Then, the mixture is dried using incubator oven at 60°C for 24 hours. The dried material is then placed in the furnace for 2 hours at 700 °C.

3.2.3.2 NaOH Activation

The alkaline-based activation is executed based on a methodology modified from a study conducted by Saad et al. (2020), with the impregnation ratio is 1:10 (mass of carbonized dabai nutshell: volume of NaOH solution with the determined concentrations). The mixture is left for 24 hours and dried at 110 °C until it is fully dried. The dried material is then activated/carbonized using LT furnace for 2 hours at 700 °C. As the process is done, the activated carbon is cooled to room temperature, and neutralized using HCl solution and deionized water until pH level is the range of 6-7.

3.2.3.3 HCl Activation

The acid-based activation process for dabai nutshell is performed using a method modified from research conducted by Grycova et al. (2018) and Sirimuangjinda et al. (2013). The precursor char is mixed with hydrochloric acid solutions at different concentrations (1%, 4%, 7%, 10% and 13%) for 3 hours and dried at 110 °C until fully dried. The mixture is further carbonized using LT furnace at 700 °C for 2 hours under less/no oxygen condition, with the ratio of the mass of the char (in gram) to the volume of HCl solution (in ml) is 1:10. To neutralize the resulting adsorbent, 0.5 M NaOH solution and distilled water is used to get the pH of the activated carbon to 6.5-7. The dried material is then activated/carbonized using

LT furnace for 2 hours at 700 °C. As the process is done, the activated carbon is cooled to room temperature and stored in a desiccator.

3.3 Characterization of Biochar and Activated Carbon

The synthesised biochar and activated carbon are analysed to determine its characteristics. This analysis helps to understand the properties of the char and its suitability to be used as an adsorbent for wastewater treatment. The characterisation of the adsorbents is performed on the percentage of yield and ash content, surface morphology (SEM) and properties (BET surface area analysis), elemental analysis (EDX), identifying functional groups (FTIR) and adsorption performance (nitrogen gas adsorption-desorption). The SEM and EDX analysis on the biochar produced from different pyrolysis parameter provides the comparison on the mass and atomic percentage of carbon. The SEM and adsorption capability evaluation on the activated carbon provides the comparison between AC synthesised with different activating agents, on pores development and adsorption performance.

3.3.1 Percentage Of Yield of Dabai Biochar and Activated Carbon

The percentage of yield of the biochar for each temperature setting in carbonization step is determined by measuring the final mass of the char after the heat treatment. The obtained value is used for the following equation.

$$\% Yield = \frac{m_f}{m_i} \times 100 \quad \text{Equation 3.1}$$

Where m_f is final mass of char and m_i is the initial mass of the precursor, will all of the mass is in g.

3.3.2 Ash Content of Dabai Biochar and Activated Carbon

To determine the ash content of the biochar or activated carbon, 2 g of char or activated carbon is combusted at a temperature of 650 °C for 4 hours (ASTM International, 2004). The ash content percentage is determined using the following equation. Figure 3.7 shows the ash content determination step.

$$\text{Ash content (\%)} = \frac{\text{Mass of ash (g)}}{\text{Mass of AC (g)}} \times 100 \quad \text{Equation 3.2}$$



Figure 3.7: Ash content determination.

3.3.3 Scanning Electron Microscopy-Energy Dispersive X-Ray Spectrometer (SEM-EDX) of Dabai Biochar and Activated Carbon

SEM is used to obtain surface images of the raw dabai nutshell, char and adsorbent derived from it. For element analysis, including carbon and oxygen mass percentages as well as surface morphology, SEM-EDS equipment was employed. A Quantax75TM Series Energy Dispersive X-Ray Spectrometer was used in combination with the Hitachi TM4000Plus desktop microscope (Hitachi Ltd., Tokyo, Japan).

3.3.4 Fourier Transform Infrared (FTIR) Spectra of Dabai Biochar and Activated Carbon

To analyse the presence of functional groups in the matter, the char and activated carbon are also subjected to Fourier transform infrared (FTIR) spectra investigation. For the Fourier transform infrared spectroscopy (FTIR) examination, a Fourier-transform infrared spectrophotometer (IRAffinity-1, Shimadzu Corporation, Kyoto, Japan) was used. The spectra of each sample were scanned throughout a wavenumber range of 4000 to 400 cm^{-1} . The samples' infrared spectral transmittance and absorption were used to create a unique chemical fingerprint spectrum using Fourier transform infrared spectroscopy. The test was performed multiple times by the IR Solution program, and the software picked the best representative results.

3.3.5 Brunauer, Emmett, and Teller (BET) Surface Analysis Dabai Biochar and Activated Carbon

The nitrogen adsorption isotherm was investigated with a Brunauer, Emmett, and Teller (BET) surface analyser (Quantachrome Autosorb iQ-MP, Automated Gas Sorption Analyzer (Boynton Beach, Florida, USA)). Using the same equipment, the surface analysis is done to get the Brunauer, Emmett, and Teller surface area (S_{BET}), total pore volume (V_{total}), and average pore size.

3.4 Optimization on Carbonization

Using Design Expert software, the optimization of carbonization is performed on the temperature setting by studying the effect of the temperature setting on the percentage of yield and ash content of the char obtained. Response Surface method is used to provide the analysis of variance (ANOVA) on the responses (percentage of yield, amount of ash content,

BET surface area and total pore volume) based on the single factor (carbonization temperature) as shown in Figure 3.8. The ANOVA is executed based on the most suitable process order by referring it to the actual data and provides the actual equation that can be used to predict the resulting responses based on the single factor.

Std	Run	Factor 1 A:Temperature C	Response 1 Percentage of yi... %	Response 2 Ash content %	Response 3 BET surface area m ² /g	Response 4 Total pore volu... cc/g
2	1	400				
15	2	400				
20	3	400				
3	4	500				
7	5	500				
4	6	500				
10	7	600				
13	8	600				
5	9	600				
11	10	700				
9	11	700				
6	12	700				
18	13	800				
12	14	800				
8	15	800				

Figure 3.8: Design Matrix of Optimization of Carbonization Temperature.

3.5 Adsorption Study and Removal of Water Pollutants

Adsorption study is performed to study the adsorptive capability of the synthesised adsorbent. Methylene blue dye is one of the common pollutant-type being used to investigate the said capability other than iodine. Heavy metal ions selected for this study are lead, zinc and chromium ions. The concentration of the methylene blue, lead, zinc, and chromium ions for adsorption uptake study is set at 30 ppm, where single concentration is used solely for the purpose of the determining the effect of using different chemical activating agents, with different impregnation concentrations on the adsorption uptake of the water pollutants.

3.5.1 Methylene Blue (MB) Adsorption

The methylene blue adsorption study is performed by using similar method in the study conducted by (Vicinisvarri et al., 2014) on the same precursor material. In 250 mL Erlenmeyer flasks, a constant quantity of AC (0.2 g) was treated with 100 mL of MB aqueous solution at 30 ppm. For 24 hours, the flasks were stirred at room temperature with the speed of 120 rpm. A UV-VIS spectrophotometer set to 664 nm was used to detect the remaining colour in the supernatant solution. The average values were utilized in data analysis after all of the trials were duplicated. Equation 3 is used to determine the quantity of MB adsorbed per gram of AC at the determined time, which is represented as q_t (mg/g).

$$q_t = \frac{(C_0 - C_t)V}{W} \quad \text{Equation 3.3}$$

C_0 (mg/L) is the initial concentration of MB solution, C_t (mg/L) is MB concentration at the determined time (t) and W (g) is the mass of activated carbon used for the experiment.

For kinetic study of the adsorption of MB solution, MB solution with concentration of 10 ppm is mixed and stirred with 0.2 g of AC replicates for 2 hours, with assumption that the equilibrium is achieved at 2 hours, where according to Ullah et al. (2017), 2 hours is optimum contact time for methylene blue dye. The concentration of the MB solution is taken every 10 minutes and 20 minutes using UV-VIS spectrophotometer, to evaluate the adsorption using the dabai AC replicates along time. The resulting concentrations were then utilized to see which of the kinetic model can describe the nature of the adsorption; either its pseudo-first-order, pseudo-second-order, intra-particle diffusions model or Elovich kinetic model. The kinetic model studied are as described in section 2.3.1.2, as shown in Table 3.2.

Table 3.4: Kinetic model of adsorption studied

Kinetic Model	Equation	
Pseudo-First-Order	$Q_t = Q_e(1 - e^{-k_1 t})$	Equation 2.11
Pseudo-Second-Order	$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \left(\frac{1}{Q_e}\right)t$	Equation 2.13
Intra-particle diffusions	$q_t = k_{id} t^{1/2} + C$	Equation 2.15
Elovich kinetic model	$q_t = \frac{1}{\beta} \ln \alpha \beta + \frac{1}{\beta} \ln t$	Equation 2.16

3.5.2 Heavy Metal Ion Adsorption

The AC is tested for its capacity to adsorb the selected heavy metal ions, lead (Pb), zinc (Zn), and chromium (Cr). The concentration of the heavy metal ion solutions is set to 30 ppm. 0.01 g of AC is added to the Pb, Zn, and Cr ion solutions, and the mixture is agitated for 24 hours to attain equilibrium. The mixture is filtered to separate the used adsorbent. Both initial ion solution and the treated solution are further diluted to the required concentration, to be analysed using Atomic Adsorption Spectroscopy (AAS) to measure the ACs' adsorption effectiveness. For this purpose, a Shimadzu AA-7000 AAS machine is used. The quantity of heavy metal ions adsorbed by the adsorbent is determined using equation 3.3.

CHAPTER 4

STUDY ON CARBONIZATION PARAMETER AND IT'S OPTIMIZATION

Overview

This chapter describes analysis on the properties of the char derived from dabai nutshell, which includes the yield and ash content, scanning electron microscopy (SEM) images, energy dispersive x-ray spectroscopy (EDX) spectrum and elemental analysis, and surface area properties. This chapter also includes the study on carbonization parameters, which are the carbonization temperatures and atmosphere conditions.

4.1 Characteristics of Biochar

The dabai char is derived through carbonization at 700 °C for 2 hours under nitrogen gas flow along the process. The following subsections explain the properties of the resulting char.

4.1.1 Percentage Of Yield and Ash Content of The Biochar

Table 4.1 shows the yield % from the carbonization of Dabai nutshell using N₂ gas. The average production was 26.52%, which was comparable to previous studies on agricultural biomass as a raw material of activated carbon (Ioannidou & Zabaniotou, 2007). The ash content analysis revealed that the average ash content in the char after carbonization was 3.67%, as shown in Table 4.2. Based on the quality requirements of activated carbon, this number was deemed adequate, although the ash content should be less than 10%, hence validating the acceptability of nutshell as an AC precursor (Zulkania et al., 2018). It was also lower than palm kernel-based AC, which had a concentration of 6.435%. (Ademiluyi & David-West, 2012). Because the presence of ash in the AC lowers adsorption capacity, the

mechanical strength of the carbon is diminished (Zulkania et al., 2018). To lower the quantity of ash in the char, further leaching processes were proposed.

Table 4.1: Yield percentage of dabai biochar

Replicate	Initial mass (g) initial	Final Mass (g)	Percentage (%)
1	20.00	5.40	27.00
2	20.00	5.28	26.40
3	20.00	5.23	26.15
Average			26.52

Table 4.2: The percentage of ash contained in the char.

Replicate	Mass of sample (g)	Mass of ash (g)	Ash content percentage (%)
1	2.00	0.08	4.00
2	2.00	0.08	4.00
3	2.00	0.06	3.00
Average			3.67

4.1.2 Fourier-Transform Infrared Spectra Analysis

The FTIR spectrum of Dabai nutshell and its char is shown in Figure 4.1. The spectra of Dabai nutshell was discovered to be extremely comparable to previous study on the same material prior to activation with phosphoric acid (Vicinisvarri et al., 2014). The wide band at 3348.42 cm^{-1} suggested hydroxyl (-OH) stretching vibration. The C-H stretching was suggested by the peak band at 2920.23 cm^{-1} . Thiocyanate stretching (S-CN) was responsible for a peak at 2166.06 cm^{-1} . The medium peak at 1984.75 cm^{-1} may indicate allene (C=C=C) stretching. A peak at 1726.29 cm^{-1} represents carbonyl group stretching (C=O). A shoulder peak at 1643.35 cm^{-1} showed C=C stretching of conjugate alkene. Aromatic C=C stretching band was observed at 1514.12 cm^{-1} , while aromatic C=O stretching band was revealed at

1643.35 cm^{-1} . The C-O-C stretching was revealed by the prominent peak at 1033.85 cm^{-1} . The C-O stretching was reflected by a tiny peak at 1238.30 cm^{-1} .

The char spectra showed a decrease in peak intensity after carbonization, which might imply a significant loss of functional groups in the material. The C-O stretching was presumably indicated by a weak band in the replicas' spectra between 1000 and 1200 cm^{-1} .

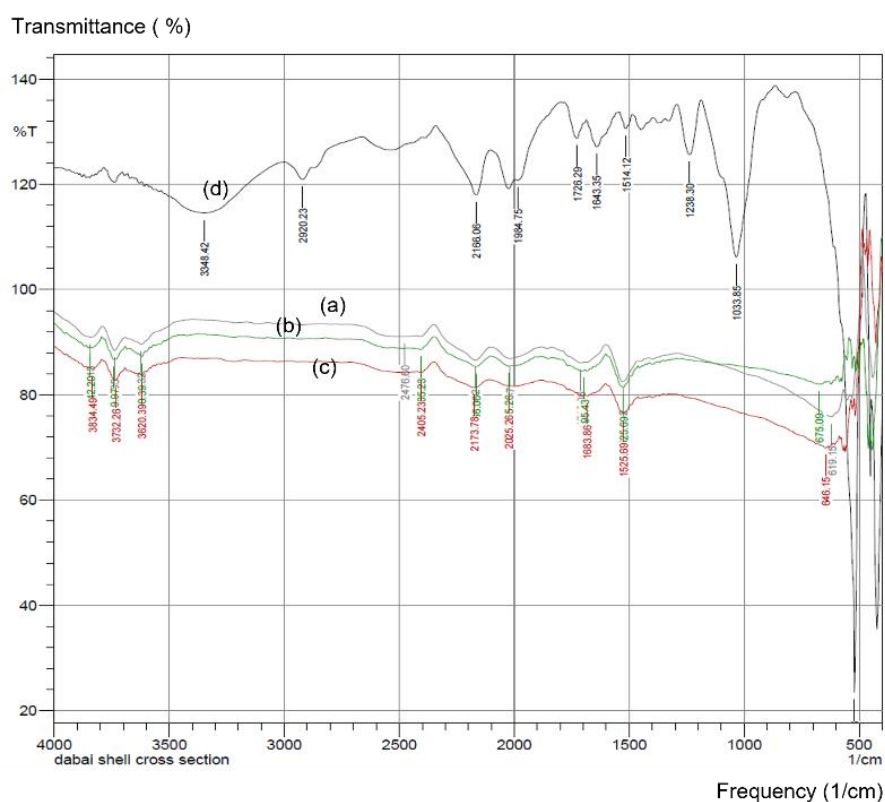
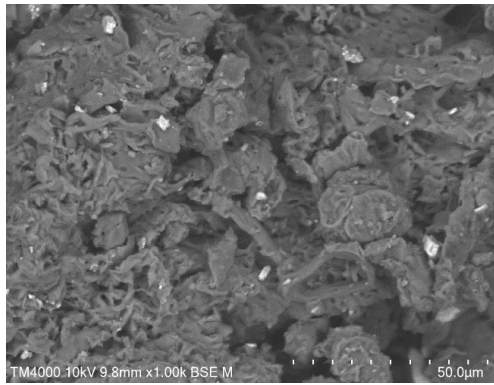


Figure 4.1: The spectra of FTIR analysis for the dabai replicates; (a) Replicate 1, (b) Replicate 2, (c) Replicate 3 and (d) raw dabai nutshell

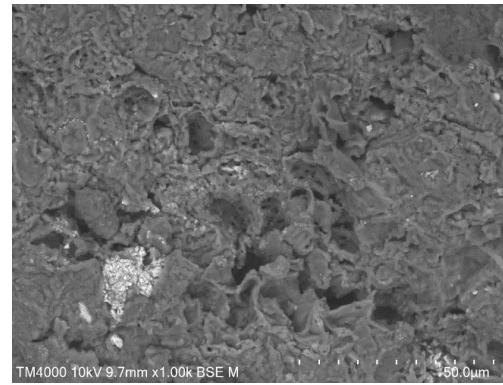
4.1.3 Surface Morphology of The Biochar

Figures 4.2 (a), (b), and (c) exhibit SEM images of char replicates, while Figure 4.2 (d) shows the raw Dabai nutshell at 1000 resolution. The Dabai nutshells image demonstrates that holes are appeared on the material's surface. The structure was stiff and packed, as is usual for lignocellulosic material. After carbonization, the porous structure began to appear

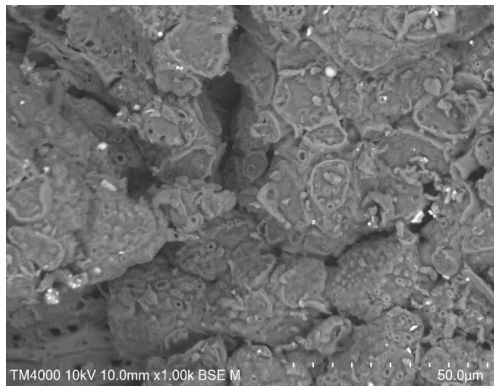
on the material, albeit in unequal and random sizes. This is consistent to the observation on the biochar derived from sugarcane biomass, obtained in a study conducted by Da Fonseca et al. (2022). The porous surfaces appears on the structure of the biomass after carbonization, which is due to the degradation of cellulose, hemicellulose, and lignin during the heat treatment (Da Fonseca et al., 2022). The presence of the white structures on the char suggested the presence of ash, as verified by energy dispersive x-ray (EDX/EDS).



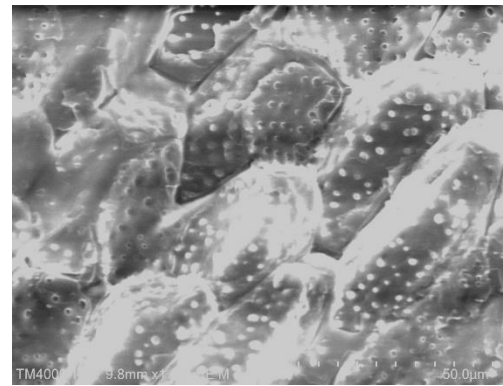
(a) Replicate 1



(b) Replicate 2



(c) Replicate 3



(d) Raw dabai nutshell

Figure 4.2: SEM figures for Dabai char replicates and raw dabai nutshell

4.1.4 Nitrogen Adsorption Isotherm and BET Surface Properties for The Dabai Biochar

Figure 4.3 depicts the Dabai char's nitrogen gas adsorption isotherm. As the relative pressure increased, N₂ adsorption increased in biochar. According to IUPAC classifications (Kecili & Hussain, 2018), the isotherm were comparable to Type I adsorption isotherms which is derived from adsorption on microporous solids exterior surfaces with a compact footprint. Although the isotherm exhibited little N₂ adsorption at low relative pressure and marginally increased adsorption as relative pressure increased.

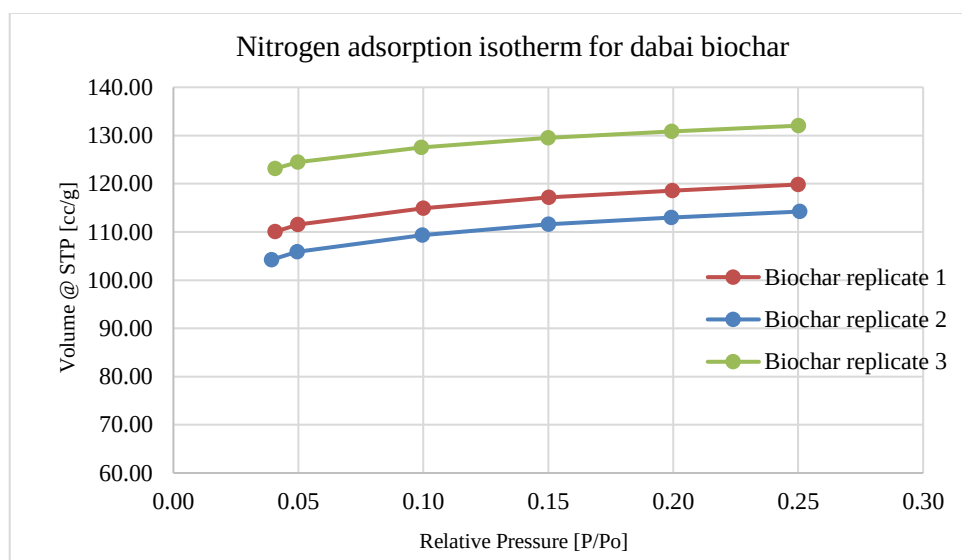


Figure 4.3: Nitrogen adsorption-desorption isotherm for dabai biochar

The BET surface area and average pore radius of the char were recorded in Table 4.3. The resultant BET surface area was equivalent to that of previous activated carbons produced from agricultural residues (Ioannidou & Zabaniotou, 2007). For the average pore radius, the biochar radii are less (10.5788) than the phosphoric acid-activated carbon from the same precursor (18.71-23.14) (Vicinivarri et al., 2014).

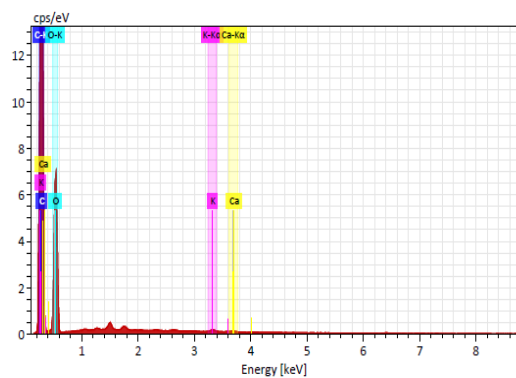
Table 4.3: BET surface area for the Dabai biochar

Replicate	BET surface area (m²/g)	Average pore radius (Å)
1	388.808	11.0658
2	370.854	10.5788
3	427.679	10.3298

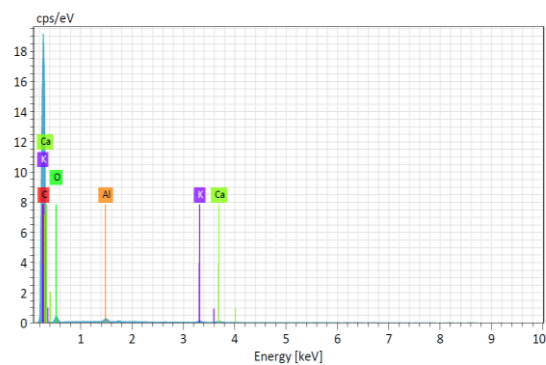
4.1.5 Elemental Mass Percentage of The Biochar

The EDX spectra of the Dabai nutshell are shown in Figure 4.4(a), which are dominated by carbon and oxygen, with a modest presence of calcium and potassium. According to Table 4.4, the amount of oxygen in the biochar was decreased from 44.29% to 5-8% after carbonization, while the percentage of carbon rose from 55.54% to the range of 86.52% to 93.57%. The presence of other elements was minimal due to their low proportion. The elemental mass composition of dabai biochar is comparable to date palm waste biochar derived in a study conducted by Salem et al. (2021), which is also dominated by carbon (more than 83%) and oxygen (more than 12%). Similar observations can be obtained in the elemental composition of palm shell biochars synthesized in a study performed by Hamza et al. (2016), where the biochars have the carbon mass percentage up to 89% and oxygen mass percentage up to 13 %.

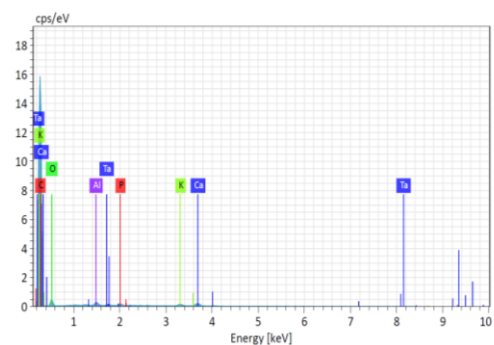
The presence of a high carbon content in the control treatment suggests that the carbonization process has been successful since the raw material has been decomposed into carbon (Hendrawan et al., 2019).



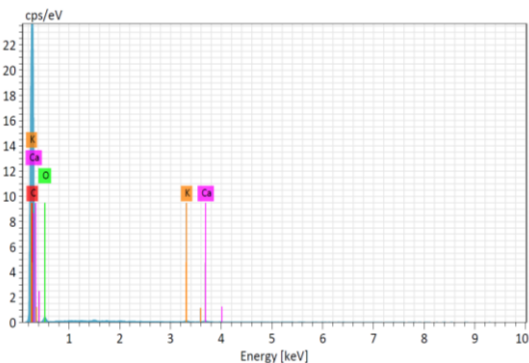
(a) Dabai nutshell



(b) Replicate 1



(c) Replicate 2



(d) Replicate 3

Figure 4.4: EDX spectra of dabai nutshell and biochars replicates derived from the precursor.

Table 4.4: The mass proportion of components in Dabai biochar.

Element	Mass percentage (%)			
	Nutshell (before carbonization)	Replicate 1	Replicate 2	Replicate 3
C	55.54	90.43	86.52	93.57
O	44.29	6.95	7.70	5.04
Ca	0.08	1.01	2.98	0.80
K	0.20	0.85	1.28	0.58
Al	-	0.77	0.78	-
P		-	0.58	-
T		-	0.16	-
Total	100.00	100.00	100.00	100.00

4.2 Study On Carbonization Parameter for Biochar

This section describes the results for the study conducted on the carbonization temperature and its atmosphere. The temperature for the process is varied from 400 to 800 °C and performed in a conventional furnace without inert gas flow. The atmosphere conditions studied are induced using nitrogen, argon, and oxygen-less condition.

