

**ALMOND SHELL BASED ACTIVATED CARBON  
PREPARED VIA MICROWAVE IRRADIATED FOR  
CHLORAMPHENICOL REMOVAL**

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CHLORAMPHENICOL REMOVAL**

**by**

**SAW WEN YI**

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## LIST OF ABBREVIATIONS

AC	Activated Carbon
ANOVA	Analysis of Variance
AS	Almond Shell
ASAC	Almond Shell based Activated Carbon
BC	Bamboo Charcoal
BET	Brunauer-Emmett-Teller
CAP	Chloramphenicol
CCD	Central Composite Design
CF	Chicken Feathers
EP	Enteromorpha Prolifera
FL	Fallen Leaves
FTIR	Fourier-Transform Infrared
HPC	Hierarchically Porous Carbons
OFAT	One-Factor-at-a-Time
PC	Petroleum Cokes
PCM	Porous Carbon Material
PFO	Pseudo First Order
PSO	Pseudo Second Order
RSM	Response Surface Methodology
SEM	Scanning Electron Microscopy
USM	Universiti Sains Malaysia
UV	Ultraviolet



## LIST OF SYMBOLS

Symbol	Description	Unit
$b$	Temkin constant related to heat of sorption	J/mol
$C_e$	Solute concentration in solution at equilibrium	mg/L
$C_i$	Thickness of boundary layer	mg/g
$C_o$	Initial solute concentration	mg/L
$C_t$	Liquid-phase CAP concentrations at time $t$	mg/L
$e_i$	Error	-
$k_1$	Pseudo first order rate constant	1/h
$k_2$	Pseudo second order rate constant	g/mg-h
$K_f$	Freundlich constant related to adsorption capacity	mg/g(L/mg) <sup>1/n</sup>
$K_L$	Langmuir Isotherm Constant	L/mg
$k_{pi}$	Intraparticle diffusion rate constant	mg/g-h <sup>1/2</sup>
$K_T$	Temkin isotherm constant	L/g
$M_1$	Concentration of stock solution	mgL
$M_2$	Concentration of desired sample solution	mgL
$N$	Total number of experiments required	-
$n$	Number of variables	-
$n_F$	Freundlich constant related to adsorption intensity	1/mg
$n_c$	Centre runs	-
$q_e$	Amount of solute adsorbed per unit mass of adsorbent	mg/g
$Q_o$	Monolayer capacity of adsorbent	mg/g
$q_t$	Amounts of adsorbate adsorbed at any time, $t$	mg/g
$R$	Universal gas constant	J/mol K

$R_L$	Separation factor	-
$T$	Absolute solution temperature	K
$t$	Time	h
$V$	Volume of sample solution	mL
$V_1$	Volume of stock solution	mL
$V_2$	Volume of desired sample solution	mL
$W$	Mass of ASAC	g
$x_1$	Radiation power	W
$x_2$	Activation time	min
$X_i, X_j$	Coded values of the AC preparation variables	-
$Y$	Predicted response	-
$Y_1$	CAP removal	%
$Y_2$	ASAC yield	%
$\beta_0$	Constant coefficient	-
$\beta_i$	Linear coefficient	-
$\beta_{ii}$	Quadratic coefficient	-
$\beta_{ij}$	Interaction coefficient	-
$\Delta S^\circ$	Standard entropy change	kJ/mol
$\Delta H^\circ$	Standard enthalpy change	kJ/mol
$\Delta G^\circ$	Standard Gibbs free energy	kJ/mol

**KARBON TERAKTIF BERASASKAN KULIT BADAM DISEDIAKAN  
MELALUI PENYINARAN GELOMBONG MIKRO UNTUK PENYINGKIRAN  
KLORAMFENIKOL**

**ABSTRAK**

Dalam kajian ini, karbon teraktif (AC) yang murah dan efisien telah dihasilkan melalui pengaktifan yang melibatkan penyinaran gelombang mikro untuk penyingkiran kloramfenikol (CAP). Keadaan penghasilan optimum bagi kekuatan kuasa gelombang mikro dan masa pengaktifan karbon teraktif berasaskan kulit badam (ASAC) untuk penjerapan CAP dilaksanakan menggunakan kaedah permukaan sambutan (RSM). Keadaan penyediaan optimum yang diperoleh untuk ASAC adalah pada 490 W kuasa radiasi dan 6 minit masa pengaktifan, yang menghasilkan penyingkiran CAP sebanyak 96.23% dan hasilan ASAC sebanyak 41.53%. ASAC yang dioptimumkan telah dicirikan melalui luas permukaan Brunauer-Emmett-Teller (BET), analisis hampiran dan elemen, imej mikroskop elektron pengimbasan (SEM) dan spektrum spektroskopi inframerah transformasi Fourier (FTIR). Untuk kajian penjerapan kelompok, pelbagai parameter operasi seperti kepekatan awal, masa hubungan, suhu larutan dan pH pada penjerapan CAP telah diselidiki. Data eksperimen telah dianalisis menggunakan tiga model garis sesuhu: Langmuir, Freundlich dan Temkin. Didapati bahawa garis sesuhu yang paling sesuai adalah Langmuir, dengan kapasiti penjerapan CAP maksimum pada 63.29 mg/g. Kajian kinetik untuk penjerapan CAP menunjukkan bahawa proses penjerapan CAP pada ASAC mengikuti model kinetik pseudo tertib kedua (PSO). Kajian termodinamik telah dilakukan untuk menentukan parameter termodinamik seperti tenaga bebas Gibbs ( $\Delta G$ ), entalpi ( $\Delta H$ ) dan entropi ( $\Delta S$ ). Berdasarkan parameter termodinamik, penjerapan CAP ke ASAC adalah proses endotermik dan spontan.

