HYDROTHERMAL CARBONISATION OF PAPAYA PEELS AS ADSORBENT FOR REMOVAL OF CHLORAMPHENICOL COMPOUNDS

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By

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AC	Activated Carbon
CAP	Chloramphenicol
HTC	Hydrothermal Carbonisation
KOH	Potassium Hydroxide
PPH	Papaya Peel-derived Hydrochar
PPAC	Papaya Peel-derived Activated Carbon
SEM	Scanning Electron Microscopy
BET	Brunauer-Emmett-Teller
FTIR	Fourier Transform Infrared Spectroscopy
UV-Vis	Ultraviolet-visible

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C_o	Initial concentration of adsorbate (mg/L)
C_e	Concentration of adsorbate at equilibrium (mg/L)
Q_e	Adsorption capacity at equilibrium (mg/g)
Q_m	Theoretical monolayer/ maximum adsorption capacity (mg/g)
Q_t	Adsorption capacity at time t (mg/g)
K_L	Langmuir constant (L/mg)
K_F	Freundlich constant corresponding to adsorption capacity $(\mathrm{mg/g})(\mathrm{L/mg})^{\frac{1}{\mathrm{n_F}}}$
K_T	Temkin equilibrium binding constant (L/g)
n_F	Freundlich constant corresponding to adsorption intensity
k_1	Kinetic rate constant of pseudo − first − order model (min^{-1})
k_2	Kinetic rate constant of pseudo − second − order model $(\mathrm{g/mg \cdot min})$
B	Temkin constant corresponding to heat of adsorption (J/mol)
b_T	Temkin constant showing the variation of adsorption energy (kJ/mol)
V	Volume of solution (L)
W	Mass of adsorbent (g)
R^2	Correlation coefficient

PENGKARBONAN HIDROTHERMA KULIT BETIK SEBAGAI PENJERAP UNTUK PENYINGKIRAN KLORAMFENIKOL

ABSTRAK

Kloramfenikol (CAP) ialah bahan farmaseutikal aktif (API) yang kerap dikesan dalam persekitaran akuatik. Akibatnya, pendedahan berterusan sisa antibiotik ini membawa kesan buruk kepada kesihatan manusia dan organisma akuatik. Antara beberapa teknologi penyingkiran antibiotik daripada sumber air, kaedah penjerapan telah mendapat perhatian penyelidik kerana kemudahan dalam sintesis, kos penyediaan karbon teraktif (AC) yang rendah serta ketersediaan bahan mentah daripada sisa biojisim yang mampan dan boleh diperbaharui. Di Malaysia, industri tanaman buah-buahan tempatan menduduki tempat keempat dalam skala hektar perladangan. Oleh itu, dalam kajian ini, kulit betik, salah satu buah tropika bukan bermusim yang paling banyak dihasilkan di Malaysia, telah disintesis menjadi AC daripada kulit betik (PPAC) dan telah diuji untuk penjerapan CAP. Dalam sintesis PPAC, pengkarbonan hidroterma (HTC) telah dijalankan diikuti dengan pengaktifan kimia menggunakan kalium hidroksida (KOH) dan radiasi gelombang mikro untuk meningkatkan luas permukaan, porositas dan kumpulan berfungsi. Kuasa radiasi gelombang mikro semasa proses pengaktifan (364-700 W) dan kepekatan awal CAP (5-100 mg/L) telah disiasat untuk mengkaji kapasiti penjerapan dan peratusan penyingkiran PPAC. Berdasarkan data eksperimen, peningkatan kuasa gelombang mikro membawa kepada peningkatan kapasiti penjerapan dan peratusan penyingkiran sehingga nilai optimum. Kapasiti penjerapan juga meningkat apabila kepekatan awal CAP meningkat kerana daya penggerak yang dihasilkan meningkat untuk mengatasi rintangan pemindahan jisim. Kapasiti penjerapan maksimum sebanyak 22.9958 mg/g dan peratusan penyingkiran maksimum sebanyak 82.40% telah dicapai. Selain itu, penyingkiran CAP melalui PPAC mematuhi model isoterma Langmuir dan model kinetik pseudo-urutan-kedua. Kajian ini menunjukkan bahawa PPAC ialah penjerap yang memuaskan dan berpotensi untuk menyahcemar CAP daripada sumber air.

HYDROTHERMAL CARBONISATION OF PAPAYA PEELS AS ADSORBENT FOR REMOVAL OF CHLORAMPHENICOL COMPOUNDS

ABSTRACT

Chloramphenicol (CAP) is an active pharmaceutical ingredient (API) frequently detected in aquatic environments. As a result, continuous exposure to this antibiotic residue brings about adverse effects on human health and aquatic organisms. Recently, among several antibiotic removal technologies from water sources, adsorption method has gained the attention of researchers due to its simplicity in design, low preparation cost of activated carbon (AC) and high availability of feedstock from sustainable and renewable biomass waste. Locally, Malaysia's fruit crop industry takes up the fourth largest land area for plantation purposes. Thus, in this study, the peel waste of papaya, one of Malaysia's most produced non-seasonal tropical fruits, was synthesised into papaya peel-derived activated carbon (PPAC) and tested for batch adsorption of CAP. In the synthesis of PPAC, hydrothermal carbonisation (HTC) was carried out followed by chemical activation via potassium hydroxide (KOH) and microwave heating to enhance its surface area, porosity and functional groups. Microwave power of activation process (364-700 W) and initial CAP concentration (5-100 mg/L) were investigated to study the PPAC adsorption capacity and percentage removal. Based on the experimental data, increased microwave power led to an increase in both adsorption capacity and percentage removal until an optimum value. Adsorption capacity also increased when initial CAP concentration increased owing to the higher driving force generated to overcome mass transfer resistance at higher initial CAP concentration. Maximum adsorption capacity of 22.9958 mg/g and maximum percentage removal of 82.40% were achieved. Moreover, the Langmuir isotherm model and pseudo-second-order kinetic model best fitted the data for CAP removal via PPAC. The findings indicated that PPAC was a promising and potential adsorbent in decontaminating CAP from water sources.