4.2.1 Carbonization Temperatures

The effect of the carbonization temperature is studied by varying the temperature setting, from 400 to 800 °C. Optimization is then performed using Design Expert software to determine the lowest possible temperature that can produce char with high yield percentage and carbon mass percentage, and low ash content and oxygen mass percentage. For the atmosphere condition, the properties of the synthesized biochar with nitrogen gas, argon gas and oxygen-less condition were compared.

4.2.1 SEM Images and EDX Spectra

Figures 4.5 (a)-(e) show SEM pictures of biochar produced from dabai nutshell at various temperature settings, and figure 4.5 (f) is a comparative SEM image of dabai nutshell from prior study (as described in Sub-section 4.1.3). The photos were captured at a magnification of 1000. After carbonization, a porous surface was clearly created on the biochar, with pores of about uniform size but distributed over the surface. According to Oginni and Singh (2020), the carbonization process caused the volatile components of the biomasses to be removed by thermal breakdown, which resulted in the formation of pores in the biochar. Biochar replicates synthesised between 400 and 700 °C is observed to have the better developed porous surface. These observation are consistent with the study of derivation of biochar from crop residue performed by Liu et al. (2018), where the rising the carbonization temperatures caused damage to the original structure and the discovery of

certain micropores in the biochars' pore walls. The biochar replicates are also observed to maintain its plant cell structure despite of the high temperature used, which is proving that carbonization temperature did not result in the total damage of the cell wall structure of the biomass (Oginni & Singh, 2020). The presence of ash on the biochar was indicated by the white particles seen in the photos.

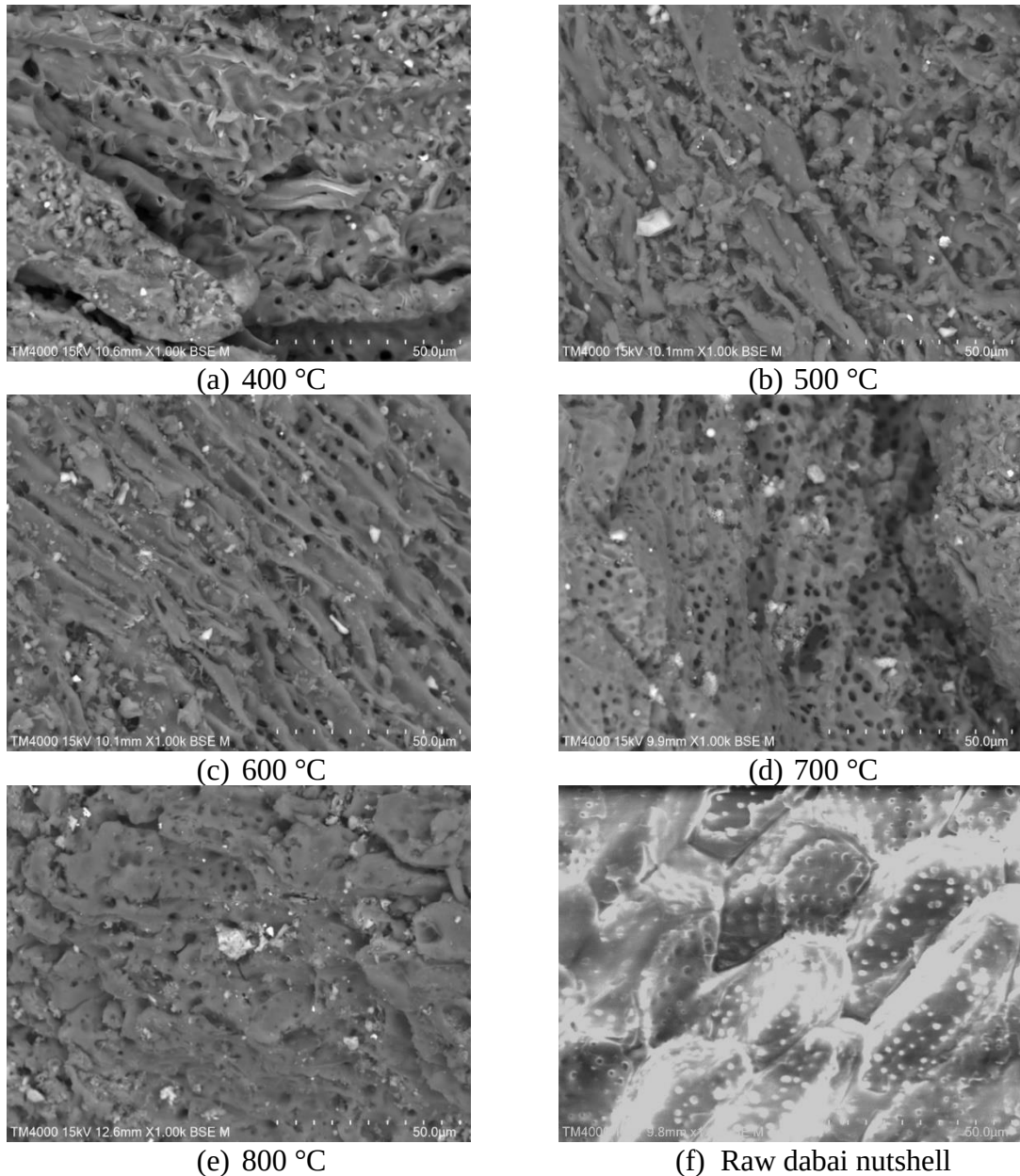


Figure 4.5: SEM images of dabai biochar synthesized from different temperature settings.

The elemental mass and atomic percentage of the dabai nutshell and the biochar generated from it are shown in Table 4.5 at various temperature settings. When the temperature is set between 500 and 800, carbonization using a conventional furnace without nitrogen or argon gas flow have raised the carbon mass percentage of the material to more than 80% and decrease the oxygen mass percentage to less than 15%. Significant differences are able to be observed on the carbon and oxygen mass percentage for biochar derived at 400 °C as compared to other replicates. The carbon appeared to be having lower mass fraction, while having higher oxygen mass fraction. According to Amer and Elwardany (2020), 400 °C is the starting temperature for high temperature carbonization (400 °C to 800 °C), which will result in a very carbon-rich biochar, if the process is performed at temperature beyond 400 °C. More lignin degradation also occurs at higher temperature (Amer & Elwardany, 2020). The decreased presence of oxygen in the replicates suggests that the carbonization treatment is capable of removing volatile substances from the raw material.

Other elements besides potassium were categorised as impurities in low and inconsequential amounts, such as aluminium from the aluminium foil used to enclose the crucible, and silica from the clay used to cover the lid of the crucible after being enclosed using aluminium foil.

Table 4.5: The mass and atomic percentage of the elements found in raw dabai nutshell and biochars obtained at various temperature settings.

Elements	Mass percentage					
	Raw dabai nutshell	400 °C	500 °C	600 °C	700 °C	800 °C
C	55.4925	74.4464	82.1726	80.8555	81.5077	80.4630
O	44.2775	23.9486	11.1827	13.3112	14.6538	13.5255
Al	-	0.3377	5.4142	3.2341	0.7498	1.1133
K	0.2300	0.2991	0.6657	1.1380	2.2006	1.6509

Ca	-	-	0.5648	0.8324	0.8881	1.3270
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Table 4.5 Continued

Si	-	0.9682	-	0.4639	-	1.9202
P	-	-	-	0.1648	-	-
Sum	100.00	100.00	100.00	100.00	100.00	100.00

4.2.2 Percentage of Yield and Ash Content

According to Table 4.6 and Figure 4.6, when the carbonization temperature increased, the yield reduced because the majority of the volatile matter in the precursor was eliminated by higher temperature carbonization. The yield quantity varied from 23.18% to 39.60% for each temperature setting, which was comparable to earlier study employing agricultural biomass as the precursor for synthesis of activated carbon (Ioannidou & Zabaniotou, 2007). The char derived at 400 °C have the highest yield percentage as most of the volatile matters are yet to be removed from the precursor.

Table 4.6: Yield percentage for biochars derived at different carbonization temperatures.

Temperature (°C)	Yield (%)			
	Trial 1	Trial 2	Trial 3	Average
400	42.39576	39.29428	37.11886	39.60297
500	31.95	28.90422	29.37119	30.07514
600	27.80166	28.50715	28.25152	28.18678
700	25.64744	25.45982	25.58488	25.56404
800	21.37	24.12276	24.04279	23.17852

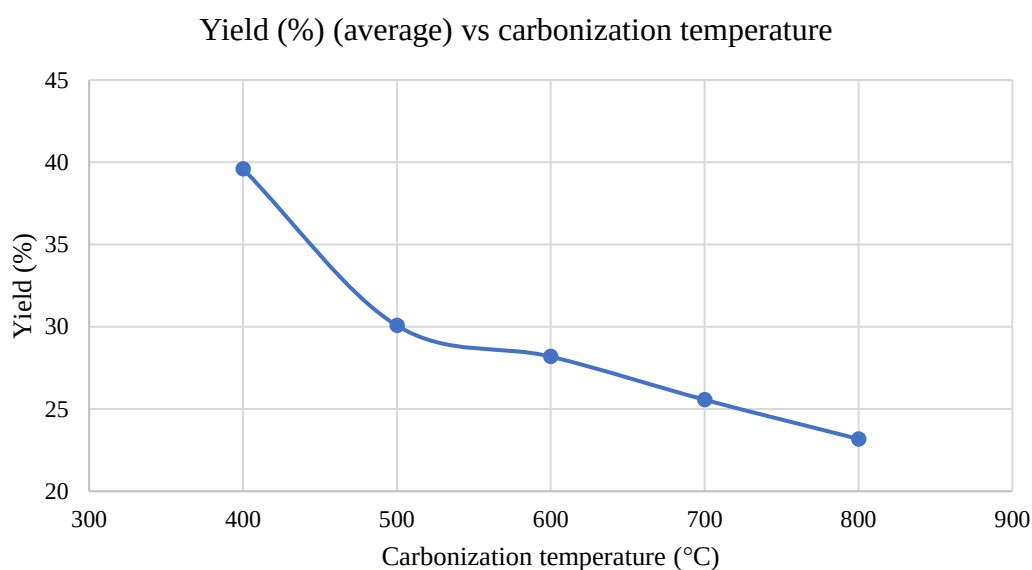


Figure 4.6: Average yield percentage of the biochars synthesised at different temperatures.

As illustrated by Table 4.7 and Figure 4.7, the linear trendline for the ash content for the char replicates derived at different temperature, shows that the ash content are increasing as the carbonization temperature increase. Higher carbonization temperatures created more ash, which was detrimental to the efficiency of activated carbon. Nonetheless, the ash content percentage range of 1.16% to 1.90% was still less than 10%, confirming the dabai nutshell's potential as a precursor for the production of activated carbon (Zulkania et al., 2018). The presence of ash reduces the performance of activated carbon. It also has an impact on reactivation efficiency. As a result, the lower the ash value, the better the activated carbon as an adsorbent (Ekpete and Horsfall, 2011).

At 500 °C, the biochar is observed to have high ash content as compared to other replicates. This is due to high presence of oxygen and aluminium content in the biochar, which is contributing to the elemental composition of ash according to Vassilev et al. (2017), as shown in Table 4.5, as compared to other biochar replicates. This is possibly one of the

drawback of using aluminium foil as part of the method to prevent combustion during carbonization.

Table 4.7: Ash content for the replicates for each carbonization temperature setting.

Temperature (°C)	Ash content (%)			
	Trial 1	Trial 2	Trial 3	Average
400	1.397205589	0.7984032	1.2948207	1.163476
500	2.002002002	2.1934197	1.4955135	1.896978
600	2.397602398	1.4925373	1.0978044	1.662648
700	1.892430279	1.5936255	1.2961117	1.594056
800	2.095808383	1.9	1.3958126	1.797207

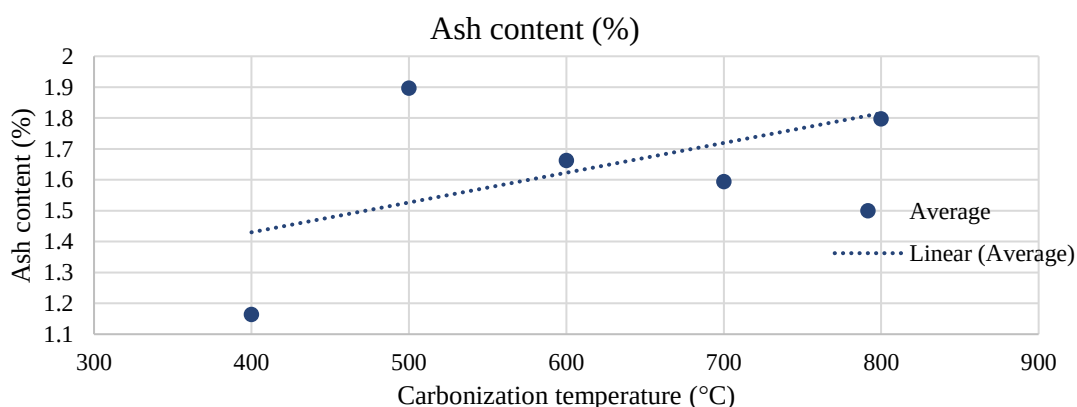


Figure 4.7: Average ash content of biochar replicates synthesised at different temperature setting.

4.2.3 Nitrogen Adsorption Isotherm and BET Surface Area

Figure 4.8 shows the nitrogen adsorption isotherm of the biochar derived at different temperature. The biochar derived at 400 °C are unable to adsorb the nitrogen gas, while the biochar derived at 500 °C and 600 °C are only able to adsorb less than 30 cm³/g and 90 cm³/g of nitrogen gas respectively. These results indicates that high adsorbent surfaces are not able to be developed through carbonization performed at 400-600 °C. These observation are consistent to the surface properties of the biochar as shown in Table 4.8, as the surface area

of the biochar derived at 400 to 600 °C are significantly lower. Higher amount of nitrogen adsorption are observed when the bio-chars were synthesized at 700 and 800 °C.

According to IUPAC classification (Thommes et al., 2015), the nitrogen adsorption isotherm for the biochars derived at 500 and 600 °C are similar to Type VI isotherm. The isotherm depicts layer-by-layer adsorption on an extremely uniform non-porous exterior. For the biochar derived at 700 °C, the nitrogen adsorption isotherm is similar to Type I isotherm, which is derived from adsorption on microporous solids exterior surfaces with a compact footprint. The nitrogen adsorption isotherm for biochars derived at 800 °C are identical to Type II isotherm, which represents the physical adsorption of gases on macroporous or non-porous structure of adsorbents (Thommes et al., 2015). The nitrogen adsorption isotherms for the dabai biochars derived at different carbonization temperature are consistent with those of the wood charcoal derived at varied carbonization temperature which is obtained in a study conducted by Yoshizawa et al. (2005). The study concluded that by increasing the carbonization temperature, the adsorption amount of nitrogen gas increases (Yoshizawa et al., 2005).

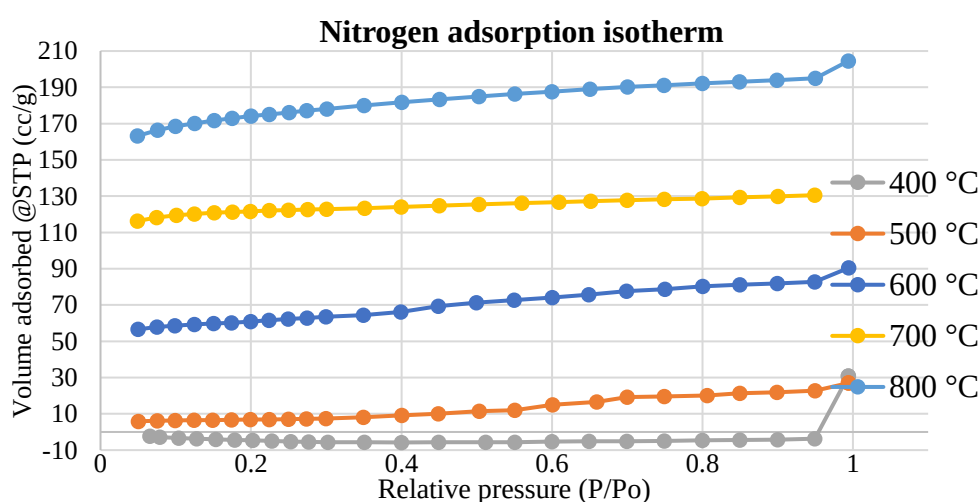


Figure 4.8: Nitrogen adsorption isotherm for biochars derived at 400 to 800 °C.

Table 4.8 shows the BET surface properties of the dabai biochars derived at 400 to 800 °C. Biochars derived at 400 °C and 500 °C have the lowest BET surface area and total pore volume, while biochar derived at 800 °C have the highest BET surface area and total pore volume. Based on this observation, increasing the temperature for carbonization process of dabai nutshell will increase the BET surface area and total pore volume. These findings are parallel to a study on carbonization of Kanlow Switchgrass and Public Miscanthus biomass, conducted by Oginni and Singh, (2020), as the researchers varied the carbonization temperature from 500 to 900 °C. The BET surface area of the resulting biochars are observed to increase as the temperature for carbonization increase. (Oginni & Singh, 2020)

The resulting properties of biochars derived at 700 are comparable with the carbonized sugarcane bagasse synthesized at the same temperature, in the study conducted by El Nemr et al. (2022). Dabai biochars derived at 500, 600, 700 and 800 °C, are considered to have porous surface within micropores range (less than 20 Å or 2 nm). The average pore size for biochar produced at 400 °C shows that the pores of the carbon material is within the range of mesopores (20 to 500 Å or 2 nm to 50 nm). The mesoporous appearance with low surface area for the biochar derived at 400 °C are similar to the biochar derived from Norway spruce needles, at 500 °C, which is synthesized in a study conducted by (Oginni & Singh, 2021), and the biochar derived from microalgae residue powder, at carbonization temperature of 400-600 °C, in a study conducted by (Yang et al., 2021). According to Lu et al. (1995), this condition are due to the release of gases and volatiles matters that soften the structure and produces bubbles, resulting to the relatively huge pores on the surface of the char. The similar phenomenon can also be observed during pyrolysis of coal materials (Lu et al., 1995).

Table 4.8: BET surface properties of the biochars derived at 400-800 °C

Temperature (°C)	BET surface area (m²/g)	Total pore volume (cm³/g)	Average pore size (Å)
400	2.01	0.04782	475.898
500	22.605	0.0116	10.2635
600	191.144	0.1399	14.6408
700	369.216	0.2019	10.9371
800	536.056	0.2754	10.2749

4.2.2 Optimization of Carbonization Temperature

The optimization of parameter includes the analysis of variance (ANOVA) and Fit Analysis for the responses, which is the percentage of yield and the ash content of the resulting biochar replicates. This chapter also includes the coded equation suggested to model and predict the responses and comparing it to the actual responses data. Software Design ExpertTM is utilized to analyse and optimize the processes.

4.2.2.1 Analysis of Variance on the Responses as Effected by Carbonization Temperature

Table 4.9 shows the single factor experimental design to analyse and optimize the carbonization temperature based on the percentage of yield, the ash content, BET surface area and total pore volume of the resulting replicates of biochar. The analysis of each response are provided by the following subsections. Both responses are recommended to fit the cubic process order. The results for BET surface area and total pore volume are obtained only for 1 replicate for each carbonization temperature, due to the limitation of the BET Surface Analyzer to process numerous samples which explains the absence of the parameters' values for Run 2, 3, 5, 6, 8, 9, 11, 12, 14 and 15.

Table 4.9: Experimental design and resulting properties of the char derived from dabai nutshell at different carbonization temperatures.

Run	Factor 1	Response 1	Response 2	Response 3	Response 4
	A: Temperature (°C)	Percentage of yield (%)	Ash content (%)	BET surface area (m ² /g)	Total pore volume (cm ³ /g)
1	400	42.3958	1.39721	2.01	0.04782
2	400	39.2943	0.798403	NR	NR
3	400	37.1189	1.29482	NR	NR
4	500	31.95	2.002	22.605	0.0116
5	500	28.9042	2.19342	NR	NR
6	500	29.3712	1.49551	NR	NR
7	600	27.8017	2.3976	191.144	0.1399
8	600	28.50715	1.49254	NR	NR
9	600	28.2515	1.0978	NR	NR
10	700	25.6474	1.89243	369.216	0.2019
11	700	25.4598	1.59363	NR	NR
12	700	25.5849	1.29611	NR	NR
13	800	21.37	2.09581	536.056	0.2754
14	800	24.1228	1.9	NR	NR
15	800	24.0428	1.39581	NR	NR
*NR- No result					

1. Response 1: Percentage of Yield

Table 4.10 shows the results of analysis of variance (ANOVA) of Response 1. The actual equation to predict the percentage of yield of char, affected by carbonization temperature is cubic, as follows;

Percentage of yield (%)

Equation 4.1

$$\begin{aligned} &= 205.30227713448 - 0.79873634797336 * T \\ &+ 0.0012071281210166 * T^2 \\ &- 6.1685582843131 \times 10^{-7} * T^3 \end{aligned}$$

Where T is the carbonization temperature. Table 4.10 shows the analysis of variance for the cubic model. Factor coding is Coded. Sum of squares is Type III – Partial. The Model F-value of 61.32 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case A^3 is a significant model term, which is 0.0283. Values greater than 0.1000 indicate the model terms are not significant. In this case, A and A^2 are not significant terms which are 0.1603 and 0.9250 respectively. These model terms are insignificant to improve or influence significant changes on the model equation for the purpose of predicting the percentage of yield as the carbonization temperature changes. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. Presence of insignificant model terms can reduce the accuracy of the model.

The Lack of Fit F-value of 1.52 implies the Lack of Fit is not significant relative to the pure error. There is a 24.59% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Table 4.10: The analysis of variance for the cubic model for the percentage of yield as affected by the carbonization temperature.

Source	Sum of Squares	df	Mean Square	F-value	p-value	Notes
Model	474.51	3	158.17	61.32	< 0.0001	Significant

Table 4.10 Continued

A-Temperature	5.85	1	5.85	2.27	0.1603	
A ²	0.0239	1	0.0239	0.0093	0.9250	
A ³	16.44	1	16.44	6.37	0.0283	
Residual	28.37	11	2.58			
Lack of Fit	3.74	1	3.74	1.52	0.2459	not significant
Pure Error	24.63	10	2.46			
Cor Total	502.89	14				

Table 4.11 shows the fit statistics for the cubic model. The Predicted R² of 0.8840 is in reasonable agreement with the Adjusted R² of 0.9282; i.e., the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 19.804 indicates an adequate signal. This model can be used to navigate the design space. Based on the cubic model equation, the model graph showing the predicted and the actual result of the percentage yield based on the carbonization temperature, is developed, and as shown in Figure 4.9.

Table 4.11: Fit statistics of the cubic model for the percentage of yield of the dabai char

Std. Dev.	1.61	R²	0.9436
Mean	29.32	Adjusted R²	0.9282
C.V. %	5.48	Predicted R²	0.8840
		Adeq Precision	19.8039

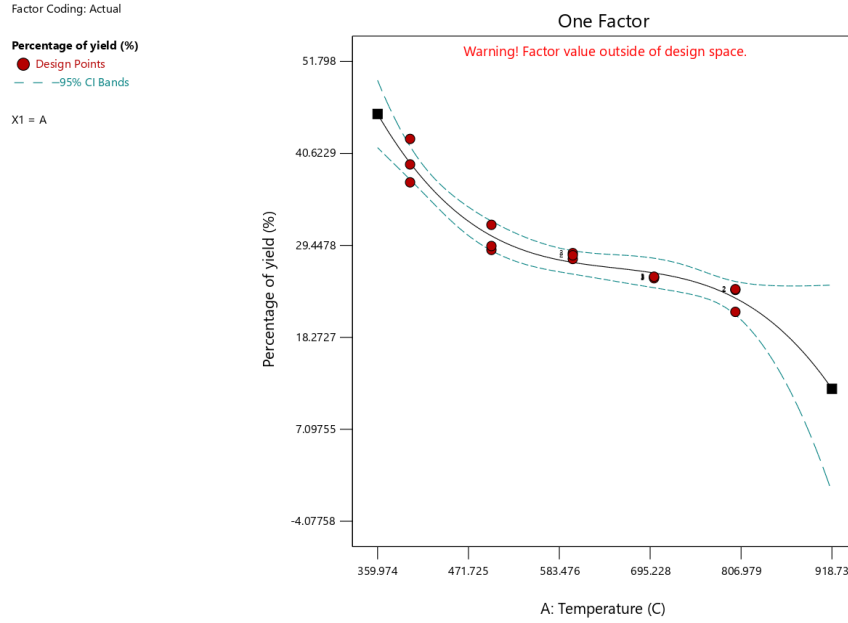


Figure 4.9: The model graph, comparing the predicted data with the actual data of the percentage of yield for the replicates of dabai char derived at different carbonization temperatures.

2. Response 2: Ash Content

Table 4.12 shows the results of ANOVA conducted on the Response 2. The actual equation to predict the percentage of ash content as the carbonization temperature varied is cubic, as follows;

$$\begin{aligned}
 \text{Ash content (\%)} &= -21.334415413567 + 0.11668533052349 * T \\
 &- 0.00019232894347916 * T^2 \\
 &+ 1.032979713003 \times 10^{-7} * T^3
 \end{aligned}
 \tag{Equation 4.2}$$

T is the carbonization temperature. The sum of squares is Type III – Partial. The Model F-value of 1.82 implies the model is not significant relative to the noise. There is a 20.18% chance that an F-value this large could occur due to noise. P-values less than 0.0500

indicate model terms are significant. In this case there are no significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. The Lack of Fit F-value of 0.25 implies the Lack of Fit is not significant relative to the pure error. There is a 62.62% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Table 4.12: ANOVA for Cubic model for the ash content of the char

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	0.9117	3	0.3039	1.82	0.2018	not significant
A-Temperature	0.2648	1	0.2648	1.59	0.2340	
A ²	0.1092	1	0.1092	0.6536	0.4360	
A ³	0.4610	1	0.4610	2.76	0.1249	
Residual	1.84	11	0.1670			
Lack of Fit	0.0453	1	0.0453	0.2525	0.6262	not significant
Pure Error	1.79	10	0.1792			
Cor Total	2.75	14				

Table 4.13 shows the fit statistics for the cubic model, to predict the ash content of the char. A negative Predicted R² implies that the overall mean may be a better predictor of your response than the current model. In some cases, a higher order model may also predict better. Adeq Precision measures the signal to noise ratio. A ratio of 3.13 indicates an inadequate signal and this model should not be used to navigate the design space. Based on the cubic model equation, the model graph showing the predicted and the actual result of the ash content based on the carbonization temperature, is developed, and as shown in Figure 4.10.