# **ALMOND SHELL BASED ACTIVATED CARBON PREPARED VIA MICROWAVE IRRADIATED FOR CHLORAMPHENICOL REMOVAL**

## **ABSTRACT**

In this study, low cost and efficient activated carbon (AC) was prepared from almond shell (AS) through microwave irradiation technique for chloramphenicol (CAP) removal. The optimization of almond shell based activated carbon (ASAC) preparation conditions of microwave irradiation power and radiation time for CAP adsorption was done by using Response Surface Methodology (RSM). The optimum preparation conditions determined were at radiation power and time of 490 W and 6 minutes, respectively, which resulted in 96.23% of CAP removal and 41.53% of ASAC yield. The optimized ASAC was characterised through Brunauer–Emmett–Teller (BET) surface area and pore structural analysis, proximate and elemental analysis, scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR). For batch adsorption study, various operational parameters such as initial concentration, contact time, solution temperature and pH on CAP adsorption were investigated. The experimental data were analyzed using three adsorption isotherm models: Langmuir, Freundlich and Temkin. It was found that the adsorption was best fitted with the Langmuir isotherm model, with maximum CAP adsorption capacity at 63.29 mg/g. Kinetic studies for CAP adsorption indicated that the adsorption process followed a pseudo second order (PSO) kinetic model. The thermodynamic parameters such as standard Gibbs free energy ( $\Delta G^\circ$ ), standard enthalpy change ( $\Delta H^\circ$ ) and standard entropy change ( $\Delta S^\circ$ ) were determined. Based on the thermodynamic parameters, the adsorption of CAP onto ASAC was an endothermic and spontaneous process.

# CHAPTER 1

## INTRODUCTION

### 1.1 Background of chloramphenicol (CAP)

In recent years, antibiotics are one of the most common pharmaceuticals that are used to treat and prevent humans and animals diseases caused by bacteria, as well as in aquaculture (Tan et al., 2017). The excessive consumption of antibiotics has aroused a new global issue and concern as it has becoming an emerging threat to the ecosystems and human health as well. It is highly identified in the aquatic environment where it generates antibiotic-resistant bacteria in the environment. Diseases caused by antibiotic-resistant bacteria are difficult, or sometimes impossible to be cured. In Europe, 25000 of patients are estimated to die under infections caused by antibiotic-resistant bacteria (Lach and Ociepa-Kubicka, 2017). In addition, the presence of antibiotic, even at a very low concentration, can lead to decrease in human immunity, possess a considerable risk to human and environment health (Kümmerer, 2009, Lach and Ociepa-Kubicka, 2017). Chloramphenicol (CAP), an effective broad spectrum antibiotic is widely employed owing to its cost effectiveness and high-availability (Xu et al., 2020). It is typically utilized to control bacterial infections, especially gram-positive and gram-negative bacteria (Balbi, 2004). Nevertheless, due to its unreasonable consumption and improper disposal, CAP has been detected frequently in surface water, ground water, and even drinking water (Guo et al., 2019). Relevant reports show that CAP raises a various adverse effects, such as bone marrow suppression, aplastic anaemia, grey baby syndrome and so on (Balbi, 2004). Conventional water treatment is not able to eliminate this containment effectively due to its low biodegradability (Guo et al., 2019). Therefore, it is crucial and mandatory to develop other approaches in order to remove CAP from the contaminated waters.

## 1.2 Removal of CAP

Throughout the years, several antibiotic removal technologies have been developed, such as photocatalysis, chemical oxidation, photodegradation, membrane processes and adsorption on activated carbon. (Lach, 2019). As we know, activated carbon (AC) is a versatile adsorbent, which extensively used for removal of various undesirable contaminants such as odour, colour, taste and other organic and inorganic impurities. It is a carbonaceous material which is well-known for its large specific surface area, well-built pore structure, high physicochemical stability, and excellent surface reactivity (Ahmad et al., 2020a). Besides that, it is widely used to remove pollutants from wastewater due to its simplicity, great efficiency, and lack of by-products. Nevertheless, the usage of AC is being restricted due to the high cost of production and regeneration, as well as the reliance on non-renewable resources as precursors (Ahmad et al., 2020a, Ahmad et al., 2020c). The employment of these non-renewable resources such as coal, pitches and coke has made the AC production non-sustainable and non-economical feasible. Thus, the preparation of AC based on various biomass such as coconut shells, palm kernel shells, rice husks and nut shells has been studied and developed by many researchers. Almond shell is a by-product from almond production which produced abundantly from the agriculture and it is typically disposed as a waste. The mean production of almond in USA, Spain, Syria, Italy, Iran and Morocco is reported to be about 1.7 million tons every year (Nabais et al., 2011). Almond shell has the potential to be used as the raw materials to produce AC as it is inexpensive and readily available. Besides, its low ash content (0.7-3.4 wt% dry), high carbon composition (45.6-50.6%) or high lignin content (23.7-32.7%) makes it suitable for the AC synthesis (Vidal et al., 2019). Thus, by employing this agriculture waste as the precursor of production of AC, the amount of waste generated is able to be reduced, yet it brings advantages to the socio-economic development to the society.