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

Chloramphenicol (CAP) is a broad-spectrum antimicrobial compound used as human antibiotics to treat bacterial infections in humans, as veterinary drugs to treat pet animals and as growth promoters in livestock farming (Lach, 2019). However, the extensive use of this antibiotic across livestock farms and aquaculture acts as pollutants to the environment. Through livestock and human intake, traces of CAP remain unmetabolised in the organism bodies and are excreted via urine and faeces. It then seeps into the soil or water via sewage and manure, leading to the accumulation of this commercial micropollutant in the water sources after being discharged from hospitals and pharmaceutical factories as one of the elements present in both untreated and treated wastewater (Lach and Ociepa-Kubicka, 2017). This pollutes the natural environment as CAP exhibits low biodegradability and persistently remains in unchanged or active forms (Ahmed *et al.*, 2017; Li *et al.*, 2018; Lach, 2019). As a result, aquatic animals and human beings experience prolonged exposure to these micropollutants through direct consumption of contaminated water or food originated from crops grown with water. Thus, this significantly threatens food safety and public health (Juela, 2022).

On top of that, the accumulation of CAP poses serious health threats as it induces resistance in bacteria strains. Low antibiotic concentrations up to several µg/L are present in surface water, groundwater, wastewater and drinking water (Lach, 2019). Consequently, bacteria are more insensitive to the existing antidotes in human disease treatment or even growth promotions in livestock due to the superbacteria resistance that emerged from prolonged exposure of bacteria to low concentrations of antibiotic residues in the environment (Lach, 2019).

As the negative impacts of antibiotics on human health and the environment are widespread and clearly demonstrated, antibiotic traces must be eliminated effectively from water sources. Ahmed *et al.* (2017) present several antibiotic removal technologies, including photocatalysis, chemical oxidation, photodegradation, membrane separation, and physicochemical approaches. Among these methods, adsorption on activated carbon (AC) is preferred due to its low cost, easy design, high efficiency, reusability, environmental friendliness and absence of harmful by-products (Reza *et al.*, 2020; Juela, 2022; Nguyen *et al.*, 2022).

AC is a carbonaceous material with a high degree of porosity, specific surface area and specific functional groups. It is suitable as an adsorbent to eliminate pharmaceutical contaminants from water resources (Benedetti *et al.*, 2018). The raw materials of AC are vast, ranging from finite resources such as coal and lignite to sustainable resources such as biomass. However, the application of commercial AC in large-scale operations is impractical due to the high cost incurred (Masoumi *et al.*, 2021). As a result, great effort has been spent developing cost-effective and renewable AC. In this case, diverse biomass feedstock is readily available in Malaysia.

In Malaysia's agriculture sector, tropical fruit crops account for 202,400 hectares of land area, with their hectarage just after oil palm, rubber and paddy. Among the fresh tropical fruits produced locally, papaya (*Carica papaya* L.) is ranked 6th, contributing to 6.3% of the total production of fresh tropical fruits in 2017, deeming its abundance and availability of this feedstock (Dardak, 2019). Papaya peels constitute 20-25% of the fruit weight (Salla *et al.*, 2016).

On top of that, food waste-derived AC is opined to contribute toward sustainability as the alternative use of fruit peels opens the new possibility of producing value-added products from the otherwise non-useful solid waste without occupying additional land use or competing with food sources (Shehzad *et al.,* 2015; Joseph *et al.*, 2020). It is further exploited to reduce agricultural waste during post-harvesting, processing, or fresh consumption instead of discarding them to landfills or as domestic compost (Dardak, 2019). It also serves to alleviate the ramification of landfill leachate to the ground and adjacent habitats which may cause soil pollution in the long run (Shehzad *et al.,* 2015).

Before the papaya peels are suitable to be utilised as adsorbents, thermochemical conversion technologies such as pyrolysis and hydrothermal carbonisation (HTC) are typically used to produce biochar and hydrochar respectively, converting biomass containing organic feedstock to carbon-rich solid products to enhance the characteristics of AC for adsorption process. Among these techniques, HTC is more promising as it can process wet feedstock (moisture content >50 wt%) directly without needing an energy-intensive pre-drying step. Besides, water as the reaction medium also requires milder process conditions with lower temperatures ranging from 150-350 °C for 2-10 hours of reaction time under supercritical water pressure, contributing to lower reactor volume and manufacturing costs more process-effective and economic-feasible. Furthermore, various HTC experimental conditions such as carbonisation temperature, biomass-to-water ratio, residence time and medium pH can be altered to better suit the feedstock type to its adsorption performance (Masoumi *et al.,* 2021).