Table 4.13: Fit statistics of the cubic model for ash content of the dabai char

Std. Dev.	0.4087	R²	0.3316
Mean	1.62	Adjusted R²	0.1494
C.V. %	25.18	Predicted R²	-0.1514
		Adeq Precision	3.1278

Factor Coding: Actual

Ash content (%)
● Design Points
— —95% CI Bands

X1 = A

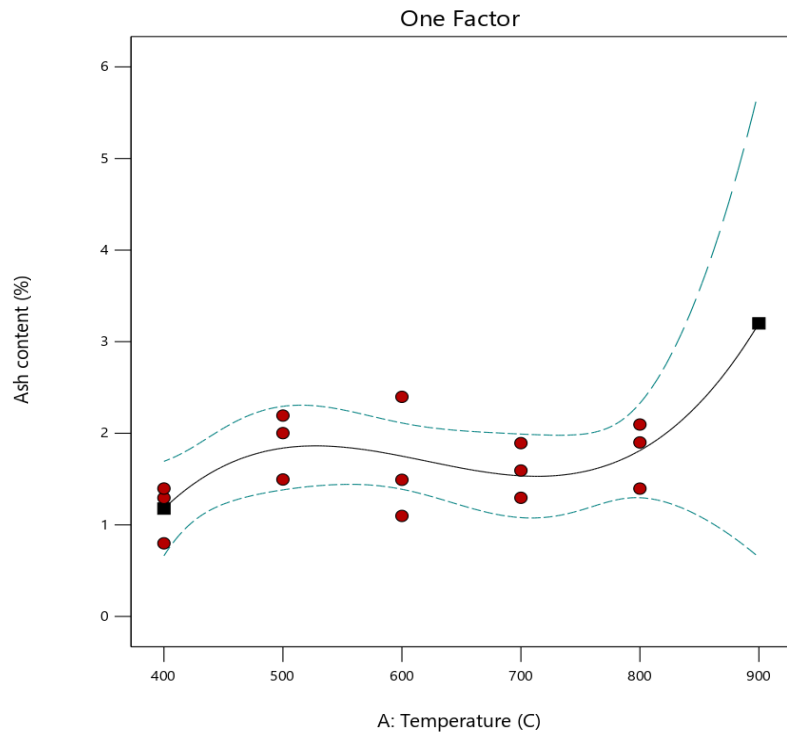


Figure 4.10: The model graph, comparing the predicted data with the actual data of the ash content for the replicates of dabai char derived at different carbonization temperatures.

3. Response 3: BET Surface Area

Table 4.14 shows the results of ANOVA on the effects of carbonization temperature on the BET surface area of the biochar. The actual equation to predict the BET surface area is linear, as follows;

$$\text{BET surface area} = -624.6156 + 1.414703 * T \quad \text{Equation 4.3}$$

Where T is the carbonization temperature. The Model F-value of 64.93 implies the model is significant. There is only a 0.40% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case A is a significant model term. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

Table 4.14: ANOVA for the linear model to predict the BET surface area of the biochar.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2.001E+05	1	2.001E+05	64.93	0.0040	significant
A-Temperature	2.001E+05	1	2.001E+05	64.93	0.0040	
Residual	9246.99	3	3082.33			
Cor Total	2.094E+05	4				

Table 4.15 shows the Fit Statistics of the linear model. The Predicted R^2 of 0.8214 is in reasonable agreement with the Adjusted R^2 of 0.9411; i.e., the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 16.116 indicates an adequate signal. This model can be used to navigate the design space. Based on the linear model, the model graph showing the predicted value of BET surface area affected by the change of temperature is developed and shown in Figure 4.11.

Table 4.15: Fit statistics of the linear model

Std. Dev.	55.52	R^2	0.9558
Mean	224.21	Adjusted R^2	0.9411
C.V. %	24.76	Predicted R^2	0.8214
		Adeq Precision	16.1159

Factor Coding: Actual

BET surface area (m²/g)

● Design Points

— 95% CI Bands

X1 = A

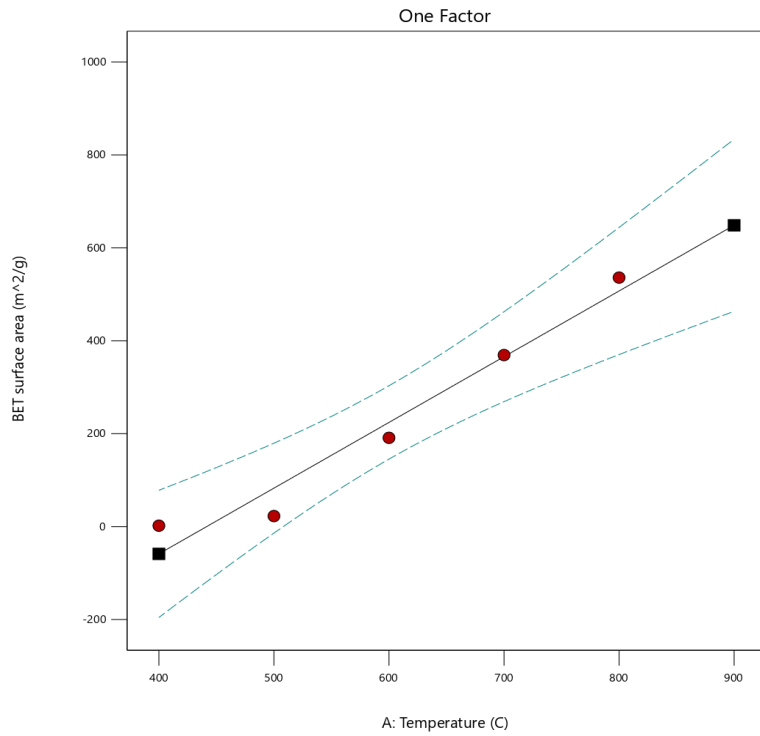


Figure 4.11: Model graph of the predicted value of BET surface area as affected by the carbonization temperature as compared to the experimental data.

4. Response 4: Total Pore Volume

Table 4.15 shows the results of ANOVA on the total pore volume of the biochars developed at different carbonization temperature. The actual equation to predict the total pore volume of the biochars is linear, as shown below;

$$\text{Total pore volume} = -0.251952 + 0.00064546 * T \quad \text{Equation 4.4}$$

Where T is the carbonization temperature. The Model F-value of 23.24 implies the model is significant. There is only a 1.70% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A is a significant model term. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model.

Table 4.16: The results of ANOVA on the total pore volume of the biochars

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	0.0417	1	0.0417	23.24	0.0170	significant
A-Temperature	0.0417	1	0.0417	23.24	0.0170	
Residual	0.0054	3	0.0018			
Cor Total	0.0470	4				

Table 4.17 shows the fit statistics of the linear model for the prediction of total pore volume of the biochars as affected by the carbonization temperature. The Predicted R^2 of 0.8214 is in reasonable agreement with the Adjusted R^2 of 0.9411; i.e., the difference is less than 0.2. Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 16.116 indicates an adequate signal. This model can be used to navigate the design space. Based on the linear model, a model graph showing the predicted values of total pore volume as affected by the carbonization and compared to the actual data is developed and as shown in Figure 4.12.

Table 4.17: Fit statistics of the linear model

Std. Dev.	0.0423	R²	0.8857
Mean	0.1353	Adjusted R²	0.8476
C.V. %	31.29	Predicted R²	0.6014
		Adeq Precision	9.6422

Factor Coding: Actual

Total pore volume (cc/g)

● Design Points
— 95% CI Bands

X1 = A

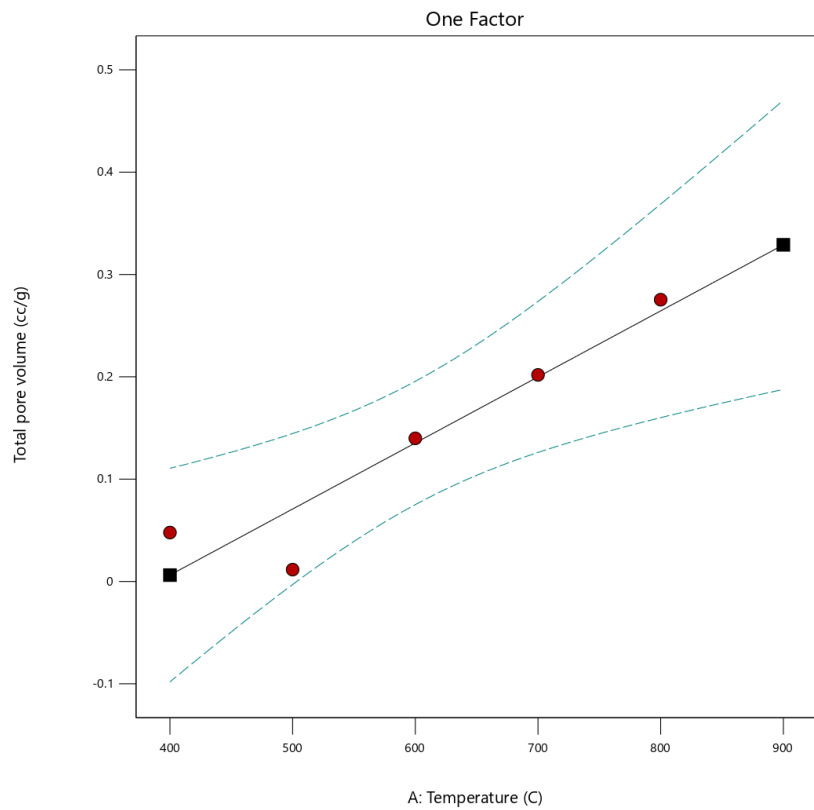


Figure 4.12: Model graph showing the predicted values of total pore volume of the biochar as affected by the carbonization temperature, compared to the actual data.

4.2.2.2 Optimization of The Carbonization Temperature

Optimization for the carbonization temperature is to determine the lowest temperature that provides the best char quality, which is with the highest yield percentage, low ash content, while having generous amount of carbon and low amount of oxygen. While having the highest yield percentage and lowest ash content, based on the EDX results (as shown in Table 4.5), char derived at 400 °C have lowest carbon mass percentage compared to others, while having more than 20% of oxygen mass percentage. Since at that temperature, the high-temperature carbonization just started, with removal of more volatile compounds are at early stages. According to the BET surface analysis and nitrogen adsorption isotherm as described in subsection 4.2.1.3, the biochar synthesized at 500 °C have very low BET

surface area, total pore volume, and adsorption of nitrogen gas. Thus, temperatures higher than 500 °C are recommended. Simplified criteria for the optimization of carbonization temperature are as follows;

- a. High percentage of yield,
- b. Low presence of ash content,
- c. High mass percentage of carbon
- d. Low presence of oxygen.
- e. High BET surface area
- f. High total pore volume

Using the criteria given and excluding the carbonization temperature of 400 and 500 °C, Design Expert suggested the following solution as shown in Figure 4.13. The biochar is suggested to be derived at 721.469 °C with the desirability of the solution is 0.610. The biochar which will have 25.72 % of percentage of yield, 1.53% of ash content, 396.049 m²/g of BET surface area and 0.214 cm³/g of total pore volume.

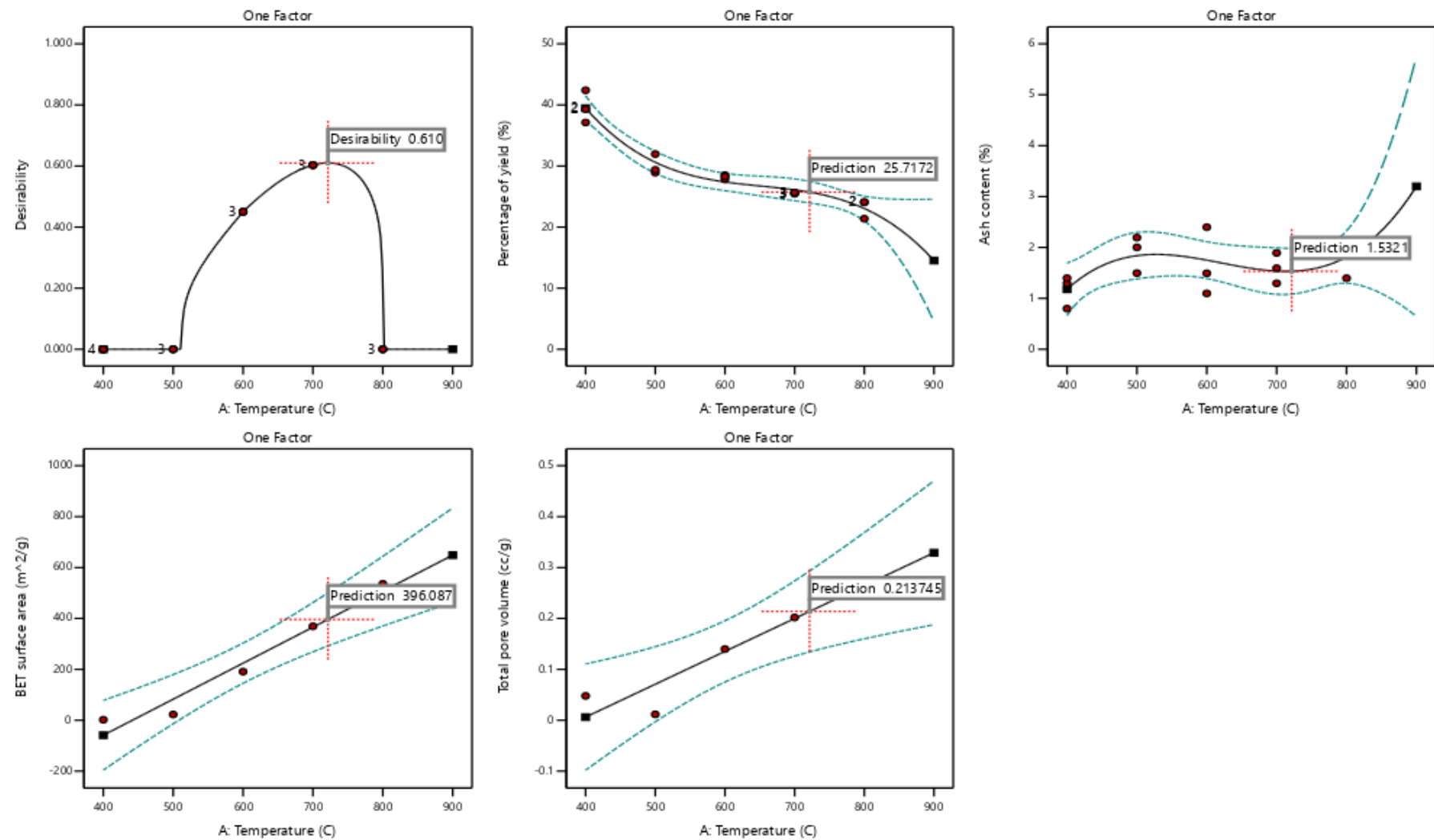


Figure 4.13: Optimization solution for the carbonization temperature

4.2.3 Carbonization Atmosphere

Comparison study is performed on the char synthesised in different pyrolysis atmosphere as listed in Table 4.18. The resulting chars of the different conditions have comparable properties, which is parallel to the research conducted for the synthesis of activated carbon from olive stones with similar conditions; with the presence of nitrogen gas flow, and self-induced atmosphere (Yousfi et al., 2020) . Basically, all conditions are able to produce char with high yield percentage and low ash content. Using nitrogen gas and argon gas flow during the carbonization are proven to derive char with higher carbon mass percentage and lower oxygen mass percentage, as compared to the oxygen-less atmosphere. These indicated that the inert gas flow is crucial to further remove the volatile compound on the raw material without degradation (Indayaningsih et al., 2017) while increasing the percentage of carbon element, which is crucial to provide essential structures for porous surface.

As for the surface area properties, argon gas is observed to develop higher BET surface area on as compared to pyrolysis conducted with the flow of nitrogen gas and without inert gas flow. This condition is similar to a study conducted on carbonization of hornet's nest which in performed under argon or nitrogen gas flow, where the resulting material derived under argon gas flow have higher BET surface area as compared to the material derived under nitrogen gas. (Z. Xu et al., 2019)

The study on the carbonization and activation of the precursor under no inert gas flow helps to determine the potential of synthesizing adsorbent using crude setup of high temperature furnaces without any gas flow inlet. The resulting biochar is observed to have several crucial adsorbent properties in acceptable range. Lower ash content are observed on the char derived without inert gas flow, as compared to other char replicates derived under

nitrogen and argon gas flow, where this indicates that placing the char in crucible with lid and covering it with aluminium foil and clay are proven to reduce amount of oxygen gas and further prevent combustion, that may turn most of the precursor directly into ash. The comparable properties of the char replicates derived under different atmosphere, have proven that it is possible to make an efficient carbon without employing a controlled atmosphere during the carbonization process (Yousfi et al., 2020). As observed in subsection 4.2.1, higher temperature in the conventional furnace is needed, to develop better surface area on the biochar. Further studies are necessary to improve this initiative.

Table 4.18: Different atmosphere conditions for carbonization of raw dabai

Atmosphere condition	Parameters of the carbonization			Resulting properties of the carbonization				
	Carbonization temperature (°C)	Mass of raw dabai nutshell (g)	Duration of carbonization (hrs)	Percentage of yield (%)	Ash content (%)	Carbon mass percentage (%)	Oxygen mass percentage (%)	BET surface area (m²/g)
Nitrogen gas flow	700	10	2	26.5	3.67	90.43	6.95	388.808
Argon gas flow	700	10	2	24.19	1.85	85.2839	11.2277	440.548
Oxygen-less condition	700	10	2	25.56	1.59	81.5077	14.6538	369.216

CHAPTER 5

STUDY ON DABAI NUTSHELL ACTIVATED CARBON AND ITS CHARACTERIZATION

Overview

This chapter describes the properties of the activated carbon (AC) derived from the dabai nutshell through chemical activation, using NaOH, HCl and KCl. The carbonization and chemical activation of the precursor material is performed using a conventional furnace, without any inert gas flow.

5.1 Fourier-Transform Infrared Spectra of the Activated Carbon

The FTIR spectra of the Dabai AC replicates are shown in Figure 5.2, 5.3 and 5.4. In comparison to the spectrum of raw dabai nutshell as stated in the research conducted by James et al., (2022), most of the initial functional groups are lost during the activation process owing to carbonization and volatilization.

For NaOH-AC replicates, as shown in Figure 5.1, there's no significant difference between the spectra of each replicate. The spectra show a faint peak extending from 1600 to 2000 cm^{-1} , which shows aromatic compound C-H bonding. Weak peaks at 2214-2177 cm^{-1} indicate the presence of C $\equiv$ C stretching of an alkyne stretching bond. Peak concentrations in the adsorbents between 1600 and 1700 cm^{-1} suggested the presence of C=O stretching, of a functional carboxylic acid group or conjugated acid. This peak is seen in absorbance bands of 1683.86, 1687.71, and 1697.36 cm^{-1} . The alkaline treatment of the precursor triggered the production of carboxylic acid compounds. C=O stretching for vinyl/phenyl ester is indicated by a strong peak at 1700 cm^{-1} . The presence of the functional groups found on the NaOH-AC are consistent to the results of the derivation of NaOH-AC from coconut shell, in a study

conducted by Sujiono et al. (2022), and derivation of KOH-AC from *Bambusa vulgaris striata*, in a research performed by Mistar et al. (2020). Sujiono et al. (2022) stated that the primary purpose of the functional groups of activated carbon, which are the O-H, C=O, and C-O stretching vibrations, is to operate as a contaminant's absorber. The oxygen-containing functional groups on the surface of the sample serve as a depositional site for the absorption of metal particles following catalyst application. (Sujiono et al., 2022)

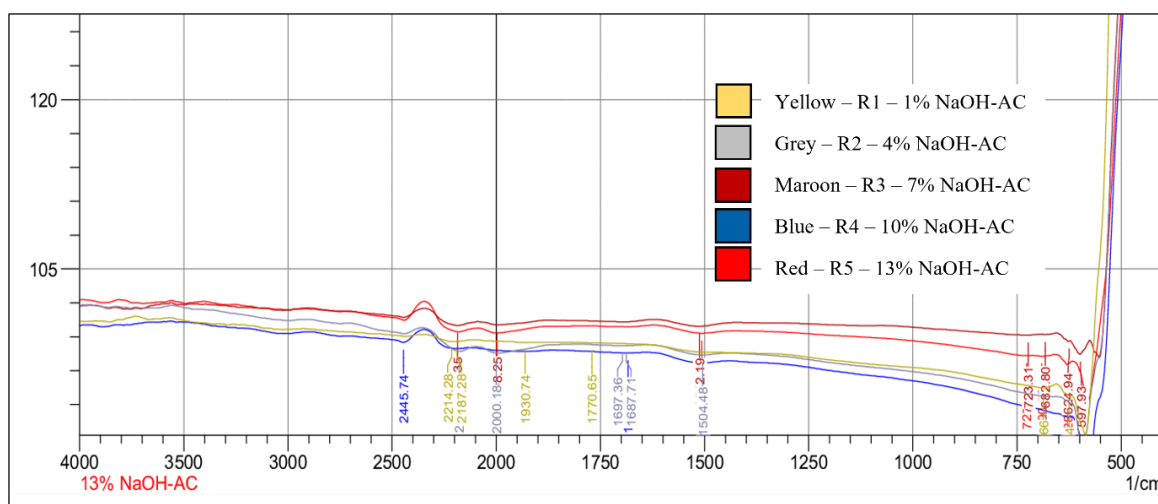


Figure 5.1: FTIR Spectra for NaOH-AC replicates

Figure 5.2 shows the FTIR spectra of HCl-AC replicates. The spectra of the replicates are very similar to each other, with no significant difference among them. The strong peak between the range of 1517 cm^{-1} to 1527 cm^{-1} indicates the possible presence of N-O stretching of nitro compound. Potential presence of C=O stretching for conjugated acid or conjugated aldehyde are represented by the strong peak between the range of 1703 cm^{-1} to 1693 cm^{-1} . The weak peaks between the range of $2400\text{--}2000\text{ cm}^{-1}$ are unidentifiable. Possible presence of alcohol with O-H stretching are represented by medium, sharp peaks ranging from 3697 to 3612 cm^{-1} . These peaks of O-H stretching within the range of $3697\text{--}3612\text{ cm}^{-1}$ and C=O stretching within the range of $1703\text{--}1693\text{ cm}^{-1}$ are consistent with the activated carbon derived from charcoal using phosphoric acid and sulphuric acid, which is synthesized

in a study conducted by Islam et al. (2022). The presence of carboxyl groups in lignin, hemicellulose, and pectin is shown by the C=O stretching. (Hameed & Daud, 2008; Islam et al., 2022) The O-H stretching are indicating the presence of cellulose, adsorbed water, lignin, pectin and hemicellulose. (Gundogdu et al., 2013; Islam et al., 2022) Peaks beyond 3700 cm^{-1} are unidentifiable.

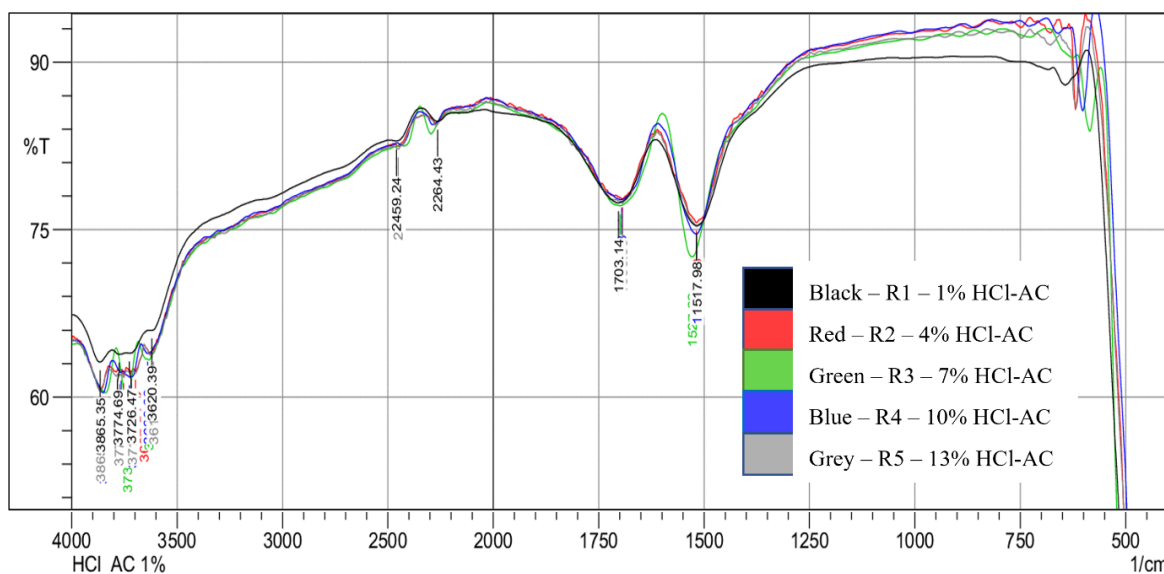


Figure 5.2: FTIR spectra of HCl-AC replicates

Figure 5.3 represents the FTIR spectra of KCl-AC replicates. The spectra of the replicates are fairly similar, with no notable differences between them. The spectra are also identical to the spectra of HCl-AC. Most of the peaks are identifiable at the strong peaks of 1517 cm^{-1} as possible presence of N-O stretching of nitro compound, and the strong peaks of 1693 to 1703 cm^{-1} , as potential presence of potential presence of C=O stretching for conjugated acid or conjugated aldehyde. Potential alcohol presence with C-O stretching are represented by the medium, sharp peaks 2697 to 3612 cm^{-1} . The peaks between the range of 2400 to 2000 cm^{-1} with weak presence, and peaks beyond 3700 cm^{-1} are unidentifiable. The presence of peaks indicating the C=O stretching are consistent with the results of activated

carbon derived from jute stick, using zinc chloride activation, which is conducted by Islam et al. (2022), where the presence of carboxyl groups in lignin, hemicellulose, and pectin is shown by the spectrum.