In general, AC is prepared by conventional heating. The carbon material is heated from the outside, and energy is transferred from the surface to the interior through convection, conduction and radiation (Duan et al., 2012). Temperature gradient from the heated surface to the inside is created until steady state conditions are attained. However, this thermal gradient makes it difficult to effectively remove gaseous products to the surroundings, leading to an extension of processing time to achieve the desired temperature and increase of energy consumption. As a consequence, the yield of products is decreased and a higher cost of energy is required (Du et al., 2016). Recently, there are spike of researches focus on preparation of AC using microwave irradiated method. This is due to the advantages of reduction in processing time, higher activation rate, lower energy consumption and higher yield of product (Khasri and Ahmad, 2018). In this method, the carbon material is heated and the energy is transferred through dipole rotations and ionic conduction (Hesas et al., 2013). The temperature gradient created is gradually increased from the surface to the interior as the heating is uniform, where the microwave absorbed is transformed into the heat supplied to the material (Duan et al., 2012). Bases on the advantages over conventional heating method, microwave-irradiated method is therefore considered as an applicable alternative to be employed to produce AC.

### 1.3 Problem statement

Nowadays, the use of CAP has been banned in many countries, such as the United State of America, Canada and China as it brings adverse effect to the environment and human health even in a low dose (mg/L) (Zhang et al., 2021). The presence of CAP in the environment might lead to severe toxicity to the aquatic and neighbouring systems, and cause serious side effects on human such as grey baby syndrome, leukaemia, fatal aplastic anaemia, and other blood disorders (Yang et al., 2020a, Idris et al., 2020).

Adsorption appears to be the best method for CAP removal compared to other methods such as photocatalysis, UV/chlorine treatment, advanced oxidation and nanoparticles treatment. This is because it is simple, efficient in environmental pollutants removal, low energy consumption and does not generate any by-products (Yang et al., 2020a, Yang et al., 2020b, Ahammad et al., 2021). Nevertheless, the adsorption process is limited by expensive cost of precursor, which is economically unfavourable.

In this study, almond shell (AS) is proposed to be the precursor for AC preparation. AS is an agricultural solid waste which is abundant, low cost and easily available. The high carbon content of AS makes it suitable to be utilized as the precursor for AC preparation. Since the AS can be employed an eco-friendly precursor, the solid waste disposal problem could be solved. This proposed research shall provide a huge opportunity to reduce the cost of removal of contaminants due to the employment of renewable precursor.

Conventional heating which is energy extensive and costly is the most common method in AC preparation. Hence, microwave irradiated method under the flow of carbon dioxide (CO<sub>2</sub>) was proposed for the AC preparation in this study. It requires less energy and processing time compared to the conventional heating. The high yield of production due to the high activation rate leads to an increase in efficiency of AC preparation. Other than that, the conversion of precursor into AC is uniform with minimal generation and emission of hazardous by-products.



Thus, an attempt was made to study the removal of CAP on ASAC prepared by microwave irradiated method.

Response surface methodology (RSM) is used in the optimization for the adsorption process instead of the traditional approach as it is able to reduce the number of investigative runs and the time required to complete series runs. It employs a variety of mathematical and statistical relationships to estimate the best beneficial values for specific process parameters and the optimal response and values may be obtained easily from the limited number of runs using central composite design (CCD).

#### **1.4 Research Objectives**

This study is carried out in order to achieve these following objectives:

- i. To prepare and characterize ASAC in terms of elemental analysis.
- ii. To optimize preparation condition (microwave irradiation power and activation time) of almond shell based activated carbon (ASAC) using Response Surface Methodology (RSM).
- iii. To investigate the effects of initial concentration and contact time, solution temperature and solution pH on adsorption of CAP onto ASAC using batch adsorption study.
- iv. To evaluate the adsorption performance of ASAC through adsorption isotherm, kinetics, mechanism and thermodynamics studies.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 Adsorption**

Adsorption is a separation process that depends on the concentration of components in the feed to be adsorbed (Seader et al., 2010). At the same time, it can also be referred as a process of retention of components of a mixture on a solid surface, where the solid is known as adsorbent, and the components being adsorbed is known as adsorbate (Dutta, 2007). It is a surface phenomenon where it occurs due to the affinity between adsorbent and adsorbate. Based on the interaction forces between the adsorbent and adsorbate, adsorption process can be classified into two types, which are physisorption and chemisorption

Generally, the interactive force in physisorption is Van der Waal's force and electrostatic force, which are relatively weak. Physisorption takes place with formation of multilayer of adsorbate on adsorbent. On the other hand, chemisorption possesses valence forces where it is significantly stronger than interactive force in physisorption. Chemisorption occurs with formation of unilayer of adsorbate on adsorbent.

#### **2.2 Adsorption isotherm**

Physical binding of a molecule onto an adsorbent's surface drives the adsorption process to occur. There are four most popular interactions under adsorption scheme, namely Van der Waals, electrostatic and hydrogen bonding. Adsorption isotherms describe the equilibrium relationships between the concentration of solute in the liquid phase and amount of solute adsorbed on adsorbents' surface. The equilibrium adsorption isotherm plays a crucial role for an adsorption system design as it describes the experimental data and parameters derived from different isotherm models. Linear regression is commonly used to find the best-fitting equilibrium adsorption isotherm. On the other hand, correlation coefficient,  $R^2$  for each

isotherm models were calculated and compared in order to determine the applicability of isotherm equations. Illustration of adsorption isotherm is presented as shown in Figure 2.1.