Besides the processing conditions of HTC, thermochemical properties such as porosity, specific surface area and presence of discrete functional groups also intimately influence CAP's adsorption capacity and removal efficiency. Generally, hydrochar exhibits inherent weaknesses in their heterogeneous surfaces as they have a low specific surface area, non-developed porous structures and poor surface chemistry (Musa *et al.*, 2017). These set back its potential function as an environmental contaminant adsorbent as scalability is needed to be evaluated as a large amount of hydrochar is needed to decontaminate CAP from water sources (Nguyen *et al.*, 2022).

However, to tackle this major setback, hydrochar can be modified to enhance its properties via chemical activation, physical activation and integration of other functional species to produce activated hydrochar or carbon. Musa *et al.* (2017) state that among these techniques, chemical activation is favoured over the other methods as it needs a lower temperature and shorter treatment time than physical activation. It also results in a larger surface area, better porous structure and higher carbon yield (Abioye and Ani, 2017; Musa *et al.*, 2017). Chemical activation is done by impregnating the hydrochar with chemical agents such as acid, alkaline, oxidising, neutral and organic agents followed by an activation process conventionally done by heating the chemical-activated material in a fixed-bed reactor under flowing nitrogen (Juela, 2022; Masoumi *et al.*, 2021). Common chemical agents involved are zinc chloride, phosphoric acid, sodium hydroxide, hydrogen peroxide, potassium carbonate and potassium hydroxide (Xue *et al.*, 2012; Ma *et al.*, 2019).

After the chemical impregnation process, instead of conventional heating, Abioye and Ani (2017) suggested an alternative by utilising microwave heating to curb the existing problems with conventional heating. These include heat loss to surroundings, heat transfer resistance and microstructure distortion due to thermal gradient from the particle’s hot surface to its interior. Microwave heating can address these issues as heat energy is converted via particle dipole rotation and ionic conduction instead of using conduction and convection as in conventional heating (Deng *et al.*, 2010). Besides, microwave irradiation also exhibits some advantages over conventional heating such as shorter heating duration, uniform temperature distribution, and energy saving (Vimalkumar *et al.*, 2018).

In previous works, Foo and Hameed (2011) recorded 4.5 times increase in BET surface area from 164m^2/g to 752m^2/g by impregnating rice husk with KOH coupled with microwave heating. Fan *et al.* (2010) also demonstrated a NaOH modification on bamboo charcoal to increase its useful functional groups, resulting in an adsorption efficiency of CAP four times higher than the pristine bamboo charcoal feedstock. These examples proof that the functionalisation of AC is needed to improve the feasibility of using agricultural biomass in eliminating residual CAP from water commercially.

1.2 PROBLEM STATEMENT

The agricultural sector in Malaysia accounted for 8% of the country's gross domestic product (GDP) in 2020 (International Trade Administration, 2021). The annual global agricultural waste production recorded a striking amount of 998 million tons whereas Malaysia contributed 1.2 million tons to the total production (Dardak, 2019). Foo and Hameed (2009) opined that modernity and industrial development not only led to more prosperous and extravagant human lifestyles and habits, but also caused higher generation of municipal solid waste. In the agricultural sector, fruit waste such as fruit peel is not suitable for disposal via conventional burning due to its high moisture content or sanitary landfilling due to the production of leachate from the composted waste (Kantakanit *et al.*, 2018). This has prompted growing research interest in finding a more reliable and promising alternative to minimise or sustain the growing amount of solid waste. One applicable method is converting agricultural waste into economic and efficient activated carbon (AC) to remove pollutants in water sources (Foo and Hameed, 2009).

Studies on the removal of antibiotics, particularly chloramphenicol (CAP) using adsorptive materials derived from agricultural waste are scarce. Present work on CAP removal from organic waste-derived AC includes *Typha orientalis*, grape slurry, corn stover, bamboo charcoal and peanut shell (Fan *et al.*, 2010; Li *et al.*, 2018; Cheng *et al.*, 2019; Chitongo *et al.*, 2019; Yang *et al.*, 2020). Earlier, Hamid and Zulkifli (2021) reported the effect of different carbonisation temperatures (150-200 ^{o}C) with a reaction time of 120 minutes on papaya peel-derived hydrochar (PPH) on mass yield, elemental compositions, higher heating value (HHV) and the effectiveness of methylene blue degradation. Nieva *et al.* (2019) also investigated the adsorption capacity of doxycycline using PPH by varying the pH and initial adsorbate concentration. Although

Hamid and Zulkifli (2021) had investigated the removal of methylene blue using PPH, no literature presents the removal of CAP using AC prepared from papaya peel despite its abundance and availability in Malaysia.

Moreover, as mentioned previously, the physiochemical properties of AC depend on the type of feedstock and the processing condition of both HTC and chemical activation. However, as recent work mainly focused on developing hydrochar from various carbonaceous sources and enhancing adsorption performance based on different carbonisation and activation conditions such as different carbonisation temperature, retention time and impregnation ratio, an in-depth discussion on microwave heating technique and its performance enhancement on the hydrochar-derived AC are limited (Chávez and Galiano, 2019). Furthermore, as the conventional heating technique is still the most widespread and known method to prepare an AC, there is no present study on the usage of microwave-irradiated biomass AC in CAP removal.