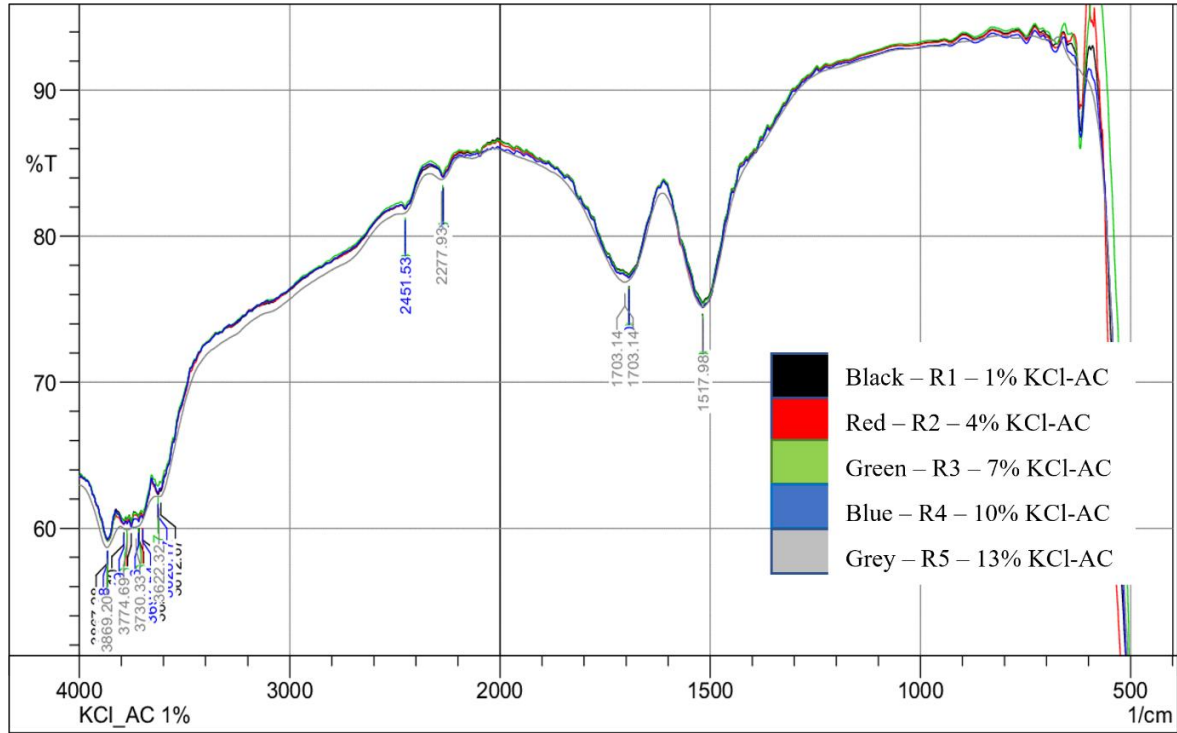


Figure 5.3: FTIR spectra of KCl-AC

5.2 Scanning Electron Microscopy (SEM) Images of Activated Carbon

The SEM images of the (a) dabai nutshell and (b)-(e) AC generated from it using NaOH solution at various concentrations are shown in Figure 5.4. All of the replicates of AC had surface fractures and pores visible in comparison to the raw precursor. Porous surfaces may be created on the precursor by carbonization and chemical activation, demonstrating the success of the synthesis of the ACs. For R5, it is shown that the porous structure has ruptured, probably as a result of high NaOH concentration. The walls between the pores are destroyed and the accessible area is drastically reduced when large concentrations of NaOH are present (Heidarinejad et al., 2020). NaOH is the well-

established potent activator of carbon compounds with disordered atoms. The reduction and oxidative modification responsible for the separation and degradation of the graphitic layer is connected to the pore enlargement brought on by NaOH (Pezoti et al., 2016).

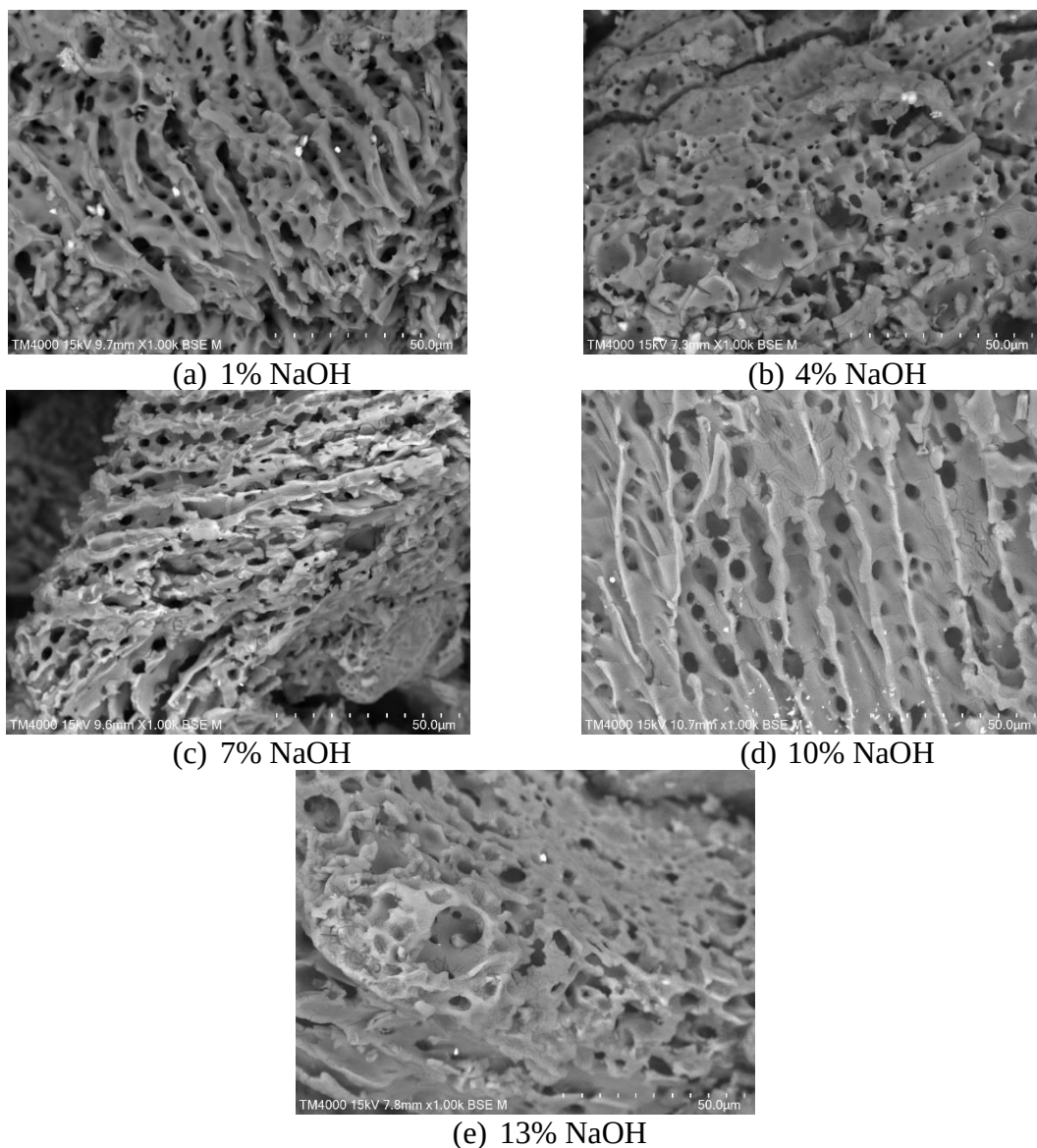


Figure 5.4: SEM images for NaOH AC at different impregnation concentrations.

Figure 5.5 shows the SEM images of all replicates for KCl derived AC, with porous surfaces are observable on all the adsorbent, basically having the similar impact from the carbonization and chemical activation using the metal chloride salt. However, for R4 and R5, the porous structures are seemed to be ruptured, possibly due to the high concentration

of KCl solution used in the chemical activation. Utilization of KCl for the chemical activation as an alternative to ZnCl_2 is due to its properties which is described to be non-toxic (Lee & Zaini, 2016).

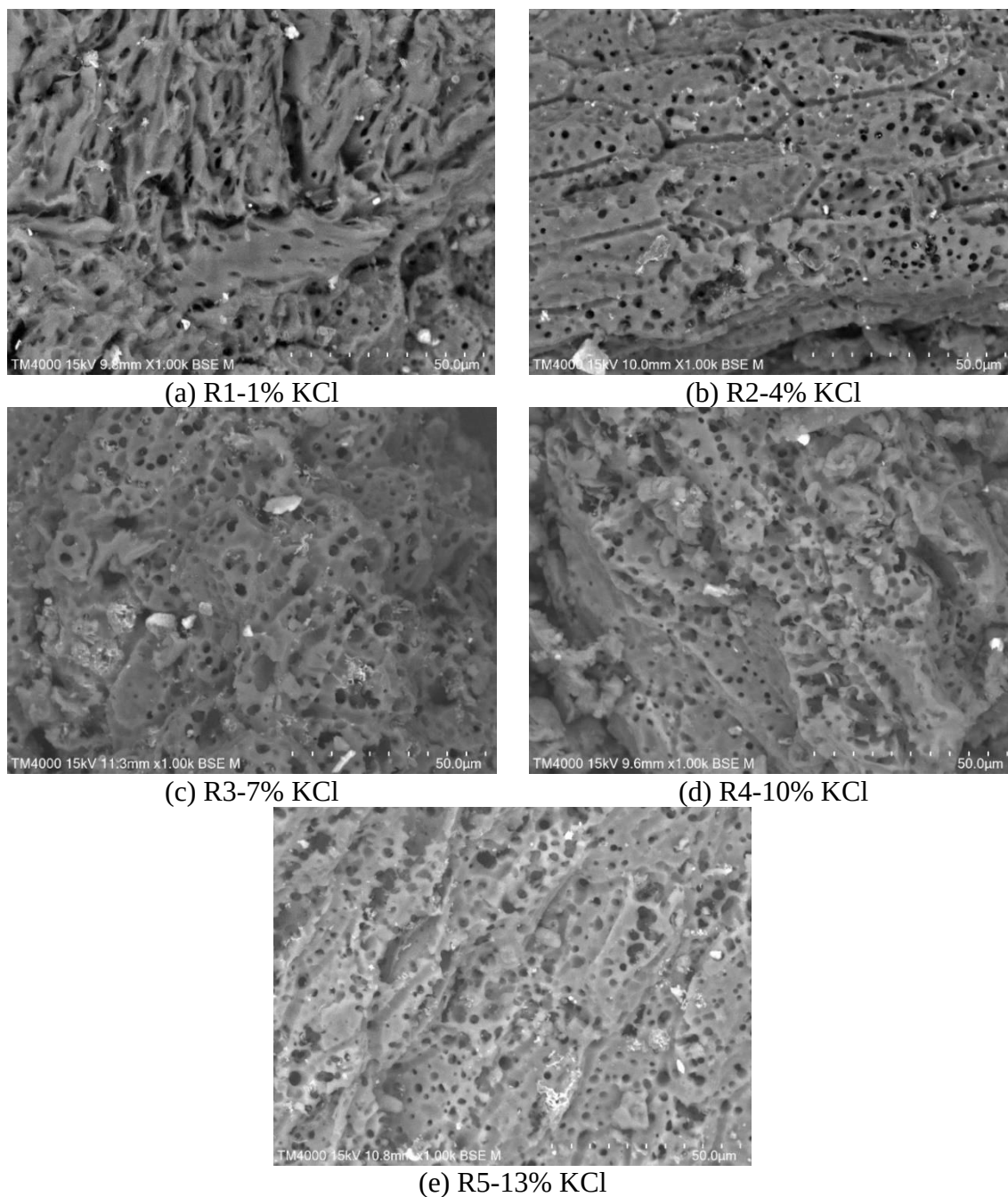


Figure 5.5: SEM images of activated carbon produced with different concentration of KCl (a) 1%, (b) 4%, (c) 7%, (d) 10% and (e) 13%.

Figure 5.6 shows the porous structure developed on the surface of the HCl-AC with different HCl concentrations. Porous surfaces are able to be observed clearly on all of the replicates. For R1 and R3, the pores are more arranged and organized, as compared to other replicates. For R2, the structure of the pores are a little ruptured.

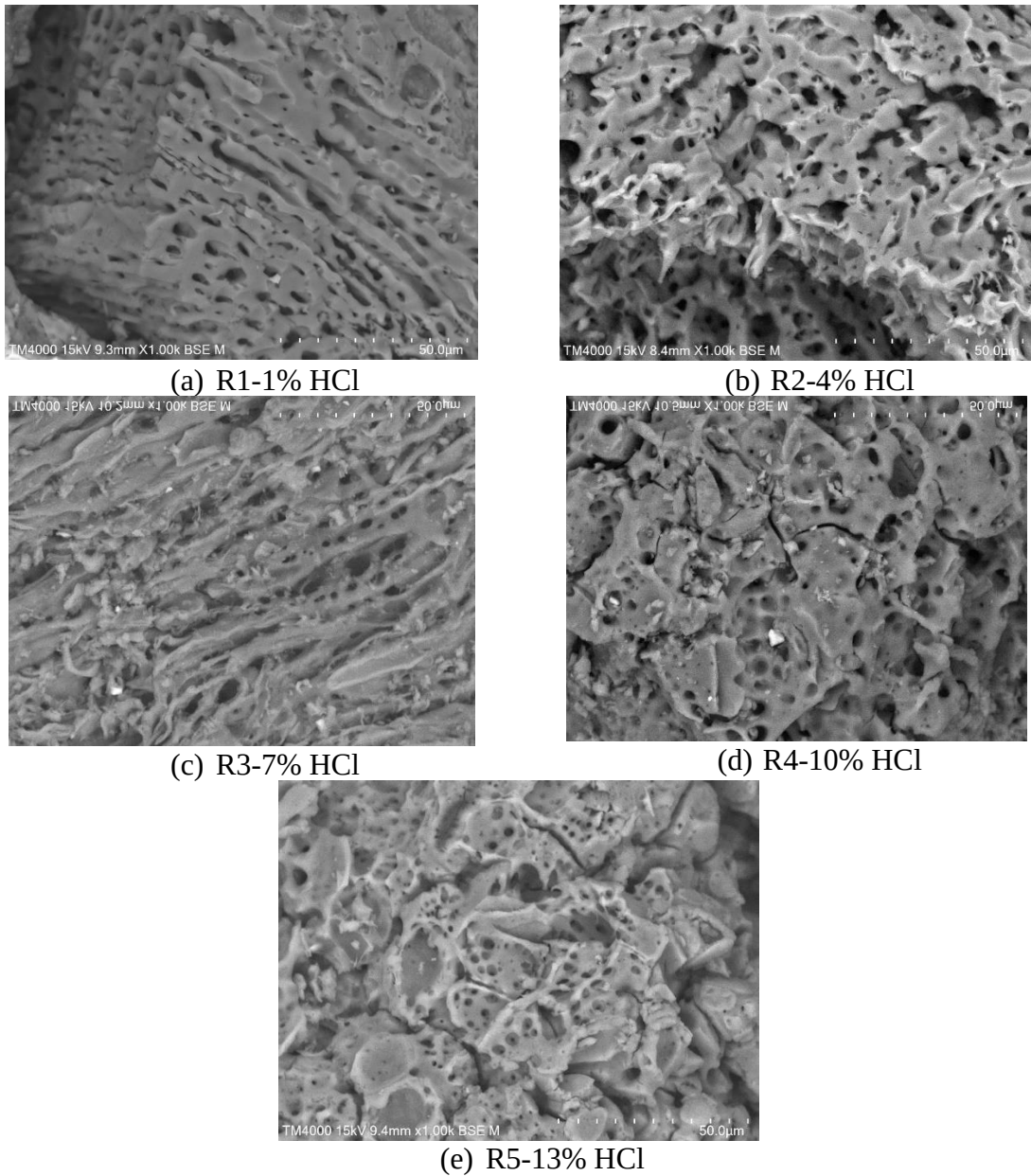


Figure 5.6: SEM images of activated carbon produced with different concentration of HCl (a) 1%, (b) 4%, (c) 7%, (d) 10% and (e) 13%.

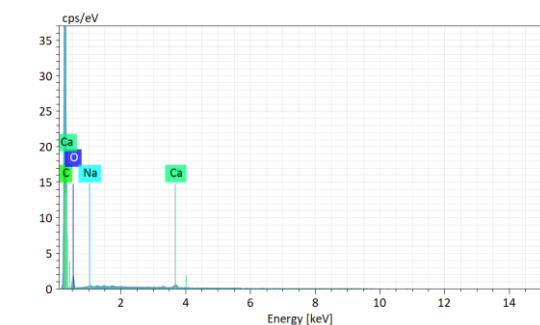
5.3 Energy Dispersive X-ray (EDX) Spectra and Elemental Analysis of Activated Carbon

Figure 5.7 displays all of the EDX spectra for the NaOH-AC replicates, and Table 5.1 displays the elemental mass composition of the NaOH-AC repeats. With mass percentages of 79–90% for carbon and 7.5–16.6% for oxygen, it can be seen that all duplicates are dominated by carbon components, suggesting that the majority of the volatile elements in the precursor were eliminated during carbonization and chemical activation. This is consistent with elemental properties of NaOH-AC derived from coconut shell in a study conducted by (Sujiono et al., 2022), where the AC are dominated by carbon and oxygen, up to 90.56% and 7.66% mass percentage respectively. The elemental composition of the NaOH-AC replicates are also comparable to those of the AC derived using KOH from agriculture wastes (coconut shell, palm kernel shell and wood sawdust), in a study conducted by Habeeb et al. (2020), where the ACs are dominated by carbon and oxygen. Impurities are trace portions of other elements, such as zinc, silicon, and aluminium, that exist as clay and aluminium foil are used in the experiment.

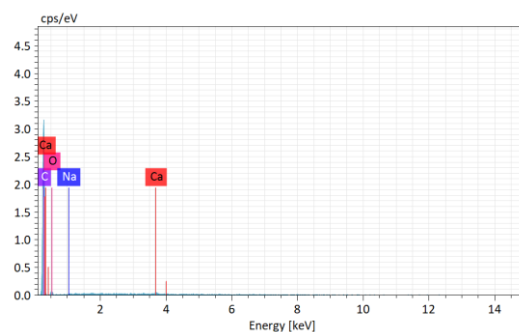
Among the replicates, NaOH-AC with 7% concentration of NaOH, have the highest carbon mass percentage, as compared to other replicates due to less presence of oxygen and calcium. The replicate are also not containing trace elements such as magnesium and zinc, which is probably coming from the reusable clay. On the other hand, NaOH-AC with 13% chemical activation is observed to have the lowest carbon mass percentage, due to high percentage of oxygen, calcium, and sodium (assumed to be the excess presence due to chemical activation). Further in section 5.5, the high percentage of oxygen and calcium caused highest presence of ash in this replicate. The sample is also observed to have trace presence of magnesium and zinc, which might come from the reusable clay.

Table 5.1: Elemental mass percentage of AC from NaOH activation

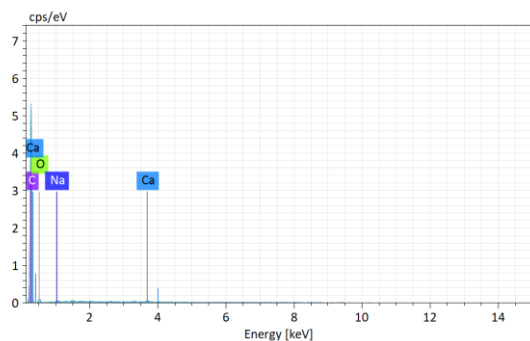
Elements	NaOH Concentration (%)				
	1	4	7	10	13
C	89.0335	89.586	90.3399	84.4292	79.1139
O	10.1068	9.1157	8.3818	7.6987	16.5483
Al	-	-	-	6.5142	-
Ca	0.6425	0.7977	0.6228	1.0202	2.5846
Na	0.2172	0.5005	0.6554	0.3378	1.4042
Mg	-	-	-	-	0.2123
Zn	-	-	-	-	0.1368
Total	100.00	100.00	100.00	100.00	100.00



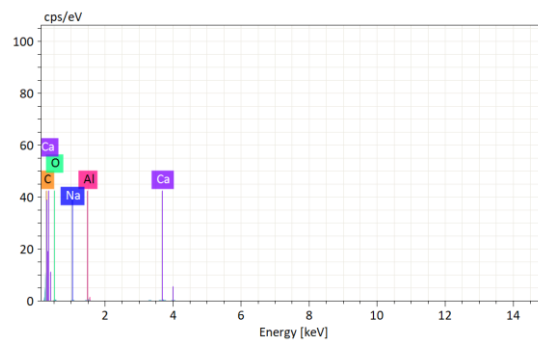
(a) R1-1%



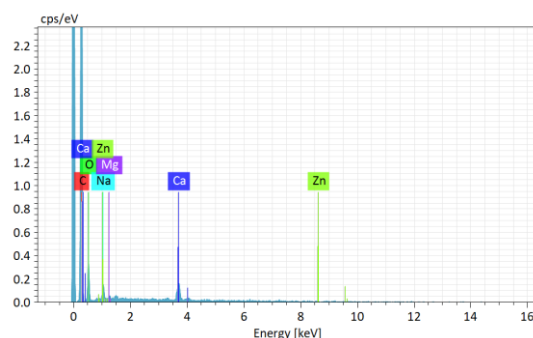
(b) R2-4%



(c) R3-7%



(d) R4-10%



(e) R5-13%

Figure 5.7: NaOH-AC EDX Spectrum

Table 5.2 and Figure 5.8 represents the elemental mass percentage of the AC synthesised through KCl-activation. The samples are observed to have similar range of C and O mass percentage to NaOH-AC, and having dominant percentage of carbon, ranging from 85-90%. The dominance of C and O in the elemental composition of the KCl-AC are comparable to AC derived using ZnCl_2 , from coconut shell, in research conducted by Sujiono et al. (2022) where the carbon and oxygen mass percentage are 90.44% and 7.45% respectively.

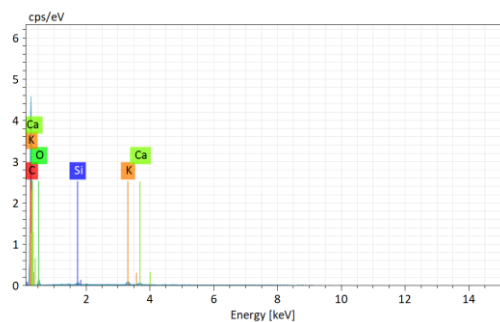
KCl-AC with 10% KCl impregnation is observed to have the highest carbon mass percentage, due to the less presence of other elements. The ash content (later explained in section 5.5) for this replicate are relatively lower as compared to other replicates. Higher percentage of oxygen can be observed for NaOH-AC replicates as compared to KCl-AC replicates. The minor presents of other elements such as aluminium and silicon are classified as impurities, which might be caused by the usage of aluminium foil and reusable clay for the experiments.

Table 5.2: Elements mass percentage for AC from KCl activation

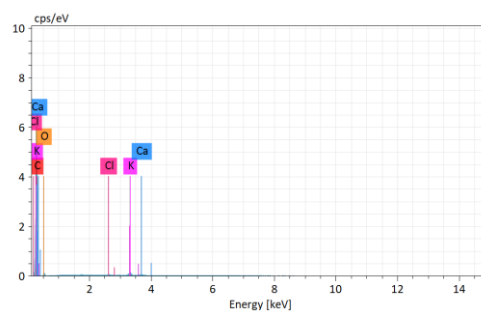
Elements	KCl Concentration %				
	1	4	7	10	13
C	85.8588	89.9874	86.4151	90.1314	89.5328

Table 5.2 Continued

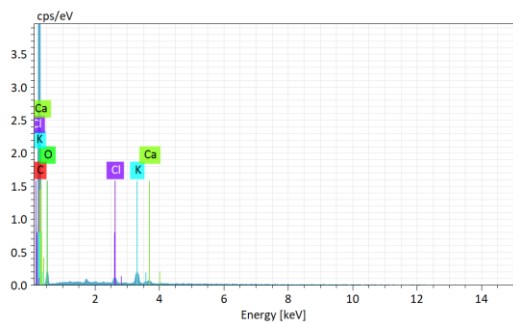
O	11.2160	7.4027	10.1907	5.7380	6.4729
K	1.4282	1.5772	2.0647	1.0735	1.1509
Ca	0.8614	0.5615	0.6099	-	-
Si	0.6355	-	-	-	-
Cl	-	0.4711	0.7195	0.5968	0.4412
Al	-	-	-	2.4602	1.9894
N	-	-	-	-	0.4129
Total	100.00	100.00	100.00	100.00	100.00



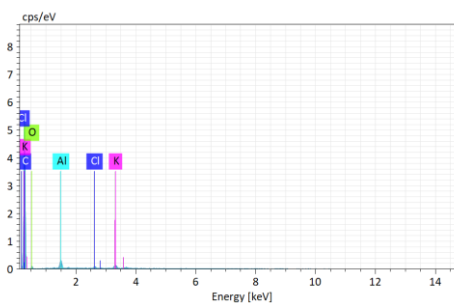
(a) R1-1%



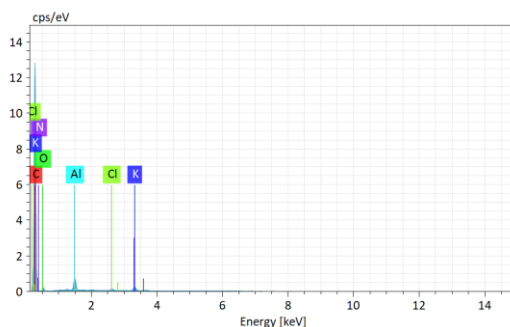
(b) R2-4%



(c) R3-7%



(d) R4-10%



(e) R5-13%

Figure 5.8: KCl-AC EDX spectrum

For HCl-AC replicates, the elemental mass percentage are as shown in Table 5.3 and Figure 5.9. The AC is dominated by carbon, which is observed to have more than 84% as compared to other elements. The elemental composition of the HCl-AC replicates are comparable to the AC derived using phosphoric acid from potato peel waste, synthesized in a study performed by Osman et al. (2019). The AC is observed to have more than 88% carbon mass percentage and less than 10% oxygen mass percentage. HCl-AC synthesised using 10% HCl has the highest carbon mass percentage, while having lowest oxygen presence in it. This is due to low percentage of elements such as Cl, Al, and N, as compared to other replicates.