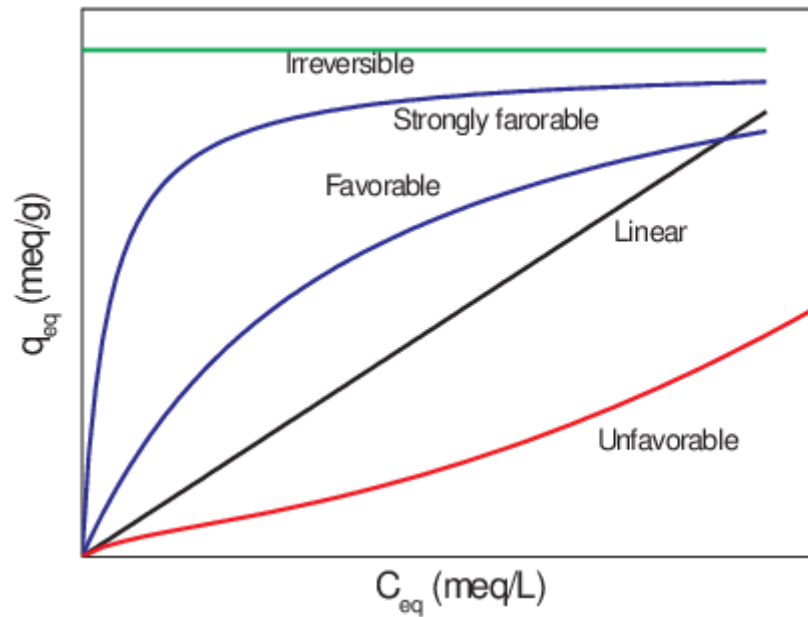


Figure 2.1 Adsorption isotherms.

Isotherms that has a convex shape are non-linear and termed favourable; these isotherms are the most useful. In favourable isotherm, large amount of adsorption occurred at a low partial pressure and the amount adsorbed is independent of the concentration down to very low value. However, the ultimate in favourable isotherms is an irreversible adsorption, where the maximum adsorption is achieved at a very low partial pressure (Gabelman, 2017).

Conversely, an unfavourable isotherm is the isotherm that having a concave shape due to low solid loadings obtained and it causes long mass-transfer zones in the bed. A relatively high partial pressure is required for an unfavourable isotherm in order to achieve an economic adsorption (Gabelman, 2017).

### 2.2.1 Langmuir isotherm

For Langmuir isotherm, it is mainly used to explain gas-solid adsorption as well as to quantify and compare the adsorptive capacity of different adsorbents (Ayawei et al., 2017). It

is applicable when there is a strong specific interaction between the solute and adsorbent, typically ion exchange and affinity type adsorptions. The adsorption is proportional to the fraction of the opened adsorbent surface while the desorption is proportional to the fraction of covered surface of adsorbent (Ayawei et al., 2017). In this isotherm, it is assumed that the adsorption occurs at homogeneous surface with uniform adsorption energy and there is no interaction between the adsorbed molecules (Ahmad and Rahman, 2011, Ahmad et al., 2020b). The maximum adsorption occurs when the surface is covered with a monolayer of adsorbate. The Langmuir adsorption isotherm is given by:

$$q_e = \frac{Q_o K_L C_e}{1 + K_L C_e} \quad (2.1)$$

Rearranging Equation (2.1) to obtain Langmuir equation in linear form:

$$\frac{C_e}{q_e} = \frac{1}{Q_o K_L} + \frac{C_e}{Q_o} \quad (2.2)$$

where

$C_e$  = Solute concentration in solution at equilibrium (mg/L)

$q_e$  = Amount of solute adsorbed per unit mass of adsorbent (mg/g)

$Q_o$  = Monolayer capacity of adsorbent (mg/g)

$K_L$  = Langmuir constant (L/g)

A dimensionless separation factor,  $R_L$  is used to explain the vital characteristics of the Langmuir isotherm.

$$R_L = \frac{1}{1 + K_L C_o} \quad (2.3)$$

where

$C_o$  = Initial solute concentration (mg/L)

The  $R_L$  value indicates the favourability of the adsorption where the result is summarized in the table below.

Table 2.1 Favourability of the adsorption for Langmuir isotherm.

$R_L$	Favourability
$>1$	Unfavourable
$=1$	Linear
$0 < R_L < 1$	Favourable
$=0$	Irreversible

### 2.2.2 Freundlich isotherm

Freundlich isotherm is applicable for adsorption processes which occur on heterogeneous surfaces surface supporting sites of varied affinities (Ayawei et al., 2017, Ahmad and Rahman, 2011). It is suitable for the strongly favourable isotherms. The logarithm form of Freundlich equation is given below:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (2.4)$$

where,

$K_f$  = Freundlich constant related to adsorption capacity ( $\text{mg/g(L/mg)}^{1/n}$ )

$n$  = Freundlich constant related to adsorption intensity (1/mg)

The  $n$  value implies the degree of nonlinearity between concentration of solution and adsorption. Table 2.2 shows the adsorption process nature based on different value of  $n$ .

Table 2.2 Nature of adsorption process for Freundlich isotherm (Desta, 2013).