Therefore, this research intends to study the effect of chemical activation on the characterisation of PPAC by examining the differences between PPH and PPAC. Next, adsorption capacity and percentage removal of CAP from PPAC activated from different microwave powers are inspected. Furthermore, change in initial concentrations of CAP is also investigated further to maximise the adsorption capacity and removal efficiency of PPAC.

1.3 RESEARCH OBJECTIVES

The objectives of this research are:

i. To produce hydrochar from papaya peels using hydrothermal carbonisation and turn it into activated carbon by utilising chemical impregnation and microwave heating.

ii. To determine the physical and chemical properties of hydrochar such as particle size, morphology and type of bonding via BET, SEM and FTIR.

iii. To test the capabilities of activated carbon produced as the adsorbent for chloramphenicol.

CHAPTER 2

LITERATURE REVIEW

2.1 BIOMASS-BASED ACTIVATED CARBON

Solid agricultural waste has since been utilised as low-cost adsorbents due to its cost-effectiveness, ease of operation, non-toxicity, low energy requirement, high accessibility, stable physical and chemical properties and versatile applications (Xu *et al.*, 2018; Ma *et al.*, 2019). Focusing on the non-food category, use of food peels from the agricultural and manufacturing sectors to produce AC are investigated by researchers in removing contaminants such as dyes from wastewater. Instances are pineapple peel, orange peel, jackfruit peel, pomelo skin and pomegranate peel (Foo and Hameed, 2012a, 2012b; Abioye and Ani, 2017; Vimalkumar *et al.*, 2018). Foo and Hameed (2012a, 2012b) observed a BET surface area, S_{BET} of 1104.45 m^2/g and 1006 m^2/g for orange peel and pineapple peel-based AC respectively. Using the same fruit peel as the present work, Hamid and Zulkifli (2021) reported a maximum methylene blue removal percentage of 92.57% using hydrothermal carbonised papaya peel hydrochar.

2.2 HYDROTHERMAL CARBONISATION FOR HYDROCHAR SYNTHESIS

To produce hydrochar, HTC, also known as wet torrefaction, was employed to convert the agricultural waste feedstock into a carbon-rich solid product. The carbonisation process removes non-carbon species such as moisture and volatile compounds from carbonaceous materials through thermal decomposition (Mohamad Nor *et al.*, 2013).

According to Kambo and Dutta (2015), HTC was operated at a temperature between 180-260 ^oC with a residence time of 5 min-12 h with a heating rate of 5-10 ^oC/min. HTC is favoured over the other conventional pretreatment methods due to its high conversion efficiency, elimination of pre-drying requirement and relatively low operating temperature (Kambo and Dutta, 2015). Unlike pyrolysis, HTC did not produce hazardous gases and the hydrochar particles are not susceptible to auto-ignition due to the high concentration of surface oxygen groups (Berge *et al.,* 2013). Nevertheless, hydrochar synthesised via this method exhibited low surface area and porosity because of hydrocarbon formation during HTC (Masoumi *et al.,* 2021). Sayğili and Güzel (2016) presented that carbonised tomato waste hydrochar at 500 ^oC for 1 h had S_{BET} of 12.79 m^2/g and total pore volume, V_{tot} of 0.012 cm^3/g. Thus, chemical activation was needed before the hydrochar is fitted for batch adsorption of contaminant.

2.3 CHEMICAL ACTIVATION OF HYDROCHAR

Proceeding to the chemical activation of hydrochar to produce AC, chemical activation involves the impregnation of hydrochar with a dehydrating agent selected based on the nature of adsorbent, adsorbate application, availability, cost and purity (Özhan *et al.,* 2014; Musa *et al.,* 2017). As the more common methods include physical, chemical and physiochemical activation, generally, this step gives rise to increased porosity, surface area and pore volume (Masoumi *et al.,* 2021).

Alkaline solution provides a chemical modification to increase the number of hydrophilic functional groups and pH value of AC (Azzaz *et al.,* 2020). Shehzad *et al.* (2015) discussed that alkaline hydroxide impregnation such as KOH and NaOH would predominantly increase the specific surface area of resulting AC. Using the previous example of tomato waste hydrochar, $ZnCl_2$ activation was done using an impregnation ratio of 4:1 and the resulting tomato AC recorded a significant increase in S_{BET} to 760 m^2/g and V_{tot} of 0.437 cm^3/g (Sayğili and Güzel, 2016). Foo and Hameed (2012) also reckoned that orange peel modified with K_2CO_3 using impregnation ratio of 1.25:1 gave S_{BET} of 1104.45 m^2/g and V_{tot} of 0.615 cm^3/g from the initial values of 6.88 m^2/g and 0.016 cm^3/g.

According to the classification adopted by IUPAC, adsorbent pores are categorised into three groups: micropores (<2 nm), mesopores (2-50 nm), and macropores (>50 nm) (Özhan *et al.,* 2014). For chemical activation using KOH at 600-800 °C, potassium from its precursor chemical diffused into the internal matrix structure and separated the lamellae of crystallites that form the carbon structure, enlarging the existing pores and making new porosities (Downie *et al.*, 2009; Chitongo *et al.*, 2019). These steps resulted in significantly improved surface area, pore structure and number of micropores and mesopores on the adsorbent surfaces (Foo and Hameed, 2011). For example, a 91.78 % mesoporosity was found in tomato AC using $ZnCl_2$ whereas an 87.80 % mesoporosity was recorded in *Typha orientalis* activated by H_3PO_4 (Sayğili and Güzel, 2016; Li *et al.*, 2018). The pore size structure was mostly mesoporous, allowinghe passage of CAP to the interior and exterior surfaces as CAP displayed an adsorbate molecule width smaller than the width of a micropore (Li *et al.,* 2018; Cheng *et al.,* 2019).