The presence of Cl in all replicates are due to the residue of the elements after the chemical activation and appeared to be the highest at 13% HCl impregnation. Other elements are considered as impurities due to its low percentages.

Table 5.3: Elements mass percentage for AC from HCl activation

Elements	HCl Concentration %				
	1	4	7	10	13
C	87.7292	84.2915	87.4566	88.0676	85.1734
O	10.5035	14.3607	12.0810	6.6314	13.9353
Si	1.6798	-	-	-	
Cl	0.0875	0.1644	0.0001	0.1389	0.2796
Ca	-	0.6865	0.4622	-	
Al	-	0.4968	-	2.3200	0.2363
N	-	-	-	2.8421	
K					0.3754
Total	100.00	100.00	100.00	100.00	100.00

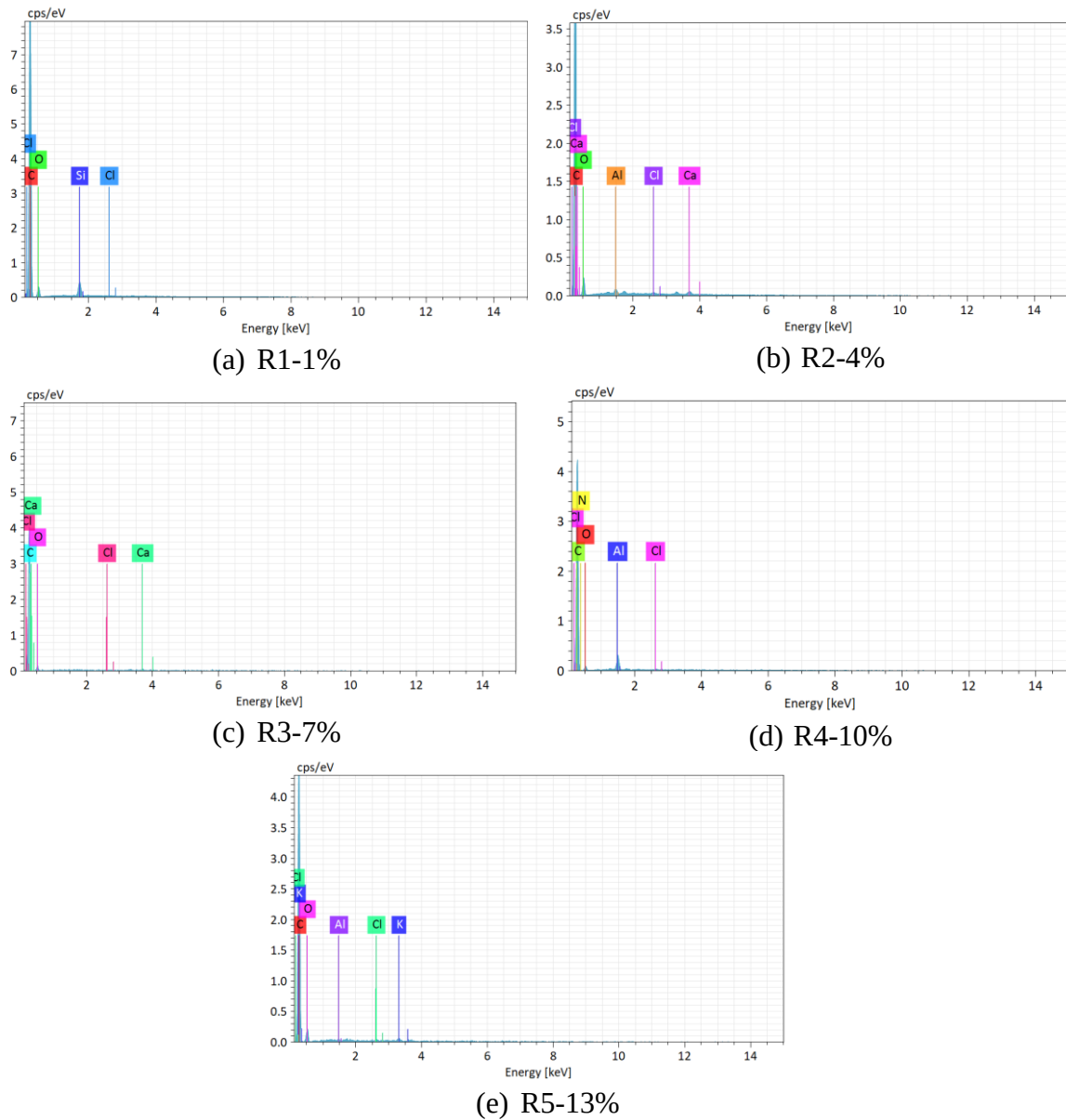


Figure 5.9: HCl-AC EDX spectrum

Figure 5.10 and Figure 5.11 shows the oxygen and carbon mass percentage respectively for NaOH-AC, KCl-AC and HCl-AC replicates. The linear trendline for the oxygen mass percentages are shown to be increasing for NaOH-AC as the impregnation of NaOH increases, while the carbon mass percentage are decreasing for the replicates. The HCl-AC replicates shows different trendline, where for both oxygen and carbon mass percentage are slightly decreasing as the HCl concentration for the impregnation increases.

For KCl-AC replicates, the linear trendline is shown to be decreasing for the oxygen mass percentage, and increasing for the carbon mass percentage, as the KCl impregnation concentration increases. Higher percentage of carbon mass are desirable as the carbon provides the skeletal structure for pores (Rodríguez-Reinoso & Sepúlveda-Escribano, 2001), while higher oxygen presence are desirable for the adsorption of volatile organic compounds by increasing the polarity of the activated carbon surfaces (Chen et al., 2020).

The presence of elements other than carbon and oxygen in the resulting replicates of AC are stated to be impurities or residue from the activating agent used. Silicon and aluminium as an example, were exist the adsorbents due to the utilization of reusable clay and aluminium foil, in order to cut off the input of oxygen into the crucible which can lead to combustion of the precursor material. In future investigations, better air insulation should be administered to further reduce presence of those impurities while maintaining the absence of inert gas flow.

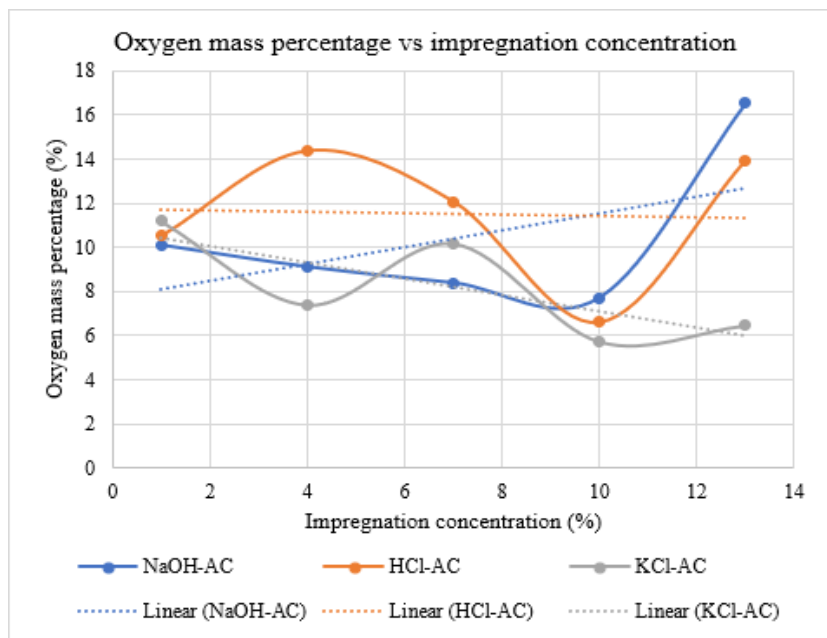


Figure 5.10: Oxygen mass percentage for the AC replicates

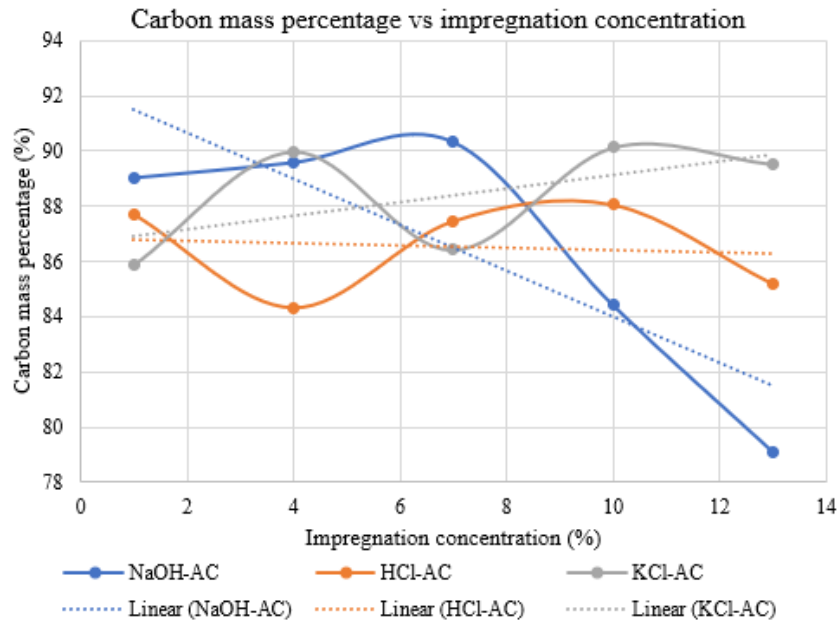


Figure 5.11: Carbon mass percentage for the AC replicates

5.4 Percentage of Ash Content of the Activated Carbon

Figure 5.12 shows the ash content percentage of the AC replicates from different chemical activation path. All replicates are observed to have acceptable range of ash content, which is below 10% (Zulkania et al., 2018), and are lower than the char's ash content as mentioned in Table 5.1, where all char replicates are having ash content percentage between 3 to 4 %. The chemical activation process are proven to help reduce the presence of ash on the adsorbent. This range is below 8% (ASTM) and 10% (Malaysia Standard and Standard National Indonesia), which is the maximum percentage of ash content allowed (Maulina and Iriansyah, 2018; Olowoyo and Orere, 2012). Vasiraja et al. (2023) stated that the high fixed carbon content value was enhanced as the ash content value decreases. A high ash percentage may diminish mechanical strength and impact carbon adsorption capability (Vasiraja et al., 2023).

The linear trendline in Figure 5.1 shows that for the replicates of NaOH-AC and KCl-AC, the ash content are observed to be increased as the concentration of the activating agents

increased. These results are consistent with the elemental composition of the AC replicates shown in Tables 5.1 and 5.2, where the percentage of oxygen and metal mass in the adsorbents increases. According to Vassilev et al. (2017), it is generally acknowledged that the components that create ash in biomass include Al, Ca, Cl, Fe, K, Mg, P, Na, S, Mn, Si, and Ti, and that these elements contribute to various technological and environmental problems during the biomass process.

For HCl-AC replicates, as the concentration of the HCl for impregnation increased, the amount of ash content only varies slightly, which is consistent to a study conducted by Mariah et al. (2023). The study discovered that the slight variation of ash content for the activated carbon derived using sulphuric acid with concentration between 5-10%, which is between 5.64-5.47%.

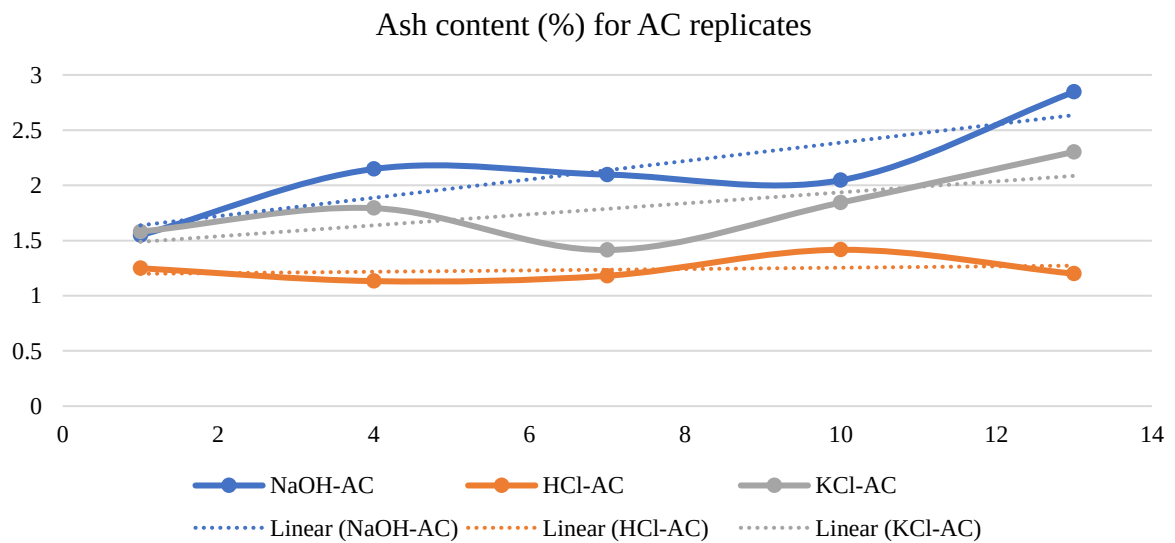


Figure 5.12: Ash content for AC replicates

5.5 Brunauer-Emmett-Teller (BET) Surface Area Analysis of Activated Carbon

This section explains the surface area analysis and nitrogen adsorption isotherm of activated carbon derived from NaOH activation only, due to the limitations of the BET surface analyser (Quantachrome Instrument) on its availability to perform analysis.

5.5.1 Surface Area Analysis of the Activated Carbon

The surface area characteristics of NaOH-AC replicates are shown in Table 5.4. All replicates' BET surface area is equivalent to that of other AC produced from renewable resources (Ioannidou & Zabaniotou, 2007). The AC replicates are at higher quality as compared to rice husk-derived AC, which is produced at a temperature of 750 °C while using the same concentration of NaOH for the activation (Saad et al., 2020). Increasing the impregnation concentration from 1-7% increases the surface area and pore volume, with the greatest value of BET surface area and total pore volume are obtained by employing 7% NaOH for the impregnation since the characteristics are not significantly different between each duplicate. Further increase in concentration of NaOH resulted the decrease in surface area and pore volume. These results are similar to a research conducted by Ramakrishna Gottipati, (2012) on synthesizing activated carbon from Bael fruit shell for chromium (IV) adsorption using KOH activation. Similar trend of increase and decrease in BET surface area and pore volume are observed in the study as the KOH impregnation increase (Gottipati, 2012). The average pore sizes for all replicates are considered to be in micropores range (less than 20 Å or 2 nm).

Surprisingly, compared to both AC and a nano-carbon combination made from the same precursor material but activated with KOH, which had BET surface areas of 5.09 m²/g and 25.8 m²/g, respectively, the synthetic AC replicates have a larger surface area. (James et al., 2022). The properties of the NaOH-AC, however, are lower than those from a related experiment using phosphoric acid, which ranged from 564 to 1024 m²/g (Vicinivarri et al., 2014).

Table 5.4: Surface area properties of the NaOH-AC replicates.

NaOH impregnation concentration (%)		BET surface area (m ² /g)	Average pore size (radius) (Å)	Total pore volume (cm ³ /g)
R1	1	344	11.628	0.200
R2	4	341	11.759	0.201
R3	7	355	11.831	0.210
R4	10	328	11.859	0.194
R5	13	349	11.859	0.207

5.5.2 Nitrogen Adsorption Isotherm of the Activated Carbon

The NaOH-AC replicates' nitrogen adsorption isotherm is shown in Figure 5.13. Similar curves can be regarded as agreeing with the Type II isotherm of the IUPAC categorization across all replicates. The physisorption of gases on non-porous or macroporous surfaces is described by this isotherm. The form is caused by uncontrolled monolayer-multilayer adsorption up to high relative pressure at the same time (Thommes et al., 2015). Because of the low range concentration of NaOH used for chemical activation, the nonporous-macroporous surface of the AC may be in this condition. Even while all SEM photos of the AC duplicates reveal porous surfaces, the success of the formation of the pores in assuring excellent adsorption capabilities cannot be determined by those representations.

As the impregnation concentration increases from 1 to 7%, nitrogen adsorption is observed to be increasing, and decreases as the concentration to 10 and 13% NaOH-AC. This is the result of the low-pressure hysteresis, which an artifact associated with the lack of equilibrium in the adsorption isotherm and/or the lack of proper outgassing, mainly found in porous solids where narrow pore constrictions are expected (Gottipati, 2012; Silvestre-Albero et al., 2012).

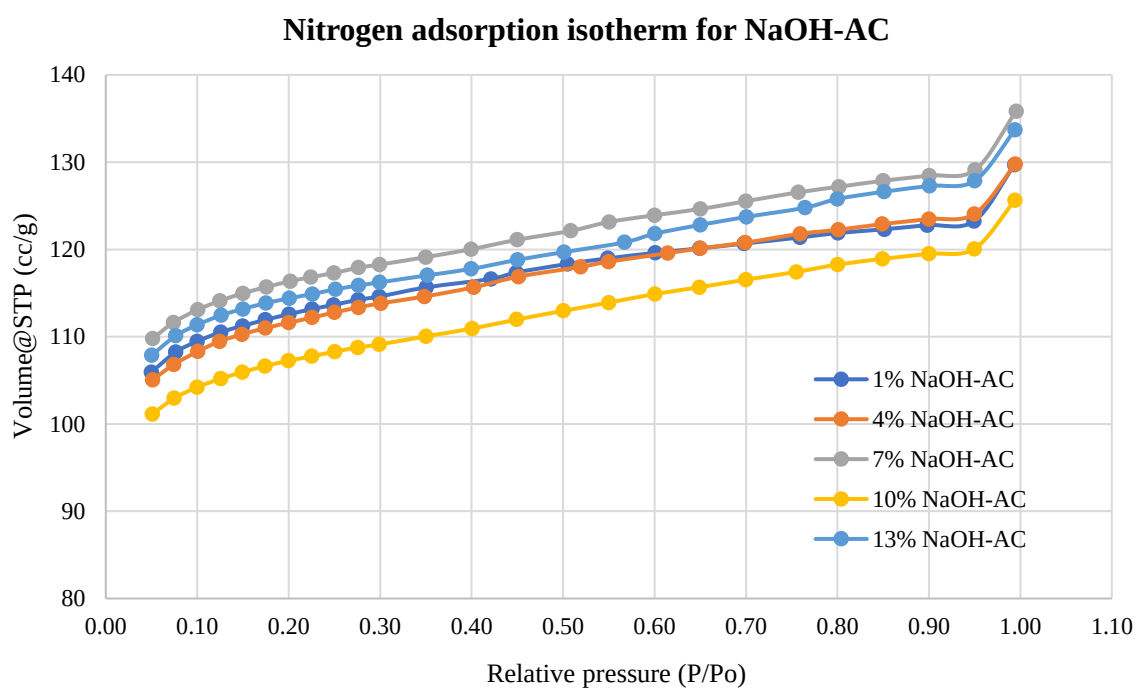


Figure 5.13: Nitrogen adsorption isotherm of the NaOH-AC replicates

CHAPTER 6

ADSORPTION PERFORMANCE OF ACTIVATED CARBON

Overview

This chapter describes the adsorption performance of the activated carbon (AC) on the dye methylene blue (MB), heavy metal ions solutions, to study the capability of the adsorbent for removal of water pollutants.

6.1 Adsorption of Methylene Blue Solution by Dabai AC.

The evaluation of adsorption of MB solution is first performed by placing 0.2g of AC into 100 ml of 30 ppm MB solution. The highest adsorbing AC is selected for kinetic study of MB adsorption.

6.1.1 Adsorption of 30 ppm MB Solution on Dabai AC Replicates

Figure 6.1 shows the methylene blue removal performance for the AC replicates derived from dabai nutshell after 24 hours. Among the AC replicates, NaOH-AC replicates are the adsorbents with adsorption rate higher than 10 mg/g, and more than 70% removal of MB. Replicates from acidic and salt activation (HCl-AC and KCl-AC) are observed to have lower MB removal, with more than 4 mg/g MB adsorbed, and 40% of MB removal.

All replicates however are having low adsorption uptake, lower than the standard (60-120 mg/g) as mentioned by Hanum et al. (2017). This condition are due to the microporous structure of the AC as described in Table 5.4, where MB uptake was significantly slower at the microporous range as stated by Ighalo et al. (2021). For NaOH-AC and KCl-AC replicates, as the impregnation concentration increases, the MB removal

decreases. HCl-AC replicates however showed a different pattern, where the MB removal percentage slightly increases as the impregnation concentration increases.

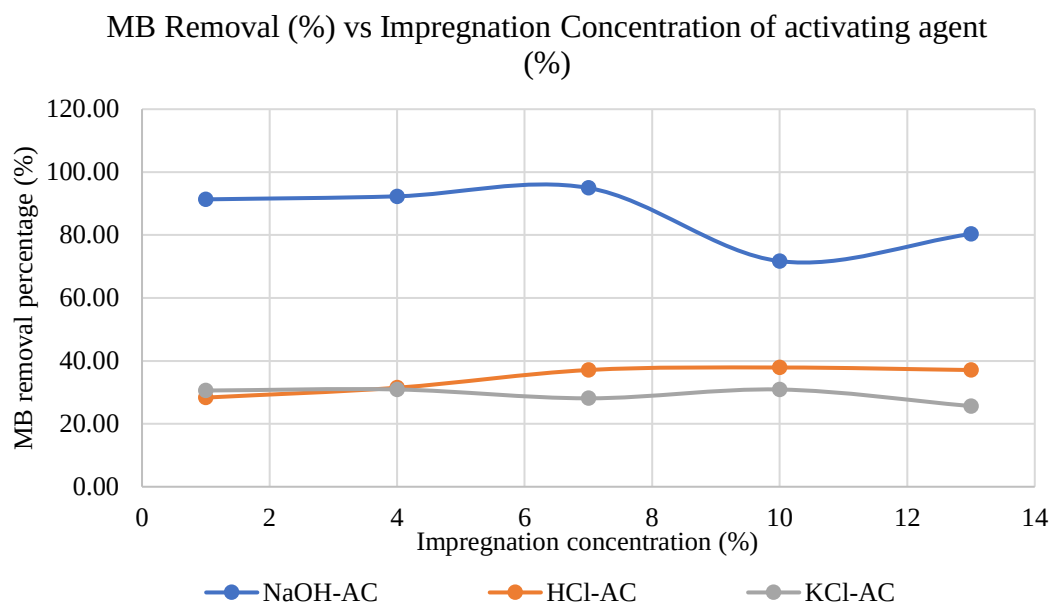


Figure 6.1: MB removal performance for the AC replicates

6.1.2 Kinetic Study of MB Adsorption on Dabai AC Replicates

Figure 6.2 shows the adsorption of 10 ppm MB solution by AC replicates for 2 hours. As the contact time progressed, the amount adsorbed onto the surface of the activated carbons increased. The adsorption for all replicates of NaOH-AC and KCl-AC is observed to achieve equilibrium after 120 minutes, but not for HCl-AC replicates. It has been observed that during dye adsorption, the dye molecules must first permeate into the adsorbent surface before slowly diffusing into the porous build of the adsorbent (Bello et al., 2021; Li et al., 2013).