$n$	Nature of Adsorption
$>1$	Physical Adsorption
$=1$	Linear
$< 1$	Chemical Adsorption

### 2.2.3 Temkin adsorption isotherm

Temkin isotherm includes a factor that considers the effect of interaction between adsorbent and adsorbate (Dada et al., 2012, Ayawei et al., 2017). It is assumed that the heat of adsorption of all molecules in the layer would decrease linearly with the increase of surface coverage. The adsorption is characterized by a homogeneous distribution of binding energies, up to a certain maximum binding energies (Dada et al., 2012). Below is the linear form of Temkin isotherm model:

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \quad (2.5)$$

where

R = Universal gas constant (8.314 J/mol K)

T = Absolute solution temperature (K)

b = Temkin constant related to heat of sorption (J/mol)

$K_T$  = Temkin isotherm constant (L/g)

### 2.3 Adsorption kinetic model

Adsorption kinetics is a key parameter to be considered in designing an adsorption system. It is a curve or line that outlines the retention or release rate of a solute from a solution to solid-phase interface at a specific amount of adsorbent, temperature and pH (Kajjumba et al., 2018). It is widely applied in identifying the suitability of an adsorbent by measuring the diffusion of adsorbate in the pores. Besides, adsorption rate also plays a vital role in determining the applicability of an adsorbent. A good adsorbent should have a good characteristic in which high adsorption uptake and fast adsorption rate. The most common kinetic models that have been widely applied in practically every sorption process are pseudo first order (PFO) and pseudo second order (PSO).

### 2.3.1 Pseudo first order kinetic model

Pseudo first order (PFO) kinetic model, or as known as Lagergren model describes the relationship between the occupied rate of adsorbent sorption site and the number of unoccupied site by following the first order mechanism (Edet and Ifelebuegu, 2020). The linear equation of PSO model is expressed as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2.6)$$

where

$q_e$  = Amount of adsorbate adsorbed at equilibrium (mg/g)

$q_t$  = Amount of adsorbate adsorbed at any time, t (h) (mg/g)

$k_1$  = Pseudo first order rate constant (1/h)

A linear plot of  $\ln (q_e - q_t)$  against time is obtained in order to determine the rate constant  $k_1$ .

### 2.3.2 Pseudo second order kinetic model

Pseudo second order (PSO) kinetic model explains the dependency of adsorption capacity of the adsorbent on time (Edet and Ifelebuegu, 2020). The rate of solute adsorption is assumed to be proportional to the active sites available on the adsorbent (Kajjumba et al., 2018).

The pseudo second order model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2.7)$$

where

$k_2$  = Pseudo second order rate constant (g/mg-h)

$q_e$  and  $k_2$  are determined from the slope and intercept, respectively from the linear plot of  $t/q_t$  versus time.

## 2.4 Adsorption mechanism

Intraparticle diffusion model was applied to further evaluate the kinetic results, by using equation as shown below:

$$q_t = k_{pi}t^{1/2} + C_i \quad (2.8)$$

where

$k_{pi}$  = Rate constant of intraparticle diffusion (mg/g-h<sup>1/2</sup>)

$C_i$  = Boundary layer thickness (mg/g)

Boyd model was used to investigate the rate controlling mechanism of an adsorption process, by employing the equation below:

$$B_t = -0.4977 - \ln\left(1 - \frac{q_t}{q_e}\right) \quad (2.9)$$

where

$q_t$  = Amount of adsorbate adsorbed at time, t (mg/g)

$q_e$  = Amount of adsorbate adsorbed at equilibrium (mg/g)

A graph of  $B_t$  against time is plotted, where if the straight line passes through the origin, the adsorption process is governed by particle diffusion mechanism; otherwise, film diffusion mechanism is governing for the adsorption process.

## 2.5 Adsorption thermodynamic

Thermodynamic is an essential element to be studied in any adsorption process as it is utilized to anticipate the equilibrium adsorbent-adsorbate nature and whether the adsorption system is spontaneous or nonspontaneous (Doke and Khan, 2013). Besides that, it also studies the temperature range at which the adsorption process is favourable or unfavourable and



predicts the ideal conditions for the viability of the adsorption process. Thermodynamic parameters such as standard Gibbs free energy ( $\Delta G^\circ$ ), standard enthalpy change ( $\Delta H^\circ$ ) and standard entropy change ( $\Delta S^\circ$ ) should be determined in order to study the thermodynamic of an adsorption system. According to Kumar and Kumaran (2005), for an isolated adsorption system where energy cannot be obtained or lost, the standard entropy change functions as the driving force. The  $\Delta H^\circ$  and  $\Delta S^\circ$  values may be computed using the equation below:

$$\ln K_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (2.10)$$

where

$K_L$  = Langmuir Isotherm constant at different temperature (L/mg)

$\Delta S^\circ$  = Standard entropy change (kJ/mol)

$\Delta H^\circ$  = Standard enthalpy change (kJ/mol)

R = Universal gas constant (8.314 J/mol-K)

T = Absolute temperature (K)

The  $\Delta H$  and  $\Delta S$  values were determined from the slope and intercept of the plot of  $\ln K_L$  versus  $1/T$  respectively. In addition, the standard Gibbs free energy ( $\Delta G^\circ$ ) can be determined by using the equation below:

$$\Delta G^\circ = -RT \ln K_L \quad (2.11)$$

where:

$\Delta G^\circ$  = Standard Gibbs free energy (kJ/mol)

$K_L$  = Constant of Langmuir isotherm at different temperature (1/mg)

R = Universal gas constant (8.314 J/mol-K)

T = Absolute temperature (K)

An exothermic adsorption process is indicated by a negative  $\Delta H^\circ$  value, whereas an endothermic adsorption process is indicated by a positive  $\Delta H^\circ$  value. On the other hand,

positive values of  $\Delta S^\circ$  indicate increased disorder and randomness at the adsorbent-adsorbate interface whereas negative values show the decrease in randomness at the interphase during adsorption process (Hema and Arivoli, 2007). In addition, the standard free energy change ( $\Delta G^\circ$ ) is the free energy change at unit concentrations of adsorbate and unit active sites of adsorbent of an adsorption process (Doke and Khan, 2013). The signs of  $\Delta G^\circ$  values indicate if an adsorption process is feasible. If the  $\Delta G^\circ$  value is lesser than 0, the adsorption process is feasible and spontaneous, while if the  $\Delta G^\circ$  value is greater than 0, the non-feasible and non-spontaneous of the adsorption process is implied.