After the chemical impregnation process, microwave heating process was carried out. Özhan *et al.* (2014) deduced that this microwave method exhibited several benefits over the conventional heating method using tubular reactor. One of them was faster irradiation time. Shehzad *et al.* (2015) summarised that the heating time required for conventional heating was remarkably longer, ranging from 1-10 h for various biomass-derived AC, whereas microwave heating took about 6-30 min depending on the types of materials (Shehzad *et al.*, 2015). The shortened activation time lowered the energy consumption as the increase in temperature via microwave was done through energy supplied to carbon particles. These particles transferred heat by dipole rotation and ionic conduction instead of the typical heat transfer techniques, leading to a homogeneous microstructure and no thermal gradient (Özhan *et al.*, 2014). Furthermore, compared to traditional heating using the same precursor, Guo and Rockstraw (2007) and Chávez and Galiano (2019) revealed that microwave heating-produced AC exhibited considerably higher surface area than conventional heating which is desirable in the adsorption process.

Impregnation ratio, activation power and activation time are the primary factors in consideration while preparing AC via microwave heating. Microwave irradiation led to the development of relatively higher surface areas of produced AC as compared with conventional heating for the same precursor used (Guo and Rockstraw, 2007). Due to the rapid rise of radiation temperature, it shortened the time of activation which in turn reduced the energy consumption. Chemical activation with microwave heating was easier to operate than conventional heating. It also induced surface area development to enhance its adsorption and removal efficiency (Chávez and Galiano, 2019). Therefore, in this paper, microwave power was altered and the effect on CAP adsorption was studied to obtain the most suitable microwave power to activate papaya peel hydrochar based on its adsorption capacity and percentage removal.

2.4 BATCH ADSORPTION OF CHLORAMPHENICOL

To investigate and enhance the adsorption performance of the synthesised PPAC on the removal of CAP, two parameters were evaluated: microwave power and initial concentration of CAP. In order to produce a better adsorbent from papaya peel, the process was split into two parts: optimisation of PPAC synthesis and optimisation of operating conditions for batch adsorption.

2.4.1 EFFECT OF MICROWAVE POWER ON PAPAYA PEEL-DERIVED ACTIVATED CARBON

In the thermal treatment process of chemical activation to produce AC from hydrochar, microwave heating was introduced to promote better porosity formation in a short radiation time than conventional heating (Foo and Hameed, 2012b). Microwave heating uses the electromagnetic spectrum of frequency around 2.45 GHz and wavelength of 12.24 cm to heat up thin-layered and large surface area materials (Abioye and Ani, 2017). As a result, large amount of micropores and mesopores were created as the spaces previously occupied by the activating agent molecules during impregnation left cavities on the adsorbent surfaces as the activating agent evaporated (Mohamad Nor *et al.*, 2013).

Shehzad *et al.* (2015) provided an overview of the optimal operating conditions for multiple food waste. The typical operating conditions for microwave heating of activated food waste ranged between 350-700 W for radiation power and 5-15 min for radiation time. After studying the effect of radiation power on the adsorption capacity of methylene blue, Foo and Hameed (2012) documented that both orange and pineapple peel ACs had the best adsorption performance at a heating power of 600 W whereas Özhan *et al.* (2014) concluded that 400 W was the prime microwave power for the adsorption of pine cone AC. On the other hand, Deng *et al.* (2010) figured that the best microwave power for cotton stalk AC was 660 W. Nevertheless, no previous work investigated the optimum microwave power for PPAC. Hence, this work focused on evaluating the optimum microwave power used to synthesise PPAC.

2.4.2 EFFECT OF INITIAL CONCENTRATION OF CHLORAMPHENICOL ON PAPAYA PEEL-DERIVED ACTIVATED CARBON

The efficiency of removing antibiotic compounds also relied on the initial concentration of the adsorbate itself. Wee *et al.* (2020) explained that the removal efficiency of compounds was reliant on the contamination level in raw water. Furthermore, Li *et al.* (2018) reported that the initial increase in adsorption capacity of CAP on *Typha orientalis*-derived AC was rapid until a certain duration when the adsorption capacity slowed down due to the gradual buildup of diffusion resistance and repulsive forces between CAP molecules adsorbed on the solid surfaces. Similarly, corn stover-derived AC had the highest CAP adsorption capacity at 30 mg/L among the six different concentrations (5-30 mg/L). Hamid and Zulkifli (2021) showed that the adsorption of methylene blue dye also observed the same result as CAP: when initial concentration of methylene blue dye increased ranging from 50-200 mg/L, adsorption capacity of methylene blue also increased where the highest adsorption capacity was 37.12 mg/g at 200 mg/L. Nevertheless, for percentage removal of CAP via KOH-modified activated grape slurry carbon adsorbents, Fagbayigbo *et al.* (2020) explained that the CAP percentage removal decreased with increasing adsorbate concentration from 30 to 100 mg/L, forming an inverse relationship. This was reasoned by the exhaustion of vacant surface binding sites as the adsorbent’s limited number of active sites became saturated at higher CAP concentrations (Chitongo *et al.*, 2019).