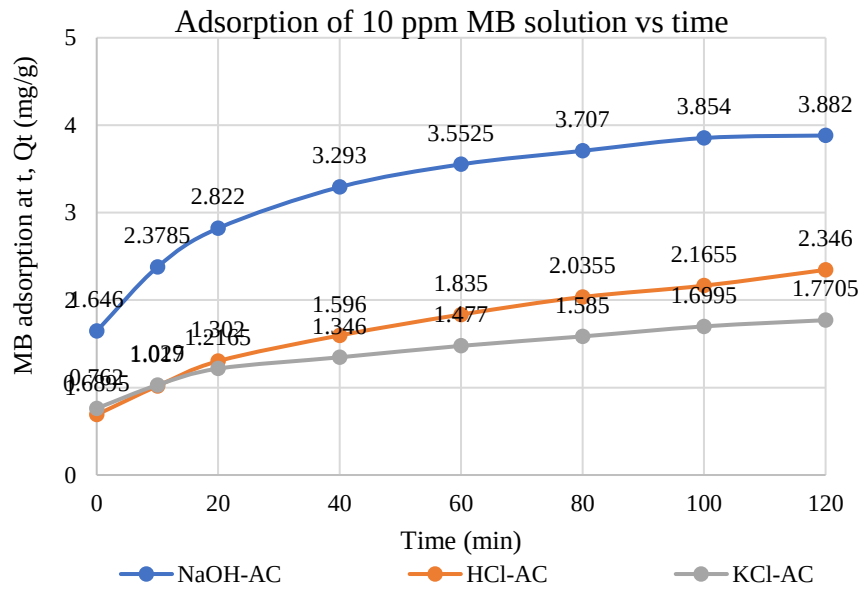


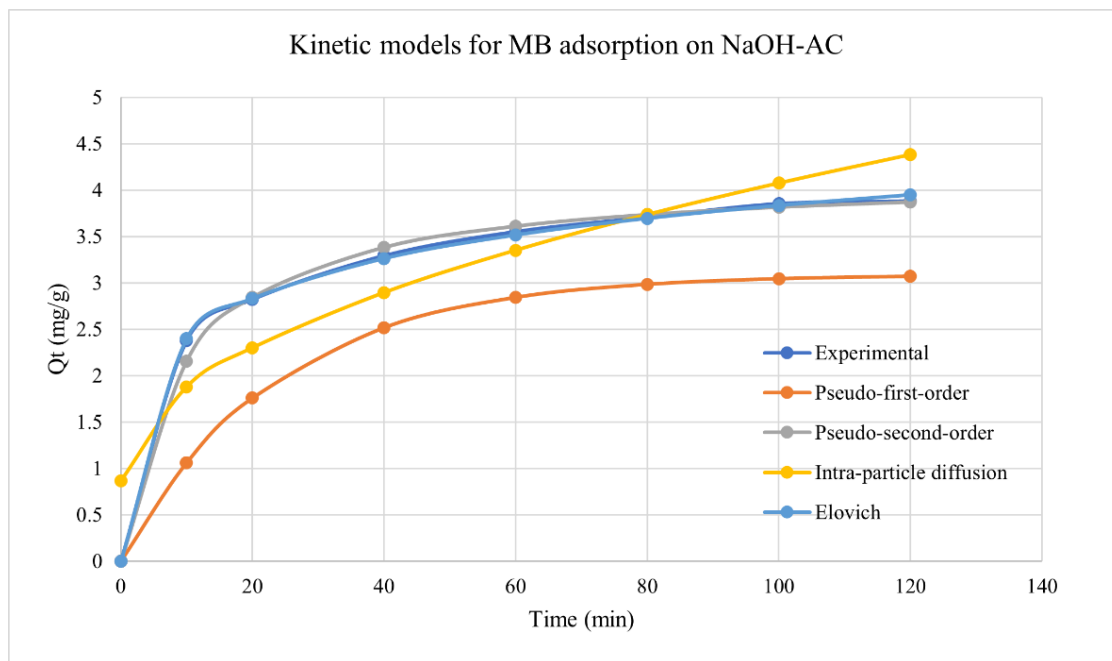
Figure 6.2: Adsorption of 10 ppm MB solution over the time using the AC replicates.

To help the calculation of kinetic parameters of the pseudo-first-order (PFO) and pseudo-second-order (PSO) models for HCl-AC replicates, the adsorption is assumed to be achieved after 120 minutes. The parameters of the PFO, PSO, intra-particle diffusion (ID) and Elovich models for all the AC replicates are stated in Table 6.1, while the representation of kinetic models are shown in Figure 6.3 (a), (b) and (c). Among all the kinetic models, the most suited model to the experimental data of MB adsorption is pseudo-second-order kinetic model. The regression correlation, R^2 of PSO for all replicates of AC are closer to 1.00 and higher than R of PFO and ID. This fit of pseudo-second-order implies that chemical interaction had a role in the adsorption of MB onto activated carbons (Bello et al., 2021; Pathania et al., 2017). However, for the duration of 0 to 60 minutes, the adsorption kinetics are observed to be more suited on Elovich model, as the R^2 (Elovich) for that duration is higher than R^2 for PSO, and curve of the experimental data is more assimilating the Elovich model. This condition indicates that chemical adsorption occurs during that first 60 minutes, and the Elovich kinetic model are usually utilized to describe adsorption occurring on the

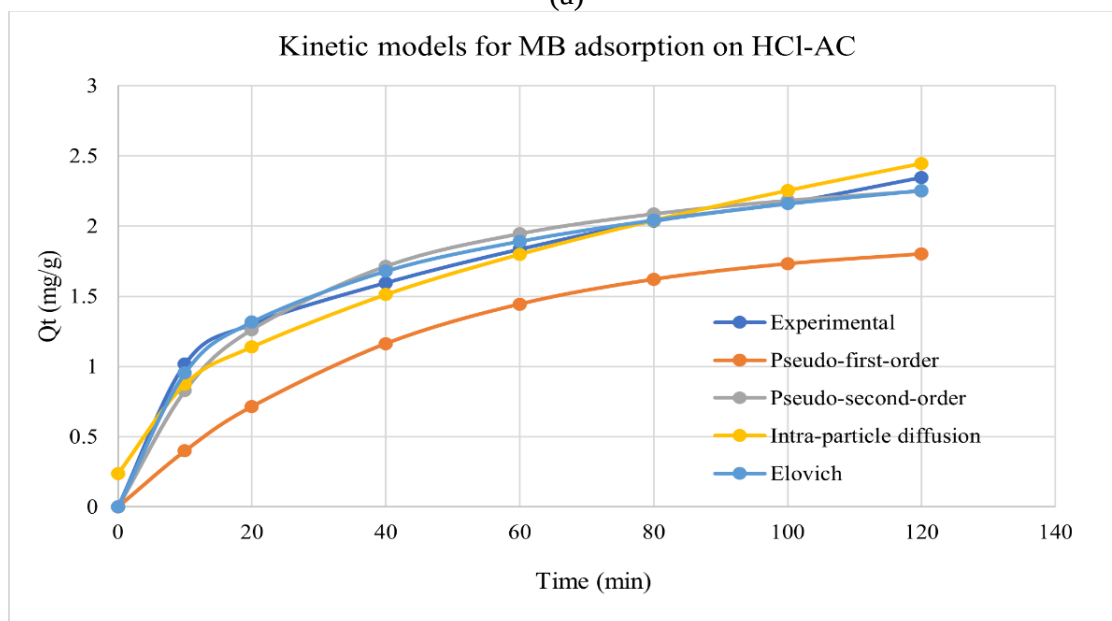
heterogeneous adsorbing surfaces (Aharoni & Tompkins, 1970; Wu et al., 2009). Aharoni and Tompkins, (1970) describes that for this model, as the amount adsorbed rises, the rate of adsorption drops exponentially.

Table 6.1: Kinetic parameters of adsorption of MB onto NaOH-AC, HCl-AC and KCl-AC

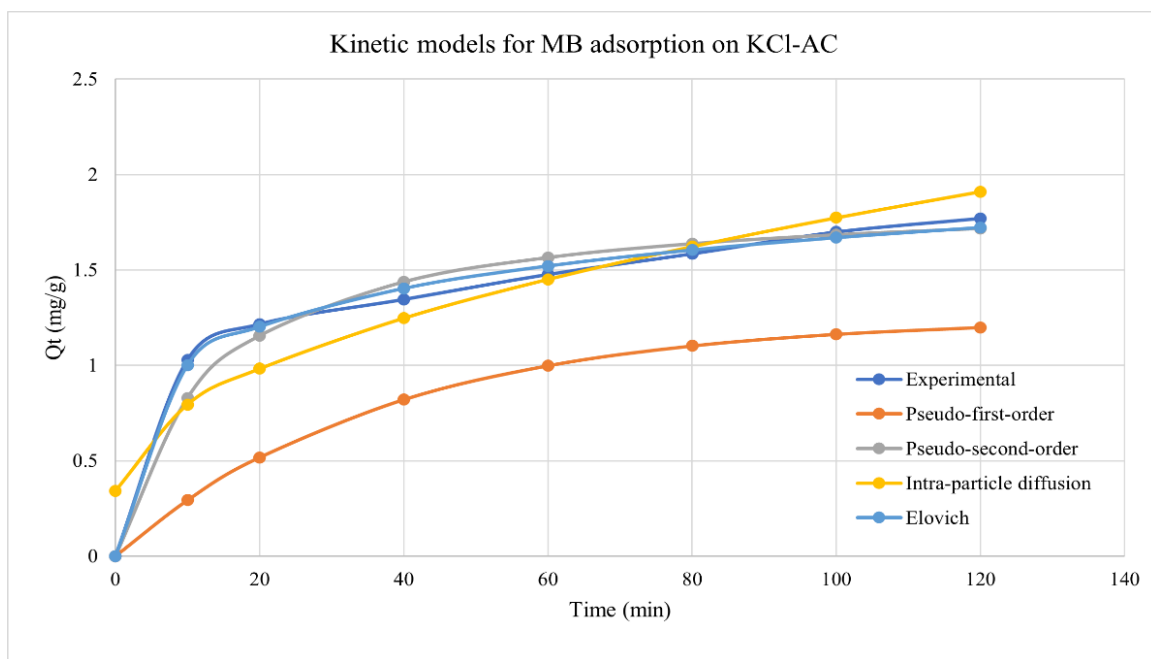
Parameter	NaOH-AC	HCl-AC	KCl-AC
<i>Pseudo First Order</i>			
$Q_{e, \text{exp}}$ (mg/g)	3.882	2.346	1.771
$Q_{e, \text{cal}}$ (mg/g)	3.0925	1.919	1.249
k_1 (min^{-1})	0.0421	0.0233	0.0267
R^2	0.9750	0.9905	0.9697
<i>Pseudo Second Order</i>			
$Q_{e, \text{exp}}$ (mg/g)	3.882	2.346	1.771
$Q_{e, \text{cal}}$ (mg/g)	4.171	2.667	1.903
k_2 (g/mg min)	0.0257	0.0169	0.0406
R^2	0.9996	0.9939	0.9960
$R^2(0\text{-}60 \text{ minutes})$	0.9994	0.9973	0.9988
<i>Intra-particle diffusion</i>			
C (mg/g)	0.8646	0.2016	0.3415
k_{id}	0.3211	0.2365	0.1432
R^2	0.9220	0.9840	0.9398
<i>Elovich kinetic model</i>			
α (mg/g min)	2.9145	0.3233	0.9117
β (g/mg)	1.6027	1.9095	3.4440
R^2	0.9980	0.9917	0.9884
$R^2(0\text{-}60 \text{ minutes})$	0.9999	0.9974	0.9960



(a)



(b)



(c)

Figure 6.3: Comparison of the experimental data of 10 ppm MB adsorption on (a) NaOH-AC, (b) HCl-AC and (c) KCl-AC, towards kinetic models of adsorption

6.2 Adsorption of Heavy Metal Ions Solutions on Dabai AC Replicates

The adsorption uptake of lead ions by the AC replicates is shown in Table 6.2 and Figure 6.4. All replicates are able to absorb more than 10 mg/g of the lead ions from 30 ppm lead ions solution, with removal performance up to 35%. For NaOH-AC and KCl-AC replicates, the q_e values are observed to increase as the concentration of NaOH increases. A different trend is observed to occur for HCl-AC replicates, where removal performance is decreasing as the HCl concentration increases. The adsorption uptake range of Pb^{2+} ions for all of the AC replicates is 10-20.575 mg/g, which is lower than commercial activated carbon which is at 42.5 mg/g (Shahrokhi-Shahraki et al., 2021) and activated carbon derived from olive branch, which is at 41.32 mg/g (Alkherraz et al., 2019). However, the adsorption uptake of lead ions for Dabai-AC replicates is comparable to AC derived from black cumin seed, which ranges from 17.19 to 17.98 mg/g (Thabede et al., 2020). As comparison to the

Malaysian Standard for AC (Department of Standards Malaysia, 2005), all dabai AC replicates are able to exceed the limit of the Pb^{2+} adsorption, which is 0.05 mg/g.

The adsorption uptake of Pb ions are increasing as the impregnation concentration of NaOH increases and are the highest as compared to other Dabai AC replicates. According to Lalhrulaitluanga et al. (2010), The adsorption capacity of biomass was increased by alkali pretreatments. The hydrolysis of certain metals by residual alkalinity may increase the adsorption capacity of biomass (Lalhrulaitluanga et al., 2010).

The decreasing trend of Pb adsorption as the impregnation concentration of HCl-AC are consistent to the result of a study conducted by Boudrahem et al. (2021), where the sorbed amount of Pb ions decreases as the concentration of the nitric acid used for chemical activation of olives stones for the synthesis of AC, increases from 1M to 3M. Similar observations are obtained in a study conducted by T. Xu and Xiaoqin, (2008), where increasing the concentration of nitric acid for chemical activation reduces the lead ions removal capacity of the activated carbon derived from peanut shell, from 35.36 mg/g to 10.93 mg/g. The researchers stated that drastic conditions used in the oxidation step led to the collapse of some pore walls, so the very low surface area and pore volume (T. Xu and Xiaoqin, 2008).

Table 6.2: Adsorption of lead ions by AC replicates

Impregnation concentration (%)	NaOH-AC	HCl-AC	KCl-AC
	Pb^{2+} adsorbed, q_e (mg/g)	Pb^{2+} adsorbed, q_e (mg/g)	Pb^{2+} adsorbed, q_e (mg/g)
1	10.790	15.431	13.641
4	12.707	17.569	15.156
7	14.407	16.808	14.054
10	13.216	6.928	16.461
13	20.575	8.509	16.940

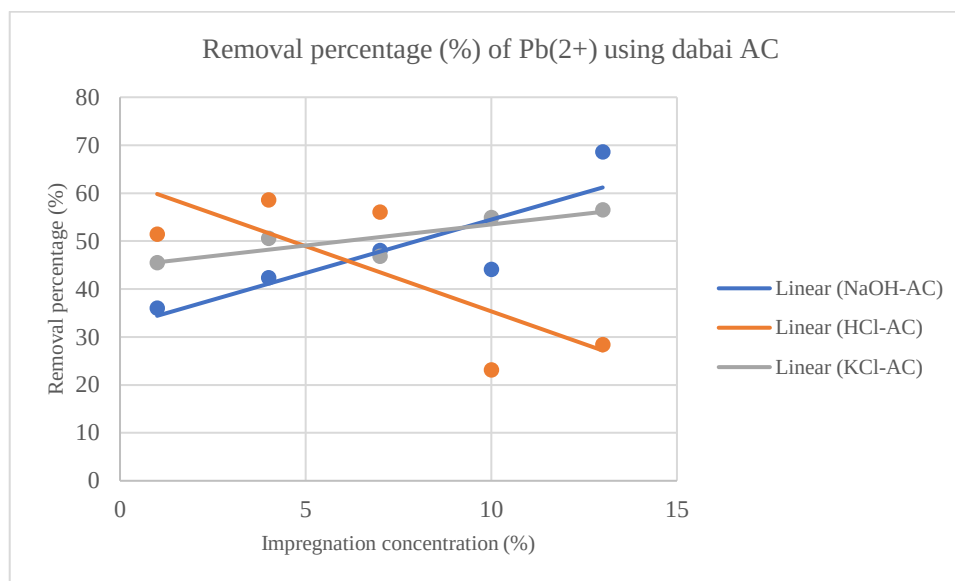


Figure 6.4 Removal percentage of lead ions using dabai AC

Table 6.3 shows the performance of Dabai AC replicates for the removal of zinc ions from 30 ppm zinc ions stock solution. The adsorption capacity of Zn^{2+} ions is more than 27 mg/g for all of the AC replicates, with removal efficiency is more than 90%. HCl-AC and KCl-AC replicates are observed to have slightly higher removal efficiency than NaOH-AC replicates. The adsorption performance of Zn^{2+} ions for all Dabai AC replicates is comparable to AC derived from olive branch, which is at 34.97 mg/g (Alkherraz et al., 2019), 95% removal efficiency for 20 mg/L of zinc ions (at initial condition), using AC derived from pinecone (G. A. Ali et al., 2023) and higher than adsorption uptake of zinc on AC derived from foxtail palm fruit which is 0.57 mg/g (Sairan et al., 2019).

The similar adsorption uptake for all of the dabai nutshell AC replicates are consistent to an experiment conducted by Hasar et al. (2003) on removal of zinc ions using AC derived from almond husk. The adsorption of the zinc on the AC surface are remain at 94% for all of the AC replicates derived with concentration of the chemical activating agent greater than 4 g/l (0.4%); where in the experiment, the researcher used up to 40 g/l (4%)

which indicates at certain range concentration of the activating agents, the adsorption intake of zinc ions did not varied. (Hasar et al., 2003).

Table 6.3: Zn ions removal using Dabai AC replicates

Impregnation concentration (%)	NaOH-AC	HCl-AC	KCl-AC
	Zn ²⁺ adsorbed, q _e (mg/g)	Zn ²⁺ adsorbed, q _e (mg/g)	Zn ²⁺ adsorbed, q _e (mg/g)
1	27.253	27.731	27.75
4	27.294	27.796	27.806
7	27.295	27.795	27.81
10	27.321	27.804	27.79
13	27.325	27.803	27.791

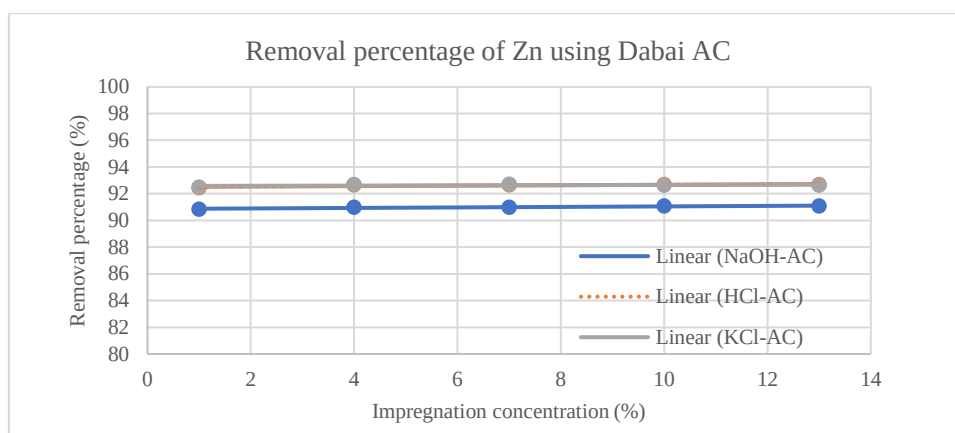


Figure 6.5: Removal performance of Zn ion using Dabai AC

Table 6.4 represents the removal performance of Cr³⁺ using the Dabai AC replicates, where the concentration of the Cr³⁺ stock solution is 30 ppm. All replicates of Dabai AC have adsorption uptakes ranging from 13.5 to 16.35 mg/g, with removal efficiency ranging from 45 to 50%. When compared to the Malaysian standard (Department of Standards Malaysia, 2005), all dabai AC replicates are able to exceed the limit, which is 0.05 mg/g. The performance for Cr³⁺ removal for all of the replicates are higher than activated carbon derived from marigold palm leaves, which is synthesised in a study conducted by Singanan

and Peters, (2013). The AC from the mentioned study able to achieve the chromium adsorption capacity of 1.902 mg/g.

Table 6.4: Chromium adsorption using Dabai AC replicates

Impregnation concentration	NaOH-AC	HCl-AC	KCl-AC
	Cr³⁺ adsorbed, q_e (mg/g)	Cr³⁺ adsorbed, q_e (mg/g)	Cr³⁺ adsorbed, q_e (mg/g)
1	14.029	16.354	15.768
4	13.992	16.089	15.247
7	13.927	16.018	14.965
10	13.737	16.056	15.478
13	13.525	16.239	15.122

CHAPTER 7

CONCLUSION

7.1 Conclusion

This study has concluded that biochar and activated carbon are successfully derived from dabai nutshell without the utilization of inert gas flow during both carbonization and chemical activation. Dabai biochar are shown to have comparable characteristics with other lignocellulosic biomass used for synthesis of activated carbon.

The char derived using a conventional furnace without the usage of any inert gas flow has similar properties with the char synthesized using high temperature muffle furnace with continuous argon or nitrogen gas flow, which indicates the suitability of the carbonization method with the absence of inert gas flow.

The study on the carbonization temperature concluded that the higher temperature setting produced char with less yield percentage and higher ash content, while having higher BET surface area and total pore volume. The ANOVA and fit analysis on the four responses derived at different carbonization temperatures, are able to provide the optimization solution, for the lowest carbonization temperature suitable to produce char with high yield percentage, carbon mass percentage, BET surface area and total pore volume, while having low ash content and oxygen mass percentage. The optimized carbonization temperature, conducted using conventional furnace without inert gas flow, is 721.469 °C.

Activated carbon replicates synthesized using NaOH, HCl and KCl have comparable properties with conventional activated carbon, with porous surfaces are observed to be present on all of the AC replicates and have ash content lower than maximum limit (8 and 10%) as referred to ASTM, Malaysian Standard and Standard National Indonesia. All

NaOH-AC, HCl-AC and KCl-AC replicates are dominated by carbon elements with more than 80% mass percentage while having less than 20% mass percentage of oxygen elements.

The ash content for all the AC replicates are shown to be increasing as the concentration of the chemical activating agent increased, while still below the recommended value of ash content. The NaOH concentration has a significant influence on the development of the porosity of the surface of the AC, with the greatest value of BET surface area attained in this experiment at 7% NaOH (R3 - 355 m²/g). R3 also has the largest quantity of MB adsorbed, 14.245 mg/g. The nitrogen adsorption isotherm of the NaOH-AC replicates are identical to Type II adsorption based on IUPAC classification.

For the adsorption performance for removal of water pollutants, NaOH-AC replicates are better adsorbent for 30 ppm methylene blue solution as compared to HCl-AC and KCl-AC replicates, where the alkaline-activated carbons have adsorption efficiency up to 94%, while the acid and salt activated carbons have the adsorption efficiency up to 37.9 % and 30.9 % respectively. The kinetic study of the adsorption of 10 ppm MB solution for all AC replicates discovers that at the first 60 minutes of the experiment, the adsorption are more suited to the Elovich kinetic model indicating the occurrence of chemisorption on heterogenous adsorbing surfaces, while the overall adsorption (from 0 minutes to 120 minutes) are more suited to pseudo-second order which indicating the effect of chemical interaction in the adsorption of MB onto the AC surfaces.

All AC replicates also are able to adsorb Pb, Zn and Cr ions with initial concentration of 30 ppm, at the adsorption efficiency of more than 23%, 90% and 45% respectively. The adsorption uptake of the heavy metal ions for all replicates of AC are beyond the Malaysian standard, specifically for adsorption of lead and chromium ions. These performances indicates that the Dabai AC are suitable for reduction of heavy metal ions concentration,

with NaOH-AC replicates with higher concentrations are significantly better adsorbents for MB solution and lead ions solution as compared to other AC replicates derived from HCl and KCl activation.

7.2 Recommendations

Dabai nutshell is proven to be suitable as the precursor material for the synthesis of activated carbon. Local farmers and industries are recommended to enhance the effort to make sure Dabai fruits are available along the year, through scientific methods and crop rotation, where these efforts may result in the reduction of price of the fruit and increases the availability of dabai nutshell.

Further studies should be done to study the potential of synthesizing activating carbon using conventional furnace without using any inert gas flow. The focus of the study is suggested to be on improving the quality of the resulting AC, match the quality of industrial AC and AC derived from other types of biomasses.

Research on the optimization of the concentrations of chemical activating agents are highly recommended to increase the porosity of the resulting adsorbent, while taking cautious steps on the pH of the activating agents. More accurate and precise elemental analysis are suggested to further determine the elemental composition of the AC. In terms of determining the accurate efficiency of adsorption, varied initial concentrations of water removals can be set to further study the potential of utilizing this adsorbent in wastewater or water treatment.