## **2.6 Different adsorbents for adsorption of chloramphenicol**

Adsorbent is a material which allows adsorbate (liquid, gas or dissolved solid) to adhere to its surface when they are in contact. Generally, adsorbent has a high selectivity where when a mixture of components passes through it, only selected components will be adsorbed to its surface. Different adsorbent has different adsorption capacity. The higher the adsorption capacity, the more adsorbate will be adsorbed, leading to a higher efficiency in adsorption. There are four major adsorbents which dominate the commercial use of adsorption, which are AC, silica gel, zeolite and activated alumina (Yang, 2003).

In the past, various adsorbents have been studied in different research works to investigate the adsorption of (CAP). Porous carbon (PCM) is a versatile material that widely applied in many industrial due to its large surface area, pore volume and pore size (Zhu et al., 2018). It is primarily applied for gas separation, water purification, catalyst supports and electrodes for electrochemical double layer capacitors and fuel cells (Lee et al., 2006). In research work of Zhu et al. (2018), petroleum cokes (PC), fallen leaves (FL), chicken feathers (CF) and *Enteromorpha prolifera* (EP) were used as the precursors to produce PCMs. Potassium tartrate was selected as the activator as it is an organic sylvite, able to produce PCMs

with large surface area and it brings less harmful secondary pollution compared to KOH. In the study, the BET surface area of PC-PCM was reported to be the lowest ( $256 \text{ m}^2/\text{g}$ ) compared to FL-PCM, CF-PCM and EP-PCM ( $1721$ ,  $1819$  and  $2152 \text{ m}^2/\text{g}$  respectively). Meanwhile, among the four raw materials, EP-PCM exhibited the highest adsorption capacity of  $892.86 \text{ mg/g}$ , where the adsorption capacities of the other materials were reported to be  $159.98 \text{ mg/g}$  (PC-PCM);  $621.12 \text{ mg/g}$  (FL-PCM);  $740.74 \text{ mg/g}$  (CF-PCM) and  $892.86 \text{ mg/g}$  (EP-PCM).

On the other hand, shrimp shell as a food waste in our daily life has the potential to be converted into carbon materials due to its high content of crude protein, crude fat, polysaccharide and calcium protein (Qin et al., 2016). Generally, carbon materials produced by simple pyrolysis exhibit poor adsorption capacity as it has a low porosity and surface area. Therefore, the introduction of chemical activation is required after the pyrolysis in order to increase the capacity of adsorption. In the research of Qin et al. (2016), novel N-doped hierarchically porous carbons (N-HPCs) was produced by shrimp shell via self-template pyrolysis followed by KOH activation. The N-HPCs produced has a high BET surface area recorded at  $3171 \text{ m}^2/\text{g}$  with a large total pore volume ( $1.934 \text{ cm}^3/\text{g}$ ). The study showed that at  $318 \text{ K}$ , the maximum adsorption capacity of N-HPCs on CAP was  $792.4 \text{ mg/g}$ .

Due to the high preparation cost and time consuming in the conventional preparation of PCMs, Dai et al. (2018) introduced a simple method to produce PCMs with high specific surface area and porosity. Potassium acetate was used as the precursor material to undergo in-situ template and self-activation under a high temperature ( $>700 \text{ }^\circ\text{C}$ ). In the research, the highest BET surface area of PCMs was  $2358.57 \text{ m}^2/\text{g}$ , prepared at a temperature of  $900 \text{ }^\circ\text{C}$ . At the same time, the prepared PCMs showed a high potential for removal of CAP, where the maximum adsorption capacity was recorded at  $588.24 \text{ mg/g}$ .

Biochar is a porous carbon-based material obtained from pyrolysis. Recently, it is widely used in wastewater treatment owing to its high thermal stability, sustainability and

enhanced adsorption abilities (Yang et al., 2020b). Yang et al. (2020b) have used peanut shell as the precursor in order to produce PCMs for CAP removal. Generally, raw biochar produced from pyrolysis has a very low adsorption capacity (about 8 mg/g) due to the weak affinity between CAP and biochar. Hence, in research work of Yang et al. (2020b), ammonium polyphosphate was utilized as heteroatoms in terms of functional groups to alter the surface polarity and enhance the affinity towards CAP. As a result, a large surface area of biochar was produced (979 m<sup>2</sup>/g) at a mass ratio of ammonium polyphosphate: peanut shell of 0.55, at a temperature of 650 °C with a retention time of 60 min. The adsorption capacity of the prepared BC was 423.7 mg/g.