2.5 ADSORPTION ISOTHERM

To understand the fundamental behaviour of AC and its interactions with adsorbents, adsorption isotherms were employed where experimental data was analysed by fitting with to isotherm models (Özhan *et al.,* 2014). Isotherm refers to the relationship, distribution and behaviour between the equilibrium adsorbate molecules in liquid phase and the equilibrium adsorption amount in solid phase when temperature is kept constant (Arampatzidou and Deliyanni, 2016; Wang and Guo, 2020a). Among the various adsorption isotherm equations, Langmuir, Freundlich and Temkin isotherms were selected in this study. Wang and Guo (2020a) concluded that Langmuir model was most commonly fitted to adsorption data of organic pollutants such as pharmaceuticals, dyes and metal ions onto adsorbents because of their simplicity in equilibrium data prediction, and it was succeeded by Freundlich isotherm.

2.5.1 LANGMUIR ISOTHERM

Langmuir adsorption model predicts that chemisorption occurred at active sites of adsorbent surface only corresponds to a monolayer of solute molecules. Assumptions made are no lateral interactions or steric hindrance between adsorbed regardless of surface coverage and only one-molecule thickness of adsorbed layer is formed when adsorbate particles adhered to the adsorbent. Adsorption can only occur at a finite number of localised active sites. Besides, homogeneous adsorption occurred where adsorption energy and enthalpy were assumed constant. The Langmuir equation is represented as (Foo and Hameed, 2010; Arampatzidou and Deliyanni, 2016):

$$Q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \tag{2.1}$$

where, $Q_e =$ Adsorption capacity at equilibrium (mg/g)

$C_e =$ Concentration of adsorbate at equilibrium (mg/L)

$Q_m =$ Theoretical monolayer/ maximum adsorption capacity (mg/g)

K_L = Langmuir constant (L/mg)

The Langmuir isotherm is linearised to evaluate the adsorption isotherm data:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \tag{2.2}$$

2.5.2 FREUNDLICH ISOTHERM

On the other hand, Freundlich adsorption model describes a non-ideal and reversible multilayer adsorption phenomenon sourced from the diversity of adsorption sites. In this model, adsorption is not restricted to monolayer. It expresses an equation for surface heterogeneity and an exponential distribution of active sites and their energy. Physisorption occurs at the surface where infinite surface coverage is assumed as saturation of the adsorbent surface is not included. The Freundlich equation is demonstrated as shown (Arampatzidou and Deliyanni, 2016; Wang and Guo, 2020a):

$$Q_e = K_F C_e^{\frac{1}{n_F}} \tag{2.3}$$

where, Q_e = Adsorption capacity at equilibrium (mg/g)

C_e = Concentration of adsorbate at equilibrium (mg/L)

K_F = Freundlich constant corresponding to adsorption capacity $(\mathrm{mg/g})(\mathrm{L/mg})^{\frac{1}{\mathrm{n_F}}}$

$\mathrm{n_F}$ = Freundlich constant corresponding to adsorption intensity

The experimental data is analysed by Freundlich isotherm model in the linearised form:

$$\ln Q_e = \ln K_F + \frac{1}{n_F} \ln C_e \tag{2.4}$$

2.5.3 TEMKIN ISOTHERM

Temkin adsorption isotherm expresses the electrostatic interaction and the heat of adsorption in chemisorption process. The interactions between adsorbent and adsorbate are considered in this model. This model implies that the heat of adsorption of all molecules is linear instead of logarithmic when the adsorbent surface becomes saturated. It postulates that the heat of adsorption is dependent on the adsorbent surface coverage but not the change in concentration. The Temkin model is written as (Foo and Hameed, 2010; Vimalkumar *et al.*, 2018; Chitongo *et al.*, 2019):

$$Q_e = B \ln K_T C_e \qquad (2.5)$$

where, $Q_e =$ Adsorption capacity at equilibrium (mg/g)

$C_e =$ Concentration of adsorbate at equilibrium (mg/L)

$K_T =$ Temkin equilibrium binding constant (L/g)

$B =$ Temkin constant corresponding to heat of adsorption (J/mol)

$b_T =$ Temkin constant showing the variation of adsorption energy $, b_T = \frac{RT}{B}\ (kJ/mol)$

The linearised form of Temkin model is computed as:

$$Q_e = \mathrm{B} \ln K_T + B \ln C_e \qquad (2.6)$$

2.6 ADSORPTION KINETICS

Adsorption kinetics provides information on the uptake of CAP onto the adsorbent with respect to contact time. Kinetic models are attributed to two types: chemical reaction and diffusion. Chemical reaction describes the relationship between chemically kinetic reactions and time without going into the steps whereas diffusion consists of film diffusion and intraparticle diffusion. Kinetic models were constructed to study adsorption and desorption rate by fitting them into linear and non-linear mathematical models to distinguish its adsorption mechanism. The more common mathematical kinetic models include pseudo-first-order and pseudo-second-order kinetic models (Nguyen *et al.*, 2022).