REFERENCES

- Abdul Aziz, M. W. H., Masre, S. F., Basri, D. F., & Ghazali, A. R. (2022). *Canarium odontophyllum* Miq. (Dabai) Leaf Phytoextracts and Their Medicinal Properties. *Pertanika Journal of Science and Technology*, 30(3), 2115–2125. <https://doi.org/10.47836/pjst.30.3.20>
- Abussaud, B., Asmaly, H. A., Ihsanullah, Saleh, T. A., Gupta, V. K., Laoui, T., & Atieh, M. A. (2016). Sorption of phenol from waters on activated carbon impregnated with iron oxide, aluminum oxide and titanium oxide. *Journal of Molecular Liquids*, 213, 351–359. <https://doi.org/10.1016/j.molliq.2015.08.044>
- Achaw, O.-W. (2012). A Study of the Porosity of Activated Carbons Using the Scanning Electron Microscope. In V. Kazmiruk (Ed.), *Scanning Electron Microscopy* (pp. 474–490). Intech. <https://doi.org/http://dx.doi.org/10.5772/57353>
- Açıkyıldız, M., Gürses, A., & Karaca, S. (2014). Preparation and characterization of activated carbon from plant wastes with chemical activation. *Microporous and Mesoporous Materials*, 198, 45–49. <https://doi.org/10.1016/j.micromeso.2014.07.018>
- Ademiluyi, F. T., & David-West, E. O. (2012). Effect of Chemical Activation on the Adsorption of Heavy Metals Using Activated Carbons from Waste Materials. *ISRN Chemical Engineering*, 2012, 1–5. <https://doi.org/10.5402/2012/674209>
- Adriano, D. C. (2001). *Trace Elements in Terrestrial Environments* (2nd ed.). Springer-Verlag New York berlin Heidelberg. <https://doi.org/10.1007/978-0-387-21510-5>

- Afroz, R., Masud, M. M., Akhtar, R., & Duasa, J. B. (2014). Water pollution: Challenges and future direction for water resource management policies in malaysia. *Environment and Urbanization ASIA*, 5(1), 63–81. <https://doi.org/10.1177/0975425314521544>
- Afroz, R., & Rahman, A. (2017). Health impact of river water pollution in Malaysia. *International Journal of Advanced and Applied Sciences*, 4(5), 78–85. <https://doi.org/https://doi.org/10.21833/ijaas.2017.05.014>
- Aharoni, C., & Tompkins, F. C. (1970). Kinetics of Adsorption and Desorption and the Elovich Equation. *Advances in Catalysis*, 21(C), 1–49. [https://doi.org/10.1016/S0360-0564\(08\)60563-5](https://doi.org/10.1016/S0360-0564(08)60563-5)
- Ahiduzzaman, M., & Sadrul Islam, A. K. M. (2016). Preparation of porous bio-char and activated carbon from rice husk by leaching ash and chemical activation. *SpringerPlus*, 5(1). <https://doi.org/10.1186/s40064-016-2932-8>
- Ali, G. A., Mohamed Salih, N. Q., Faroun, G. A., & Chyad Al-Hamadani, R. F. (2023). Adsorption technique for the removal of heavy metals from wastewater using low-cost natural adsorbent. *IOP Conference Series: Earth and Environmental Science*, 1129(1). <https://doi.org/10.1088/1755-1315/1129/1/012012>
- Ali, S. S., Al-Tohamy, R., & Sun, J. (2022). Performance of *Meyerozyma caribbica* as a novel manganese peroxidase-producing yeast inhabiting wood-feeding termite gut symbionts for azo dye decolorization and detoxification. *Science of the Total Environment*, 806. <https://doi.org/10.1016/j.scitotenv.2021.150665>
- Alkheraz, A. M., Ali, A. K., & Elsherif, K. M. E. (2019). Removal of Pb(II), Zn(II), Cu(II) and Cd(II) from aqueous solutions by adsorption onto olive branches activated carbon:

- Equilibrium and thermodynamic studies. *Chemistry International*, 6(1).
<https://doi.org/https://doi.org/10.5281/zenodo.2579465>
- Allwar, A., Hartati, R., & Fatimah, I. (2017). Effect of nitric acid treatment on activated carbon-oil palm shell. *AIP Conference Proceedings*.
<https://doi.org/https://doi.org/10.1063/1,4978202>
- Almroth, B. C., Cartine, J., Jönander, C., Karlsson, M., Langlois, J., Lindström, M., Lundin, J., Melander, N., Pesqueda, A., Rahmqvist, I., Renaux, J., Roos, J., Spilsbury, F., Svalin, J., Vestlund, H., Zhao, L., Asker, N., Ašmonaitė, G., Birgersson, L., ... Sturve, J. (2021). Assessing the effects of textile leachates in fish using multiple testing methods: From gene expression to behavior. *Ecotoxicology and Environmental Safety*, 207. <https://doi.org/10.1016/j.ecoenv.2020.111523>
- Altmann, J., Rehfeld, D., Träder, K., Sperlich, A., & Jekel, M. (2016). Combination of granular activated carbon adsorption and deep-bed filtration as a single advanced wastewater treatment step for organic micropollutant and phosphorus removal. *Water Research*, 92, 131–139. <https://doi.org/10.1016/j.watres.2016.01.051>
- Al-Tohamy, R., Ali, S. S., Li, F., Okasha, K. M., Mahmoud, Y. A. G., Elsamahy, T., Jiao, H., Fu, Y., & Sun, J. (2022). A critical review on the treatment of dye-containing wastewater: Ecotoxicological and health concerns of textile dyes and possible remediation approaches for environmental safety. *Ecotoxicology and Environmental Safety*, 231, 113160. <https://doi.org/10.1016/J.ECOENV.2021.113160>
- Amer, M., & Elwardany, A. (2020). Biomass Carbonization. In *Renewable Energy - Resources, Challenges and Applications* (pp. 211–300).
<https://doi.org/10.5772/intechopen.90480>

- ASTM International. (2004). Standard Test Method for Total Ash Content of Activated Carbon. *ASTM Standards*, 15(1), 1–2. <https://doi.org/10.1520/D2866-11.2>
- Aulakh, M. S., Khurana, M. P. S., & Singh, D. (2009). Water pollution related to agricultural, industrial, and urban activities, and its effects on the food chain: Case studies from punjab. *Journal of New Seeds*, 10(2), 112–137. <https://doi.org/10.1080/15228860902929620>
- Aziz, K. H. H., Mustafa, F. S., Omer, K. M., Hama, S., Hamarawf, R. F., & Rahman, K. O. (2023). Heavy metal pollution in the aquatic environment: efficient and low-cost removal approaches to eliminate their toxicity: a review. In *RSC Advances* (Vol. 13, Issue 26, pp. 17595–17610). Royal Society of Chemistry. <https://doi.org/10.1039/d3ra00723e>
- Azrina, A., Nurul Nadiah, M. N., & Amin, I. (2010). Antioxidant properties of methanolic extract of *Canarium odontophyllum* fruit. *International Food Research Journal*, 17(2), 319–326.
- Bán, A., Schäfer, A., & Wendt, H. (1998). Fundamentals of electrosorption on activated carbon for wastewater treatment of industrial effluents. *Journal of Applied Electrochemistry*, 28(3), 227–236. <https://doi.org/10.1023/A:1003247229049>
- Basri, D. F., Fairuzishak, S., & Zin, N. M. (2014). Shell Extract of Seed from *Canarium odontophyllum* Miq. (dabai) Fruit as Potential Source of Antibacterial Agent. *International Journal of Pharmaceutical Sciences Review and Research*, 28(46), 257–262.

- Basu, P. (2018). Torrefaction. In *Biomass Gasification, Pyrolysis and Torrefaction: Practical Design and Theory* (pp. 93–154). Elsevier. <https://doi.org/10.1016/B978-0-12-812992-0.00004-2>
- Batool, F., Akbar, J., Iqbal, S., Noreen, S., & Bukhari, S. N. A. (2018). Study of Isothermal, Kinetic, and Thermodynamic Parameters for Adsorption of Cadmium: An Overview of Linear and Nonlinear Approach and Error Analysis. *Bioinorganic Chemistry and Applications*, 2018. <https://doi.org/10.1155/2018/3463724>
- Bello, M. O., Abdus-Salam, N., Adekola, F. A., & Pal, U. (2021). Isotherm and kinetic studies of adsorption of methylene blue using activated carbon from ackee apple pods. *Chemical Data Collections*, 31. <https://doi.org/10.1016/j.cdc.2020.100607>
- Bolisetty, S., Peydayesh, M., & Mezzenga, R. (2019). Sustainable technologies for water purification from heavy metals: review and analysis. *Chemical Society Reviews*, 48(2), 463–487. <https://doi.org/10.1039/c8cs00493e>
- Boudrahem, F., Aissani-Benissad, F., Audonnet, F., & Vial, C. (2021). Kinetics and equilibrium adsorption of lead (II) ions on olive residues: Effects of chemical activation. *Algerian Journal of Environmental Science and Technology March Edition*, 7(1). www.aljest.org
- Briffa, J., Sinagra, E., & Blundell, R. (2020). Heavy metal pollution in the environment and their toxicological effects on humans. *Heliyon*, 6(9), e04691. <https://doi.org/10.1016/j.heliyon.2020.e04691>
- Brooke, P., & Yuon, L. C. (2013). *Dabai Planting Material and Propagation Technique*. Agriculture Research Centre, Semongok. <http://myagric.upm.edu.my/id/eprint/12092>

- Budi, E., Umiatin, Nasbey, H., Bintoro, R. A., Wulandari, F., & Erlina. (2016). Activated coconut shell charcoal carbon using chemical-physical activation. *AIP Conference Proceedings*, 1712(February 2016), 1–7. <https://doi.org/10.1063/1.4941886>
- Carabineiro, S. A. C., Pereira, M. F. R., Orfao, J. J. M., & Figueiredo, J. L. (2012). Surface Chemistry of Activated Carbons. In J. F. Kwiatkowski (Ed.), *Activated Carbon: Classifications, Properties and Applications* (pp. 125–167). Nova Science Publishers, Inc.
- Çeçen, F. (2011). Water and Wastewater Treatment: Historical Perspective of Activated Carbon Adsorption and its Integration with Biological Processes. In F. Cecen & O. Aktas (Eds.), *Activated Carbon for Water and Wastewater Treatment* (First Edit, Issue July, pp. 1–11). WILEY-VCH. <https://doi.org/10.1002/9783527639441.ch1>
- Chai, K. L., Dayang, A. W. A., Lau, C. Y., & Sim, S. L. (2010). Control of in vitro contamination of explants from field-grown dabai (*canarium odontophyllum* miq.) trees. *Asia-Pacific Journal of Molecular Biology and Biotechnology*, 18(1), 113–116.
- Chakrapani, C., Babu, C. S., Vani, K. N. K., & Rao, K. S. (2010). Adsorption kinetics for the removal of fluoride from aqueous solution by activated carbon adsorbents derived from the peels of selected citrus fruits. *E-Journal of Chemistry*, 7(SUPPL. 1), 419–427. <https://doi.org/10.1155/2010/582150>
- Chen, C. X., Huang, B., Li, T., & Wu, G. F. (2012). Preparation of phosphoric acid activated carbon from sugarcane bagasse by mechanochemical processing. *BioResources*, 7(4), 5109–5116. <https://doi.org/10.15376/biores.7.4.5109-5116>
- Chen, R., Han, N., Li, L., Wang, S., Ma, X., Wang, C., Li, H., Li, H., & Zeng, L. (2020). Fundamental understanding of oxygen content in activated carbon on acetone

- adsorption desorption. *Applied Surface Science*, 508. <https://doi.org/10.1016/j.apsusc.2019.145211>
- Cherifi, H., Fatiha, B., & Salah, H. (2013). Kinetic studies on the adsorption of methylene blue onto vegetal fiber activated carbons. *Applied Surface Science*, 282, 52–59. <https://doi.org/10.1016/j.apsusc.2013.05.031>
- Chowdhury, Z. Z., Hamid, S. B. A., Das, R., Hasan, M. R., Zain, S. M., Khalid, K., & Uddin, M. N. (2013). Preparation of carbonaceous adsorbents from lignocellulosic biomass and their use in removal of contaminants from aqueous solution. *BioResources*, 8(4), 6523–6555. <https://doi.org/10.15376/biores.8.4.6523-6555>
- Chua, H. P., Nicholas, D., & Yahya, M. N. A. (2015). Physical properties and nutritional values of dabai fruit (*Canarium odontophyllum*) of different genotypes. *Journal of Tropical Agriculture and Food Science*, 43(1), 1–10. <https://doi.org/10.13140/2.1.2944.3366>
- Contescu, C., Adhikari, S., Gallego, N., Evans, N., & Biss, B. (2018). Activated Carbons Derived from High-Temperature Pyrolysis of Lignocellulosic Biomass. *Journal of Carbon Research*, 4(3), 51. <https://doi.org/10.3390/c4030051>
- Crini, G., Lichtfouse, E., Wilson, L. D., & Morin-Crini, N. (2019). Conventional and non-conventional adsorbents for wastewater treatment. In *Environmental Chemistry Letters* (Vol. 17, Issue 1, pp. 195–213). Springer Verlag. <https://doi.org/10.1007/s10311-018-0786-8>
- Da Fonseca, G. C., Oliveira, M. S., Martins, C. V. C., & De Souza, J. C. P. (2022). How the Carbonization Time of Sugarcane Biomass Affects the Microstructure of Biochar and

- the Adsorption Process? *Sustainability* (Switzerland), 14(3).
<https://doi.org/10.3390/su14031571>
- Dash, R. R., Balomajumder, C., & Kumar, A. (2009). Removal of cyanide from water and wastewater using granular activated carbon. *Chemical Engineering Journal*, 146(3), 408–413. <https://doi.org/10.1016/j.cej.2008.06.021>
- Daud, W. M. A. W., Ali, W. S. W., & Sulaiman, M. Z. (2001). Effect of carbonization temperature on the yield and porosity of char produced from palm shell. *Journal of Chemical Technology and Biotechnology*, 76(12), 1281–1285.
<https://doi.org/10.1002/jctb.515>
- Deliyanni, E. A. (2019). Low-cost activated carbon from rice wastes in liquid-phase adsorption. In *Interface Science and Technology* (Vol. 30). Elsevier.
<https://doi.org/10.1016/B978-0-12-814178-6.00005-4>
- Deng, Y., & Zhao, R. (2015). Advanced Oxidation Processes (AOPs) in Wastewater Treatment. In *Current Pollution Reports* (Vol. 1, Issue 3, pp. 167–176).
<https://doi.org/10.1007/s40726-015-0015-z>
- Department of Standards Malaysia. (2005). *Powdered Activated Carbon For Use of Potable Water Supply - Specification (First Revision) MS 873:2005*.
- Dimpe, K. M., Ngila, J. C., & Nomngongo, P. N. (2017). Application of waste tyre-based activated carbon for the removal of heavy metals in wastewater. *Cogent Engineering*, 4(1). <https://doi.org/10.1080/23311916.2017.1330912>
- Ding, P., & Tee, Y. K. (2011). Physicochemical characteristics of dabai (*Canarium odontophyllum* Miq.) fruit. *Fruits*, 66(1), 47–52.
<https://doi.org/10.1051/fruits/2010040>

- Dolas, H., Sahin, O., Saka, C., & Demir, H. (2011). A new method on producing high surface area activated carbon: The effect of salt on the surface area and the pore size distribution of activated carbon prepared from pistachio shell. *Chemical Engineering Journal*, 166(1), 191–197. <https://doi.org/10.1016/j.cej.2010.10.061>
- Donohue, M. D., & Aranovich, G. L. (1998). Classification of Gibbs adsorption isotherms. *Advances in Colloid and Interface Science*, 76–77, 137–152. [https://doi.org/10.1016/S0001-8686\(98\)00044-X](https://doi.org/10.1016/S0001-8686(98)00044-X)
- Ekpete, O. A., & Horsfall, M. J. (2011). Preparation and Characterization of Activated Carbon derived from Fluted Pumpkin Stem Waste (*Telfairia occidentalis* Hook F). *Research Journal of Chemical Sciences*, 1(3). www.isca.in
- El Nemr, A., Aboughaly, R. M., El Sikaily, A., Masoud, M. S., Ramadan, M. S., & Ragab, S. (2022). Microporous-activated carbons of type I adsorption isotherm derived from sugarcane bagasse impregnated with zinc chloride. *Carbon Letters*, 32(1). <https://doi.org/10.1007/s42823-021-00270-1>
- Farzaneh, H., & Mokshapathy, S. (2018). Overview of Filtration in Water Treatment Plant No . 1 (Hesar Branch), Karaj City - Iran. *International Journal of Life Sciences Research*, 1(1), 1–5.
- Fatriansyah, J. F., Matari, T., & Harjanto, S. (2018). The preparation of activated carbon from coconut shell charcoal by novel mechano-chemical activation. *Materials Science Forum*, 929 MSF, 50–55. <https://doi.org/10.4028/www.scientific.net/MSF.929.50>
- Fern, A., & Morris, R. (2019). *Canarium odontophyllum* - *Useful Tropical Plants*. Tropical Plants Database. <http://tropical.theferns.info/viewtropical.php?id=Canarium+odontophyllum>

- Foo, K. Y., & Hameed, B. H. (2009). A short review of activated carbon assisted electrosorption process: An overview, current stage and future prospects. *Journal of Hazardous Materials*, 170(2–3), 552–559. <https://doi.org/10.1016/j.jhazmat.2009.05.057>
- Foo, K. Y., & Hameed, B. H. (2012). Potential of jackfruit peel as precursor for activated carbon prepared by microwave induced NaOH activation. *Bioresource Technology*, 112, 143–150. <https://doi.org/10.1016/j.biortech.2012.01.178>
- Fredalina Basri, D. (2015). Leaves Extract from *Canarium odontophyllum* Miq. (Dabai) Exhibits Cytotoxic Activity against Human Colorectal Cancer Cell HCT 116. *Natural Products Chemistry & Research*, 3(1). <https://doi.org/10.4172/2329-6836.1000166>
- Gai, X. J., & Kim, H. S. (2008). The role of powdered activated carbon in enhancing the performance of membrane systems for water treatment. *Desalination*, 225(1–3), 288–300. <https://doi.org/10.1016/j.desal.2007.07.009>
- Ganjoo, R., Sharma, S., Kumar, A., & Daouda, M. M. A. (2023). Activated Carbon: Fundamentals, Classification, and Properties. In *Activated Carbon: Progress and Applications* (pp. 1–22). [https://doi.org/https://doi.org/10.1039/BK9781839169861-00001](https://doi.org/10.1039/BK9781839169861-00001)
- Gautam, P. K., Gautam, R. K., Banerjee, S., Chattopadhyaya, M. C., & Pandey, J. D. (2016). Heavy metals in the environment: Fate, transport, toxicity and remediation technologies. *Heavy Metals: Sources, Toxicity and Remediation Techniques*, February, 101–130.
- Gomez-Delgado, E., Nunell, G. V., Cukierman, A. L., & Bonelli, P. R. (2022). Influence of the carbonization atmosphere on the development of highly microporous adsorbents

- tailored to CO₂ capture. *Journal of the Energy Institute*, 102, 184–189.
<https://doi.org/10.1016/J.JOEI.2022.03.003>
- Grycova, B., Pryszcz, A., Matejova, L., & Lestinsky, P. (2018). Influence of activating reagents on the porous structure of activated carbon. *Chemical Engineering Transactions*, 70, 1897–1902. <https://doi.org/10.3303/CET1870317>
- Gundogdu, A., Duran, C., Senturk, H. B., Soylak, M., Imamoglu, M., & Onal, Y. (2013). Physicochemical characteristics of a novel activated carbon produced from tea industry waste. *Journal of Analytical and Applied Pyrolysis*, 104, 249–259.
<https://doi.org/10.1016/J.JAAP.2013.07.008>
- Habeeb, O. A., Kanthasamy, R., Saber, S. E. M., & Olalere, O. A. (2020). Characterization of agriculture wastes based activated carbon for removal of hydrogen sulfide from petroleum refinery waste water. *Materials Today: Proceedings*, 20, 588–594.
<https://doi.org/10.1016/j.matpr.2019.09.194>
- Hameed, B. H., & Daud, F. B. M. (2008). Adsorption studies of basic dye on activated carbon derived from agricultural waste: Hevea brasiliensis seed coat. *Chemical Engineering Journal*, 139(1), 48–55. <https://doi.org/10.1016/J.CEJ.2007.07.089>
- Hamza, U. D., Nasri, N. S., Amin, N. A. S., Mohammed, J., & Zain, H. M. (2016). Characteristics of oil palm shell biochar and activated carbon prepared at different carbonization times. *Desalination and Water Treatment*, 57(17), 7999–8006.
<https://doi.org/10.1080/19443994.2015.1042068>
- Hamzah, M. H., Mohd Basri, M. S., Maringgal, B., Mohd Ali, M., Wondi, M. H., Che Man, H., & Gatuk Abdulloh, S. (2022). Exploring Dabai (*Canarium odontophyllum*), Indigenous Fruit of Borneo: A Review of Nutritional Values, Potential Uses, Emerging

- Application in Essential Oil Processing, and Health Benefits. In *Plants* (Vol. 11, Issue 19). MDPI. <https://doi.org/10.3390/plants11192646>
- Han, Q., Wang, J., Goodman, B. A., Xie, J., & Liu, Z. (2020). High adsorption of methylene blue by activated carbon prepared from phosphoric acid treated eucalyptus residue. *Powder Technology*, 366, 239–248. <https://doi.org/10.1016/j.powtec.2020.02.013>
- Han, Y., Quan, X., Chen, S., Zhao, H., Cui, C., & Zhao, Y. (2006). Electrochemically enhanced adsorption of phenol on activated carbon fibers in basic aqueous solution. *Journal of Colloid and Interface Science*, 299(2), 766–771. <https://doi.org/10.1016/j.jcis.2006.03.007>
- Hanum, F., Bani, O., & Wirani, L. I. (2017). Characterization of Activated Carbon from Rice Husk by HCl Activation and Its Application for Lead (Pb) Removal in Car Battery Wastewater. *1st Annual Applied Science and Engineering Conference*, 1, 1–11. <https://doi.org/10.1088/1757-899X/180/1/012151>
- Haq, I., Raj, A., & Markandeya. (2018). Biodegradation of Azure-B dye by *Serratia liquefaciens* and its validation by phytotoxicity, genotoxicity and cytotoxicity studies. *Chemosphere*, 196, 58–68. <https://doi.org/10.1016/j.chemosphere.2017.12.153>
- Hasar, H., Cuci, Y., Obek, E., & Fatih Dilekoglu, M. (2003). Removal of Zinc(II) by Activated Carbon Prepared from Almond Husks Under Different Conditions. *Adsorption Science & Technology*, 21(9), 799–808. <https://doi.org/https://doi.org/10.1260/02636170360744056>
- Hayashi, J., Kazehaya, A., Muroyama, K., & Watkinson, A. P. (2000). Preparation of activated carbon from lignin by chemical activation. *Carbon*, 38(13), 1873–1878. [https://doi.org/10.1016/S0008-6223\(00\)00027-0](https://doi.org/10.1016/S0008-6223(00)00027-0)

- Hayashi, J., Yamamoto, N., Horikawa, T., Muroyama, K., & Gomes, V. G. (2005). Preparation and characterization of high-specific-surface-area activated carbons from K₂CO₃-treated waste polyurethane. *Journal of Colloid and Interface Science*, 281(2), 437–443. <https://doi.org/10.1016/j.jcis.2004.08.092>
- Heidarinejad, Z., Dehghani, M. H., Heidari, M., Javedan, G., Ali, I., & Sillanpää, M. (2020). Methods for preparation and activation of activated carbon: a review. *Environmental Chemistry Letters*, 18(2), 393–415. <https://doi.org/10.1007/s10311-019-00955-0>
- Hendrawan, Y., Sajidah, N., Umam, C., Fauzy, M. R., Wibisono, Y., & Hawa, L. C. (2019). Effect of Carbonization Temperature Variations and Activator Agent Types on Activated Carbon Characteristics of Sengon Wood Waste (*Paraserianthes falcataria* (L.) Nielsen). *IOP Conference Series: Earth and Environmental Science*, 239(1). <https://doi.org/10.1088/1755-1315/239/1/012006>
- Huang, P. H., Jhan, J. W., Cheng, Y. M., & Cheng, H. H. (2014). Effects of carbonization parameters of Moso-bamboo-based porous charcoal on capturing carbon dioxide. *Scientific World Journal*, 2014. <https://doi.org/10.1155/2014/937867>
- Ighalo, J. O., Iwuzor, K. O., Igwegbe, C. A., & Adeniyi, A. G. (2021). Verification of pore size effect on aqueous-phase adsorption kinetics: A case study of methylene blue. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 626. <https://doi.org/10.1016/j.colsurfa.2021.127119>
- Ilomuanya, M., Nashiru, B., Ifudu, N., & Igwilo, C. (2017). Effect of pore size and morphology of activated charcoal prepared from midribs of *Elaeis guineensis* on adsorption of poisons using metronidazole and *Escherichia coli* O157:H7 as a case

- study. *Journal of Microscopy and Ultrastructure*, 5(1), 32.
<https://doi.org/10.1016/j.jmau.2016.05.001>
- Indayaningsih, N., Destyorini, F., Purawiardi, R. I., Insiyanda, D. R., & Widodo, H. (2016). Production of activated carbon by using pyrolysis process in an ammonia atmosphere. *Journal of Physics: Conference Series*, 755(1), 1–6. <https://doi.org/10.1088/1742-6596/755/1/011001>
- Indayaningsih, N., Destyorini, F., Purawiardi, R. I., Insiyanda, D. R., & Widodo, H. (2017). Production of activated carbon by using pyrolysis process in an ammonia atmosphere. *Journal of Physics: Conference Series*, 817. <https://doi.org/10.1088/1742-6596/817/1/012006>
- Ioannidou, O., & Zabaniotou, A. (2007). Agricultural residues as precursors for activated carbon production-A review. *Renewable and Sustainable Energy Reviews*, 11(9), 1966–2005. <https://doi.org/10.1016/j.rser.2006.03.013>
- Islam, M. N., Khatton, A., Sarker, ahid, Sikder, H. A., & Chowdhury, A. M. S. (2022). Preparation and Characterization of Activated Carbon from Jute Stick by Chemical Activation: Comparison of Different Activating Agents. *Saudi Journal of Engineering and Technology*, 7(2), 112–117. <https://doi.org/10.36348/sjet.2022.v07i02.008>
- James, A. A., Rahman, M. R., Huda, D., Aqlan, F. M., Matin, M. M., Bakri, M. K. Bin, Kuok, K. K., & Rahman, M. M. (2022). Synthesis and Characterization of Novel Nano-carbon Mixture from Dabai (*Canarium odontophyllum*) Nutshell. *BioResources*, 17(3), 4452–4469. <https://doi.org/10.15376/biores.17.3.4452-4469>
- Jawad, A. H., Mohd Firdaus Hum, N. N., Abdulhameed, A. S., & Mohd Ishak, M. A. (2020). Mesoporous activated carbon from grass waste via H₃PO₄-activation for methylene

- blue dye removal: modelling, optimisation, and mechanism study. *International Journal of Environmental Analytical Chemistry*.
<https://doi.org/10.1080/03067319.2020.1807529>
- Jawad, A. H., Saud Abdulhameed, A., Wilson, L. D., Syed-Hassan, S. S. A., ALOthman, Z. A., & Rizwan Khan, M. (2021). High surface area and mesoporous activated carbon from KOH-activated dragon fruit peels for methylene blue dye adsorption: Optimization and mechanism study. In *Chinese Journal of Chemical Engineering* (Vol. 32, pp. 281–290). Materials China. <https://doi.org/10.1016/j.cjche.2020.09.070>
- Jiang, C., Cui, S., Han, Q., Li, P., Zhang, Q., Song, J., & Li, M. (2019). Study on Application of Activated Carbon in Water Treatment. *IOP Conference Series: Earth and Environmental Science*, 237(2). <https://doi.org/10.1088/1755-1315/237/2/022049>
- Kadir, N. A. A. A., Azlan, A., Abas, F., & Ismail, I. S. (2018). Beneficial effect of supercritical carbon dioxide extracted (SC-CO₂) Dabai (*Canarium odontophyllum*) pulp oil in hypercholesterolemia-induced SPF sprague-dawley rats. *Natural Product Communications*, 13(12), 1583–1586. <https://doi.org/10.1177/1934578x1801301205>
- Kasron, N., Rozana, N., Masdek, N., Saari, N. A., & Saari, A. (2020). Indigenous fruits consumption in Sabah and Sarawak (Penggunaan buah-buahan nadir di Sabah dan Sarawak). In *Economic and Technology Management Review* (Vol. 15).
- Katesa, J., Junpiromand, S., & Tangsathitkulchai, C. (2013). Effect of Carbonization Temperature On Properties of Char And Activated Carbon From Coconut Shell. *Suranaree Journal of Science and Technology*, 20(4), 269–278.
- Kecili, R., & Hussain, C. M. (2018). Mechanism of Adsorption on Nanomaterials. In C. M. Hussain (Ed.), *Nanomaterials in Chromatography: Current Trends in*

Chromatographic Research Technology and Techniques (pp. 89–115). Elsevier Inc.

<https://doi.org/10.1039/9781782623625-00090>

Kim, H. S., Takizawa, S., & Ohgaki, S. (2007). Application of microfiltration systems coupled with powdered activated carbon to river water treatment. *Desalination*, 202(1–3), 271–277. <https://doi.org/10.1016/j.desal.2005.12.064>

Koehlert, K. (2017). Activated carbon: Fundamentals and new applications. *Chemical Engineering (United States)*, 124(7), 32–40.

Kristiana, I., Joll, C., & Heitz, A. (2011). Powdered activated carbon coupled with enhanced coagulation for natural organic matter removal and disinfection by-product control: Application in a Western Australian water treatment plant. *Chemosphere*, 83(5), 661–667. <https://doi.org/10.1016/j.chemosphere.2011.02.017>

Lalhruaitluanga, H., Jayaram, K., Prasad, M. N. V., & Kumar, K. K. (2010). Lead(II) adsorption from aqueous solutions by raw and activated charcoals of *Melocanna baccifera* Roxburgh (bamboo)-A comparative study. *Journal of Hazardous Materials*, 175(1–3), 311–318. <https://doi.org/10.1016/j.jhazmat.2009.10.005>

Lamine, S. M., Ridha, C., Mahfoud, H. M., Mouad, C., Lotfi, B., & Al-Dujaili, A. H. (2014). Chemical activation of an activated carbon prepared from coffee residue. *Energy Procedia*, 50, 393–400. <https://doi.org/10.1016/j.egypro.2014.06.047>

Lee, L. Z., & Ahmad Zaini, M. A. (2016). Metal chloride salts in the preparation of activated carbon and their hazardous outlook. *Desalination and Water Treatment*, 57(34), 16078–16085. <https://doi.org/10.1080/19443994.2015.1077348>

- Li, H., Gao, Y., Pan, L., Zhang, Y., Chen, Y., & Sun, Z. (2008). Electrosorptive desalination by carbon nanotubes and nanofibres electrodes and ion-exchange membranes. *Water Research*, 42(20), 4923–4928. <https://doi.org/10.1016/j.watres.2008.09.026>
- Li, Y., Du, Q., Liu, T., Peng, X., Wang, J., Sun, J., Wang, Y., Wu, S., Wang, Z., Xia, Y., & Xia, L. (2013). Comparative study of methylene blue dye adsorption onto activated carbon, graphene oxide, and carbon nanotubes. *Chemical Engineering Research and Design*, 91(2), 361–368. <https://doi.org/10.1016/J.CHERD.2012.07.007>
- Limousin, G., Gaudet, J. P., Charlet, L., Szenknect, S., Barthès, V., & Krimissa, M. (2007). Sorption isotherms: A review on physical bases, modeling and measurement. *Applied Geochemistry*, 22(2), 249–275. <https://doi.org/10.1016/j.apgeochem.2006.09.010>
- Liu, Z., Niu, W., Chu, H., Zhou, T., & Niu, Z. (2018). Effect of the Carbonization Temperature on the Properties of Biochar Produced from the Pyrolysis of Crop Residues. *BioResources*, 13(2), 3429–3446.
- Lu, G. Q., Low, J. C. F., Liu, C. Y., & Lua, A. C. (1995). Surface area development of sewage sludge during pyrolysis. In *Fuel* (Vol. 74, Issue 3).
- Mariah, M. A. A., Rovina, K., Vonnice, J. M., & Erna, K. H. (2023). Characterization of activated carbon from waste tea (*Camellia sinensis*) using chemical activation for removal of methylene blue and cadmium ions. *South African Journal of Chemical Engineering*, 44, 113–122. <https://doi.org/10.1016/j.sajce.2023.01.007>
- Mariana, M., Abdul, A. K., Mistar, E. M., Yahya, E. B., Alfatah, T., Danish, M., & Amayreh, M. (2021). Recent advances in activated carbon modification techniques for enhanced heavy metal adsorption. *Journal of Water Process Engineering*, 43, 102221. <https://doi.org/10.1016/J.JWPE.2021.102221>

- Marsh, H., & Rodríguez-Reinoso, F. (2006a). Activated Carbon (Origins). *Activated Carbon*, 1997, 13–86. <https://doi.org/10.1016/b978-008044463-5/50016-9>
- Marsh, H., & Rodríguez-Reinoso, F. (2006b). Activation Processes (Chemical). *Activated Carbon*, i, 322–365. <https://doi.org/10.1016/b978-008044463-5/50020-0>
- Maulina, S., & Iriansyah, M. (2018). Characteristics of activated carbon resulted from pyrolysis of the oil palm fronds powder. *IOP Conference Series: Materials Science and Engineering*, 309(1). <https://doi.org/10.1088/1757-899X/309/1/012072>
- Menéndez-Díaz, J. A., & Martín-Gullón, I. (2006). Types of carbon adsorbents and their production. In *Interface Science and Technology* (Vol. 7, pp. 1–48). Elsevier. [https://doi.org/10.1016/S1573-4285\(06\)80010-4](https://doi.org/10.1016/S1573-4285(06)80010-4)
- Misran, E., Bani, O., Situmeang, E. M., & Purba, A. S. (2022). Banana stem based activated carbon as a low-cost adsorbent for methylene blue removal: Isotherm, kinetics, and reusability. *Alexandria Engineering Journal*, 61(3), 1946–1955. <https://doi.org/10.1016/j.aej.2021.07.022>
- Mistar, E. M., Alfatah, T., & Supardan, M. D. (2020). Synthesis and characterization of activated carbon from *Bambusa vulgaris striata* using two-step KOH activation. *Journal of Materials Research and Technology*, 9(3), 6278–6286. <https://doi.org/10.1016/j.jmrt.2020.03.041>
- Mohanty, K., Das, D., & Biswas, M. N. (2006). Preparation and characterization of activated carbons from *Sterculia alata* nutshell by chemical activation with zinc chloride to remove phenol from wastewater. *Adsorption*, 12(2), 119–132. <https://doi.org/10.1007/s10450-006-0374-2>

- Muruges, S., Msagati, T. A. M., Sivasankar, V., & Hariharan, R. (2016). Adsorption investigations: Kinetic and isotherm models, determination of thermodynamic parameters. In *Surface Modified Carbons as Scavengers for Fluoride from Water* (pp. 147–178). Springer International Publishing. https://doi.org/10.1007/978-3-319-40686-2_7
- Nazem, M. A., Zare, M. H., & Shirazian, S. (2020). Preparation and optimization of activated nano-carbon production using physical activation by water steam from agricultural wastes. *RSC Advances*, 10(3), 1463–1475. <https://doi.org/10.1039/c9ra07409k>
- Nor, N. M., Lau, L. C., Lee, K. T., & Mohamed, A. R. (2013). Synthesis of activated carbon from lignocellulosic biomass and its applications in air pollution control - A review. *Journal of Environmental Chemical Engineering*, 1(4), 658–666. <https://doi.org/10.1016/j.jece.2013.09.017>
- Oginni, O., & Singh, K. (2020). Influence of high carbonization temperatures on microstructural and physicochemical characteristics of herbaceous biomass derived biochars. *Journal of Environmental Chemical Engineering*, 8(5), 104169. <https://doi.org/10.1016/J.JECE.2020.104169>
- Oginni, O., & Singh, K. (2021). Effect of carbonization temperature on fuel and caffeine adsorption characteristics of white pine and Norway spruce needle derived biochars. *Industrial Crops and Products*, 162. <https://doi.org/10.1016/j.indcrop.2021.113261>
- Okhovat, A., Ahmadpour, A., Ahmadpour, F., & Khaki Yadegar, Z. (2012). Pore Size Distribution Analysis of Coal-Based Activated Carbons: Investigating the Effects of Activating Agent and Chemical Ratio. *ISRN Chemical Engineering*, 2012, 1–10. <https://doi.org/10.5402/2012/352574>

- Olowoyo, D. N., & Orere, E. E. (2012). Preparation and Characterization of Activated Carbon Made From Palm-Kernel Shell, Coconut Shell, Groundnut Shell and Obeche Wood (Investigation of Apparent Density, Total Ash Content, Moisture Content, Particle Size Distribution Parameters. *International Journal of Research in Chemistry and Environment*, 2(32), 32–35. www.ijrce.org
- Oren, Y. (2008). Capacitive deionization (CDI) for desalination and water treatment - past, present and future (a review). *Desalination*, 228(1–3), 10–29. <https://doi.org/10.1016/j.desal.2007.08.005>
- Örkün, Y., Karatepe, N., & Yavuz, R. (2012). Influence of temperature and impregnation ratio of H₃PO₄ on the production of activated carbon from hazelnut shell. *Acta Physica Polonica A*, 121(1), 277–280. <https://doi.org/10.12693/APhysPolA.121.277>
- Osman, A. I., Blewitt, J., Abu-Dahrieh, J. K., Farrell, C., Al-Muhtaseb, A. H., Harrison, J., & Rooney, D. W. (2019). Production and characterisation of activated carbon and carbon nanotubes from potato peel waste and their application in heavy metal removal. *Environmental Science and Pollution Research*, 26(36), 37228–37241. <https://doi.org/10.1007/s11356-019-06594-w>
- Oubagaranadin, J. U. K., & Murthy, Z. V. P. (2012). Activated Carbons: Classifications, Properties and Applications. In J. F. Kwiatkowski (Ed.), *Activated Carbon* (pp. 239–266). Nova Science Publishers, Inc.
- Pan, R., Chen, Y. J., Chen, C., Chang, H., & Ding, A. F. (2019). Research on Adsorption of Cr(VI) in Water by Potassium Chloride Modified Peanut Shell Carbon. *IOP Conference Series: Earth and Environmental Science*, 330(4). <https://doi.org/10.1088/1755-1315/330/4/042033>

- Pathania, D., Sharma, S., & Singh, P. (2017). Removal of methylene blue by adsorption onto activated carbon developed from *Ficus carica* bast. *Arabian Journal of Chemistry*, 10, S1445–S1451. <https://doi.org/10.1016/J.ARABJC.2013.04.021>
- Pezoti, O., Cazetta, A. L., Bedin, K. C., Souza, L. S., Martins, A. C., Silva, T. L., Santos Júnior, O. O., Visentainer, J. V., & Almeida, V. C. (2016). NaOH-activated carbon of high surface area produced from guava seeds as a high-efficiency adsorbent for amoxicillin removal: Kinetic, isotherm and thermodynamic studies. *Chemical Engineering Journal*, 288, 778–788. <https://doi.org/10.1016/j.cej.2015.12.042>
- Pillai, S. B. (2020). Adsorption in Water and Used Water Purification. *Handbook of Water and Used Water Purification*, 1–22. https://doi.org/10.1007/978-3-319-66382-1_4-1
- Prakash, N. B., Sockan, V., & Jayakaran, P. (2014). Waste Water Treatment by Coagulation and Flocculation. *Certified International Journal of Engineering Science and Innovative Technology*, 9001(2), 2319–5967.
- Prasad, K. N., Chew, L. Y., Khoo, H. E., Yang, B., Azlan, A., & Ismail, A. (2011). Carotenoids and antioxidant capacities from *Canarium odontophyllum* Miq. fruit. *Food Chemistry*, 124(4), 1549–1555. <https://doi.org/10.1016/j.foodchem.2010.08.010>
- Prasad, K. N., Ismail, A., Chew, L. Y., Khoo, H. E., Kong, K. W., & Azlan, A. (2010). Antioxidant capacities of peel, pulp, and seed fractions of *canarium odontophyllum* Miq. fruit. *Journal of Biomedicine and Biotechnology*, 2010. <https://doi.org/10.1155/2010/871379>
- Gottipati, R. (2012). *Preparation and Characterization of Microporous Activated Carbon from Biomass and its Application in the Removal of Chromium(VI) from Aqueous Phase*. National Institute of Technology.

- Reza, M. S., Yun, C. S., Afroze, S., Radenahmad, N., Bakar, M. S. A., Saidur, R., Taweekun, J., & Azad, A. K. (2020). Preparation of activated carbon from biomass and its' applications in water and gas purification, a review. *Arab Journal of Basic and Applied Sciences*, 27(1), 208–238. <https://doi.org/10.1080/25765299.2020.1766799>
- Rodríguez, P. U., Burgos, A. J., & López, J. S. (2015). *Activated Carbon Adsorption - Series: Tertiary Treatments*. July, 18.
- Rodríguez-Reinoso, F., & Sepúlveda-Escribano, A. (2001). Porous Carbons in Adsorption and Catalysis. *Handbook of Surfaces and Interfaces of Materials*, 5, 309–355. <https://doi.org/10.1016/b978-012513910-6/50066-9>
- Rodriguez-Reinoso, F., & Silvestre-Albero, J. (2016). Activated Carbon and Adsorption. *Reference Module in Materials Science and Materials Engineering*, April 2016, 1–14. <https://doi.org/10.1016/b978-0-12-803581-8.02289-x>
- Rufford, T. E., Hulicova-Jurcakova, D., Zhu, Z., & Lu, G. Q. (2010). A comparative study of chemical treatment by FeCl₃, MgCl₂, and ZnCl₂ on microstructure, surface chemistry, and double-layer capacitance of carbons from waste biomass. *Journal of Materials Research*, 25(8), 1451–1459. <https://doi.org/10.1557/jmr.2010.0186>
- Saad, M. J., Hua, C. C., Misran, S., Zakaria, S., Sajab, M. S., & Abdul Rahman, M. H. (2020). Rice husk activated carbon with NaOH activation: Physical and Chemical properties. *Sains Malaysiana*, 49(9), 2261–2267. <https://doi.org/10.17576/jsm-2020-4909-23>
- Şahin, Ö., Saka, C., Ceyhan, A. A., & Baytar, O. (2015). Preparation of High Surface Area Activated Carbon from *Elaeagnus angustifolia* Seeds by Chemical Activation with ZnCl₂ in One-Step Treatment and its Iodine Adsorption. *Separation Science and*

Technology (Philadelphia), 50(6), 886–891.
<https://doi.org/10.1080/01496395.2014.966204>

Sairan, N. S., Subki, N. S., Raihan, N., & Yusoff, N. (2019). Removal of Pb(II), Fe(II) and Zn(II) using activated carbon produced from foxtail palm fruit chemically activated by KOH and H₃PO₄. In *J. Trop. Resour. Sustain. Sci* (Vol. 7).

Salem, I. Ben, Saleh, M. B., Iqbal, J., El Gamal, M., & Hameed, S. (2021). Date palm waste pyrolysis into biochar for carbon dioxide adsorption. *Energy Reports*, 7, 152–159.
<https://doi.org/10.1016/j.egyr.2021.06.027>

Saravanan, A., Senthil Kumar, P., Jeevanantham, S., Karishma, S., Tajsabreen, B., Yaashikaa, P. R., & Reshma, B. (2021). Effective water/wastewater treatment methodologies for toxic pollutants removal: Processes and applications towards sustainable development. *Chemosphere*, 280.
<https://doi.org/10.1016/j.chemosphere.2021.130595>

Schwarzenbach, R. P., Egli, T., Hofstetter, T. B., Von Gunten, U., & Wehrli, B. (2010). Global water pollution and human health. *Annual Review of Environment and Resources*, 35, 109–136. <https://doi.org/10.1146/annurev-environ-100809-125342>

Shahrokhi-Shahraki, R., Benally, C., El-Din, M. G., & Park, J. (2021). High efficiency removal of heavy metals using tire-derived activated carbon vs commercial activated carbon: Insights into the adsorption mechanisms. *Chemosphere*, 264, 128455.
<https://doi.org/10.1016/J.CHEMOSPHERE.2020.128455>

Silvestre-Albero, A. M., Juárez-Galán, J. M., Silvestre-Albero, J., & Rodríguez-Reinoso, F. (2012). Low-pressure hysteresis in adsorption: An artifact? *Journal of Physical Chemistry C*, 116(31), 16652–16655. <https://doi.org/10.1021/jp305358y>

- Sing, K. S. W. (1982). Reporting physisorption data for gas/solid systems. *Pure and Applied Chemistry*, 54(11), 2201–2218. <https://doi.org/10.1351/pac198254112201>
- Singanana, M., & Peters, E. (2013). Removal of toxic heavy metals from synthetic wastewater using a novel biocarbon technology. *Journal of Environmental Chemical Engineering*, 1(4), 884–890. <https://doi.org/10.1016/J.JECE.2013.07.030>
- Sirimuangjinda, A., Atong, D., & Pechyen, C. (2013). Comparison on pore development of activated carbon produced from scrap tire by hydrochloric acid and sulfuric acid. *Advanced Materials Research*, 626, 706–710. <https://doi.org/10.4028/www.scientific.net/AMR.626.706>
- Sujiono, E. H., Zabrian, D., Zurnansyah, Mulyati, Zharvan, V., Samnur, & Humairah, N. A. (2022). Fabrication and characterization of coconut shell activated carbon using variation chemical activation for wastewater treatment application. *Results in Chemistry*, 4. <https://doi.org/10.1016/j.rechem.2022.100291>
- Tadda, M. A., Ahsan, A., Shitu, A., ElSergany, M., Arunkumar, T., Jose, B., Razzaque, M. A., & Daud, N. N. N. (2016). A Review On Activated Carbon: Process, Application And Prospects. *Journal of Advanced Civil Engineering Practice and Research*, 2(1), 7–13. www.ababilpub.com/jacepr<http://dx.doi.org/xxhttp://ababilpub.com/download/jacepr2-1-3/>
- Thabede, P. M., Shooto, N. D., & Naidoo, E. B. (2020). Removal of methylene blue dye and lead ions from aqueous solution using activated carbon from black cumin seeds. *South African Journal of Chemical Engineering*, 33, 39–50. <https://doi.org/10.1016/j.sajce.2020.04.002>

- Thommes, M., Kaneko, K., Neimark, A. V., Olivier, J. P., Rodriguez-Reinoso, F., Rouquerol, J., & Sing, K. S. W. (2015). Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure and Applied Chemistry*, 87(9–10), 1051–1069. <https://doi.org/10.1515/pac-2014-1117>
- Ting, J., Ho, W., & Tawan, C. (2017). *Flora morphology and sex specific marker development of a Sarawak ' s specialty fruit species Canarium odontophyllum*. 6(11), 1621–1637.
- Trishitman, D., Cassano, A., Basile, A., & Rastogi, N. K. (2019). Reverse osmosis for industrial wastewater treatment. In *Current Trends and Future Developments on (Bio-) Membranes: Reverse and Forward Osmosis: Principles, Applications, Advances*. Elsevier Inc. <https://doi.org/10.1016/B978-0-12-816777-9.00009-5>
- Tseng, R. L. (2006). Mesopore control of high surface area NaOH-activated carbon. *Journal of Colloid and Interface Science*, 303(2), 494–502. <https://doi.org/10.1016/j.jcis.2006.08.024>
- Tzvetkov, G., Mihaylova, S., Stoitchkova, K., Tzvetkov, P., & Spassov, T. (2016). Mechanochemical and chemical activation of lignocellulosic material to prepare powdered activated carbons for adsorption applications. *Powder Technology*, 299, 41–50. <https://doi.org/10.1016/j.powtec.2016.05.033>
- Ukanwa, K. S., Patchigolla, K., Sakrabani, R., Anthony, E., & Mandavgane, S. (2019). A review of chemicals to produce activated carbon from agricultural waste biomass. *Sustainability (Switzerland)*, 11(22), 1–35. <https://doi.org/10.3390/su11226204>

- Ullah, M., Khan, K., Kamal, R., Sohail, M., Ullah, A., Ullah, K., Ullah, A., Shaheen, S., Ullah, I., & Shah, Z. A. (2017). Removal of Methylene Blue Dye from Aqueous Solution by Using Powdered *Saccharum Arundinaceum* Leaves. *Transylvanian Review*, XXV(18). <https://www.researchgate.net/publication/319260364>
- Vasiraja, N., Saravana Sathiya Prabhakar, R., & Joshua, A. (2023). Preparation and Physio-Chemical characterisation of activated carbon derived from *Prosopis juliflora* stem for the removal of methylene blue dye and heavy metal containing textile industry effluent. *Journal of Cleaner Production*, 397, 136579. <https://doi.org/10.1016/J.JCLEPRO.2023.136579>
- Vassilev, S. V., Vassileva, C. G., Song, Y. C., Li, W. Y., & Feng, J. (2017). Ash contents and ash-forming elements of biomass and their significance for solid biofuel combustion. In *Fuel* (Vol. 208, pp. 377–409). Elsevier Ltd. <https://doi.org/10.1016/j.fuel.2017.07.036>
- Vicinisvarri, I., Shanker Kumar, S., Nor Aimi, A. W., Norain, I., & Nurul Izza, H. (2014). Preparation and characterization of phosphoric acid activated carbon from *Canarium Odontophyllum* (Dabai) nutshell for methylene blue adsorption. *Research Journal of Chemistry and Environment*, 18(2), 57–62.
- Wu, F. C., Tseng, R. L., & Juang, R. S. (2009). Characteristics of Elovich equation used for the analysis of adsorption kinetics in dye-chitosan systems. *Chemical Engineering Journal*, 150(2–3), 366–373. <https://doi.org/10.1016/J.CEJ.2009.01.014>
- Xu, T., & Xiaoqin, L. (2008). Peanut Shell Activated Carbon: Characterization, Surface Modification and Adsorption of Pb²⁺ from Aqueous Solution. In *Chinese Journal of Chemical Engineering* (Vol. 16, Issue 3).

- Xu, Z., Chen, J., Wu, M., Chen, C., Song, Y., & Wang, Y. (2019). Effects of Different Atmosphere on Electrochemical Performance of Hard Carbon Electrode in Sodium Ion Battery. *Electronic Materials Letters*, 15(4), 428–436. <https://doi.org/10.1007/s13391-019-00143-w>
- Yahya, M. A., Mansor, M. H., Zolkarnaini, W. A. A. W., Rusli, N. S., Aminuddin, A., Mohamad, K., Sabhan, F. A. M., Atik, A. A. A., & Ozair, L. N. (2018). A brief review on activated carbon derived from agriculture by-product. *AIP Conference Proceedings*, 1972(June). <https://doi.org/10.1063/1.5041244>
- Yang, Z., Hou, J., Wu, J., & Miao, L. (2021). The effect of carbonization temperature on the capacity and mechanisms of Pb(II) adsorption by microalgae residue-derived biochar. *Ecotoxicology and Environmental Safety*, 225. <https://doi.org/10.1016/j.ecoenv.2021.112750>
- Yoshizawa, S., Utsugi, T., Shibanol, K., Goto, S., & Yajima, H. (2005). Effect of Carbonization Temperature on Adsorption Isotherms of Wood Charcoals. In *Transactions of the Materials Research Society of Japan* (Vol. 30).
- Yousfi, N., Fettaka, H., Velasco, L. F., Lodewyckx, P., Boutillara, Y., & Tazibet, S. (2020). Efficiency comparison of activated carbons prepared in inert and in self-generated atmospheres. *Materials and Manufacturing Processes*, 35(9), 993–1001. <https://doi.org/10.1080/10426914.2020.1753881>
- Yuliusman, Y., Puspitasari, M., & Nafisah, A. R. (2019). Preparation of activated carbon by chemical activation using KOH and acetone from low density polyethylene (LDPE) wastes. *AIP Conference Proceedings*, 2175(November). <https://doi.org/10.1063/1.5134591>

- Zabaniotou, A. A., & Stavropoulos, G. (2003). Pyrolysis of used automobile tires and residual char utilization. *Journal of Analytical and Applied Pyrolysis*, 70(2), 711–722. [https://doi.org/10.1016/S0165-2370\(03\)00042-1](https://doi.org/10.1016/S0165-2370(03)00042-1)
- Zawawi, N. M., Hamzah, F., Sarif, M., Manaf, S. F. A., & Idris, A. (2017). Characterization of Activated Carbon Using Chemical Activation Via Microwave Ultrasonic System. *Malaysian Journal of Analytical Science*, 21(1), 159–165. <https://doi.org/10.17576/mjas-2017-2101-18>
- Zhigao Liu, Yuxiang Huang, and G. Z. (2016). Preparation and Characterization of Activated Carbon Fibers from Liquefied Wood by ZnCl₂ Activation. *BioResources*, 11(2001), 3178–3190.
- Zulkania, A., Hanum, G. F., & Sri Rezki, A. (2018). The potential of activated carbon derived from bio-char waste of bio-oil pyrolysis as adsorbent. *MATEC Web of Conferences*, 154, 1–6. <https://doi.org/10.1051/mateconf/201815401029>

APPENDIX

Journal Publications

No	Publication
1	Bin Mohd Khairulzaim, A. A., Rahman, M. R., Roslana, L., Bin Bakri, M. K., Khan, A., and Matin, M. M. (2021). Analysis of char prepared by pyrolysis of dabai (<i>Canarium odontophyllum</i>) nutshells as a potential precursor of biocarbon used for wastewater treatment. <i>BioResources</i> 16(3), 5036-5046. https://doi.org/10.15376/biores.16.3.5036-5046