2.6.1 PSEUDO-FIRST-ORDER KINETIC MODEL

In first order reaction, molar concentration of only one reactant is determining the rate of reaction. Instead, for pseudo-first-order model, second order chemical reaction in this case, behaves as a first order reaction. Rate of reaction should be dependant of two reactants. Still, the concentration of one of the reactants is so high that it overwhelms the other reactant and thus, the second reactant's change in concentration becomes negligible. Simonin (2016) reported that it also corresponds to a diffusion-controlled process. The differential form for pseudo-first-order model is (Simonin, 2016; Wang and Guo, 2020b):

$$\frac{dQ}{dt} = k_1(Q_e - Q_t) \qquad (2.7)$$

where, $Q_e =$ Adsorption capacity at equilibrium (mg/g)

$Q_t =$ Adsorption capacity at time t (mg/g)

$k_1 = \text{Kinetic rate constant of pseudo} - \text{first} - \text{order model } (\text{min}^{-1})$

The linearised and simplified form of pseudo-first-order kinetic model is calculated by integrating its differential equation with respect to time:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \qquad (2.8)$$

2.6.2 PSEUDO-SECOND-ORDER KINETIC MODEL

The pseudo-second-order model assumes that the adsorption reaction rate is controlled by chemisorption reaction at the interface between the aqueous and solid phases in the adsorbent. The differential equation is denoted as (Simonin, 2016; Nguyen *et al.*, 2022):

$$\frac{dQ}{dt} = k_2(Q_e - Q_t)^2 \qquad (2.9)$$

where, $Q_e = \text{Adsorption capacity at equilibrium (mg/g)}$

$Q_t = \text{Adsorption capacity at time t (mg/g)}$

$k_2 = \text{Kinetic rate constant of pseudo} - \text{second} - \text{order model } (\text{g/mg} \cdot \text{min})$

Transforming the non-linear mathematical model to its linearised version:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \qquad (2.10)$$

CHAPTER 3

METHODOLOGY

This section describes the materials and equipment required to start the experiment, the step-by-step procedures for the synthesis and characterisation of PPAC, as well as the batch adsorption of CAP.

3.1 MATERIALS AND EQUIPMENT

The materials and equipment used in producing PPH, PPAC and the subsequent characterisation and batch adsorption of CAP are tabulated in Table 3.1 and Table 3.2 respectively:

Table 3.1: Materials Used in Producing AC from Papaya Peel

Material	Purpose
Papaya Fruit (*Carica papaya* L.)	Raw Material for the synthesis of PPH and PPAC
Potassium Hydroxide (KOH)	Alkaline activating agent for the synthesised PPH Alter the pH of CAP
Hydrochloric Acid (HCl)	Washing agent for PPAC
Chloramphenicol (CAP)	Antibiotics to determine the adsorption capacity and removal efficiency of PPAC
Distilled Water	Washing agent Diluting agent
Nitrogen Gas	Provide an inert flow for microwave heating of PPAC

Table 3.2: Equipment Used for the Experiment

Material	**Purpose**
Oven	Dry PPH and PPAC
Blender	Powderise and decrease the size of dry papaya peel pieces
Sieve	Filter out larger particles from fine powdered papaya pieces
Analytical Weighing Balance	Weigh the raw and dried hydrochar powder
Hydrothermal Reactor	Carry out HTC
pH Meter	Measure the pH of sample solution during washing
Microwave Oven	Carry out chemical activation of hydrochar
BET surface area analyser (BET)	Determine the BET surface area of samples
Scanning Electron Microscopy (SEM)	Produce surface morphological characteristics of samples
Fourier Transform Infrared Spectroscopy (FTIR)	Evaluate the functional groups of samples
Membrane Filter	Retain solid AC from the sample solution of CAP and AC
Water Bath Shaker	Shake and mix samples at constant temperature during batch adsorption
UV-Vis Spectrophotometer	Measure the absorbance of solution and concentration of CAP

3.2 FLOW CHART OF METHODOLOGY

In overall, the project can be divided into two parts, the synthesis and characterisation of PPH and PPAC and the batch adsorption of CAP using PPAC.

3.2.1 SYNTHESIS OF PAPAYA PEEL-DERIVED ACTIVATED CARBON

Figure 3.1 shows the flow chart for synthesis of PPH and PPAC as well as the characterisation of and optimisation for CAP batch adsorption:

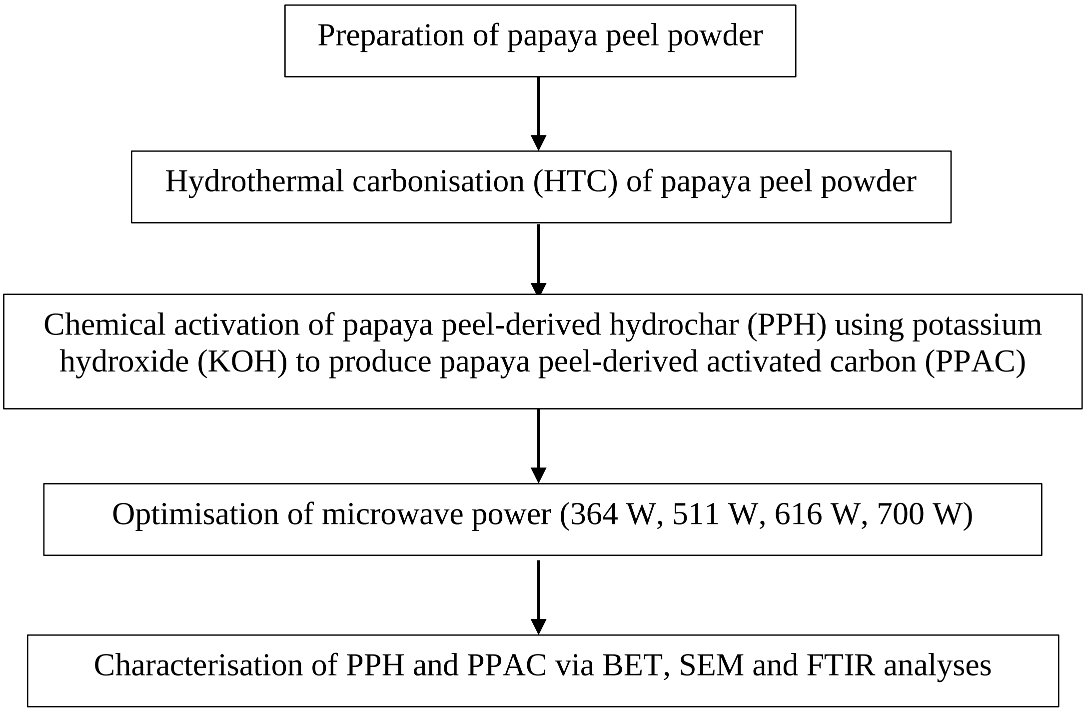

Figure 3.1: Flow Chart for Synthesis of AC

3.2.2 REMOVAL OF CHLORAMPHENICOL

Figure 3.2 depicts the batch adsorption process on the removal of CAP:

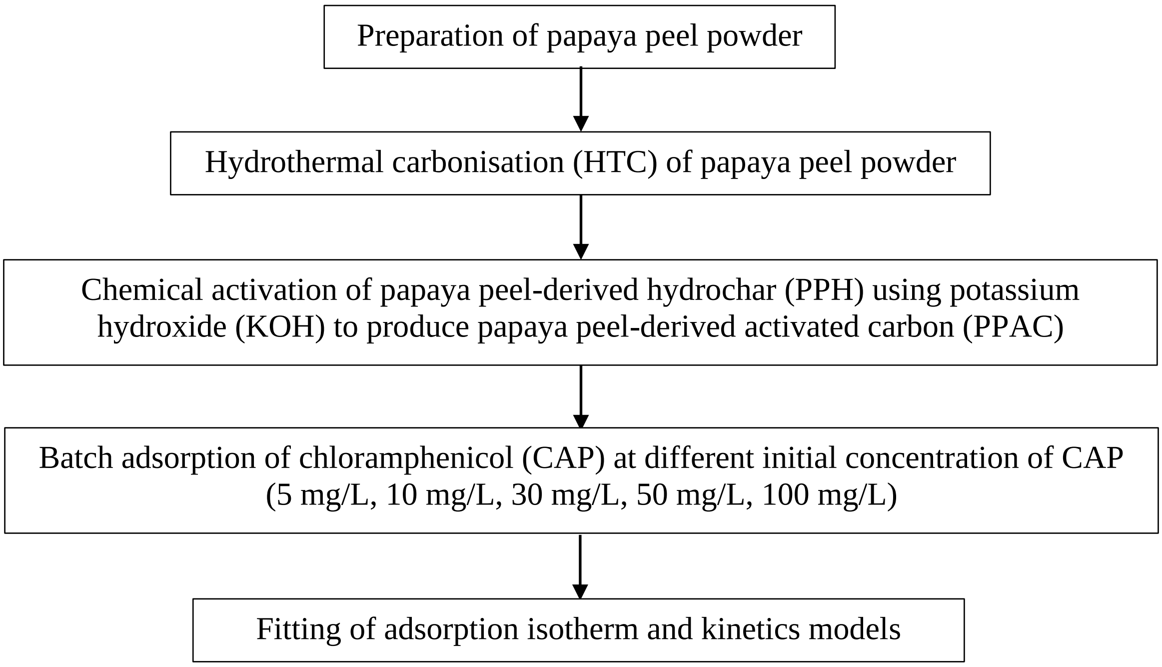

Figure 3.2: Flow Chart for Removal of CAP

3.3 EXPERIMENTAL PROCEDURES

The experimental procedures to produce PPH, PPAC and the subsequent characterisation and batch adsorption of CAP are as follows:

3.3.1 PRETREATMENT OF RAW MATERIAL

The ripened papaya fruit was washed with distilled water to remove dirt from its surface and then peeled. Papaya peels were then cut into smaller pieces and dried in an oven for 18 h at 120 ºC. Next, the small papaya peel pieces were ground using a blender to powderise them before being filtered using an 80-mesh sieve to obtain uniformly-sized powder. Finally, the raw papaya peel powder is weighed using an analytical weighing balance.

3.3.2 HYDROTHERMAL CARBONISATION OF HYDROCHAR

15 g papaya peel powder was mixed with 150 mL distilled water and poured into a 200 mL stainless steel hydrothermal reactor. The hydrothermal reactor was then heated in an oven for 2 h at 150 ºC. After cooling to room temperature, the content was filtered and washed repeatedly with distilled water using a Buchner funnel, filtration flask, pump and filter paper to separate the solid and liquid products. The washed solid hydrochar was collected in a ceramic evaporating dish and further dried using an oven at 120 ºC for 18 h. 2 g of solid hydrochar was put aside in a container labelled PPH for the characterisation process.