Adsorption of bamboo charcoal (BC) on contaminants has attracted significant attention of researchers as it is an environmental friendly yet cost-effective porous structure. However, raw BC has a poor adsorption capacity and modification is a mandatory step in order to increase the adsorption capacity of BC. There were two modification methods carried out by researchers, heating the adsorbents under a high temperature and a certain atmosphere to create more pores in the adsorbent; or impregnate the adsorbent with certain solution to produce more characteristic surface functional groups. Fan et al. (2010) studied on adsorptive removal of CAP from wastewater by modified BC. In the research work, adsorption of CAP on BC, H<sub>2</sub>SO<sub>4</sub> modified BC, and NaOH modified BC were investigated. Impregnation has been selected as the modification method as it is more convenient and cost-effective compared to heating. The study shows that NaOH modified BC has the highest adsorption capacity on CAP due to the increment of  $\pi-\pi$  interaction between the adsorbent and adsorbate, which is CAP.

In 2019, a research had studied on the adsorption of CAP on commercial and modified AC (Lach, 2019). F-100, F-300, WG-12, ROW 08, Picabiol were the commercial AC used in the study. Among the five commercial AC, Picabiol showed the highest adsorption capacity of

214 mg/g. Besides, AC WG-12 was modified with carbon dioxide showed a great increment in adsorption capacity from 195 mg/g (unmodified carbon) to 343.12 mg/g.

## **2.7 Activated carbon**

(AC) is a porous amorphous carbonaceous material with high degree of porosity, which has a complicated structure consisting mostly of channels produced within a rigid skeleton of disordered carbon atoms layer, connected together by chemical bonds (Bansal and Goyal, 2005). Generally, AC is produced by thermal decomposition of carbon-rich raw precursors in a furnace under a controlled atmosphere and elevated temperature. The precursors of AC can be classified into non-renewable resources such as coal, pitches, coke, and renewable biomass such as coconut shells, palm kernel shells, rice husks and nut shells. AC has been proven as an efficient adsorbent as it offers several advantages such as large porous surface area, good thermostability at high temperature and chemical stabilization (Ao et al., 2018, Zhu et al., 2017). It is widely used in industrial due to its simplicity of preparation and cost-effectivity. Generally, an AC with higher internal surface area have greater efficiency. The most widely used ACs have a specific surface area ranging from 800 to 1500 m<sup>2</sup>/g and a pore volume of 0.20 – 0.60 cm<sup>3</sup>/g (Bansal and Goyal, 2005). The pore of AC can be classified into three major groups, which are micropores (pore size < 2 nm), mesopores (pore size 2 – 50 nm) and macropores (pore size > 50 nm) according to International Union of Pure and Applied Chemistry (IUPAC). During adsorption, the pores of AC give a vast surface area for adsorbate to be adsorbed on its surface.

## **CHAPTER 3**

### **MATERIALS AND METHOD**

This chapter consists of materials, chemicals as well as equipment that required for this study. Besides, methodology of this experiment such as preparation and characterization of ASAC, adsorption and analysis study of CAP are outlined in this chapter.

#### **3.1 Experimental activities**

All the experimental activities that conducted for this study are summarized in the schematic diagram below:

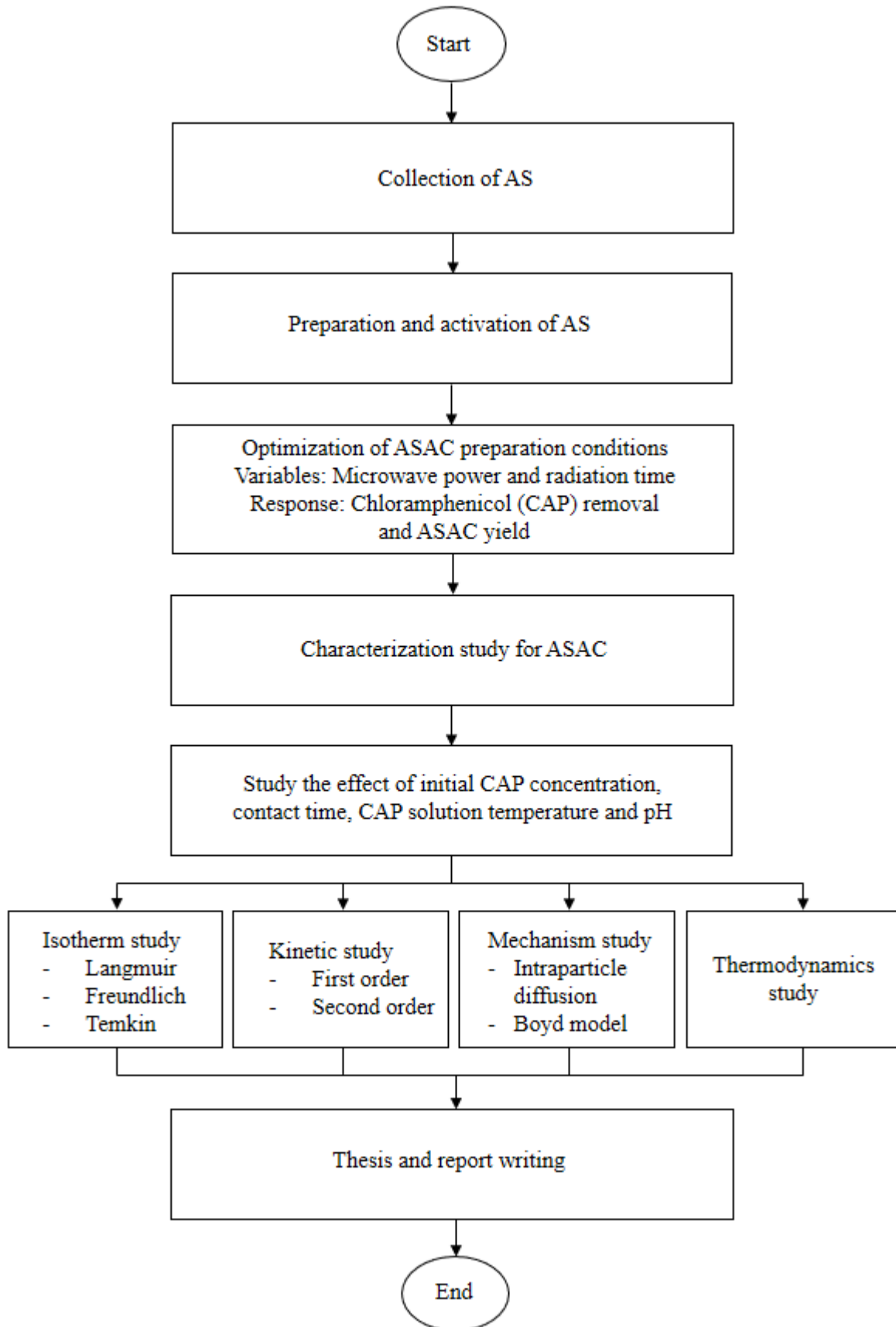


Figure 3.1 Schematic flow diagram of experimental activities.

## 3.2 Materials and chemicals

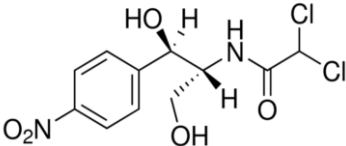
### 3.2.1 Raw materials

Almond was purchased from an e-commerce online shopping platform — Shopee. In order to obtain almond shell (AS) as the raw material, the almond was shelled before carrying out the experiment.

### 3.2.2 Chemicals

Chloramphenicol (CAP) was used as adsorbate in this experiment and it was acquired from Sigma-Aldrich (M) Sdn. Bhd, Malaysia. The properties of CAP are listed in Table 3.1. Deionized water (DI water) that used to prepare the stock solution was supplied by laboratory of School of Chemical Engineering, USM.

Table 3.1 Properties of CAP (Lach, 2019).

Properties	Description
<b>Chemical Name</b>	2,2-Dichloro-N-[1,3-dihydroxy-1-(4-nitrophenyl)propan-2-yl] acetamide
<b>Common Name</b>	Chloramphenicol
<b>CAS Number</b>	<a href="#">56-75-7</a>
<b>Maximum Wavelength</b>	278 nm
<b>Molecular Formula</b>	C <sub>11</sub> H <sub>12</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>5</sub>
<b>Molecular Weight</b>	323.13 g/mol
<b>Molecular Structure</b>	

### 3.2.3 Gases

Carbon dioxide (CO<sub>2</sub>) with purity of 99 % was used as activating agent and inert gas for the preparation of ASAC in this study. It is supplied by MOX Gases Berhad, Malaysia.



### **3.3 Equipment**

In this section, the detail information for all the equipment used in this studies such as ASAC preparation, batch adsorption system and characterization system are outlined.

#### **3.3.1 Preparation of almond shell based activated carbon (ASAC)**

In order to remove any moisture content in the AS, it was first dried in a drying oven (Model Memmert 600, Germany) at temperature of 100 °C for 24 hours.

After that, the dried AS were activated in a modified microwave. The modified microwave consists of a power controller to alter the heating power (700, 616, 490, 364, 284 and 140 Watt) and a timer to adjust the heating time (1 – 30 minutes). Besides that, the microwave was connected to a gas piping system and gas flow meter to measure the flowrate of CO<sub>2</sub>.

#### **3.3.2 Batch adsorption and analysis system**

For batch adsorption studies, an isothermal water-bath shaker with temperature and agitation speed controller was used. Conical flask with 200 mL of sample solution and 0.2 g of ASAC was placed inside the water-bath shaker for adsorption. A double beam UV-Visible spectrometer (Model Shimadzu UV-1800, Japan) was used to measure the concentration of sample solution for analysis studies.

#### **3.3.3 Characterization of ASAC**

Surface area, total pore volume and average pore diameters of the ASAC prepared were determined by using a volumetric adsorption analyser (Micromeritics ASAP 2020). Brunauer-Emmett-Teller (BET) equation was used to determine the BET surface area of the sample from the adsorption isotherm. The total pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of 0.98. The surface morphology of the ASAC was evaluated via

scanning electron microscope (SEM) (JEOL JSM- 6460LV, Japan). The proximate analysis was performed using simultaneous thermal analysis equipment (Perkin Elmer STA 6000, USA), while elemental analysis was carried out using an Elemental Analyzer (Perkin Elmer Series II 2400, USA). Fourier-transform infrared (FTIR) spectroscopy (Shimadzu Prestige 21, Japan) was employed to study the chemical structural properties of the prepared ASAC.

### 3.4 Experimental design

AC is generally prepared with “one-factor-at-a-time” (OFAT) approach, where the desired parameter is varied while the rest of the parameters remained constant (Ahmad et al., 2020c). However, this conventional approach has some limitations where it requires several numbers of experiment and fails to explain the interaction of parameters with the selected response. As a result, RSM arises as a useful tool for establishing, refining and optimizing the conditions of AC preparation. Based on the CAP removal efficiency and ASAC yield, standard Response Surface Methodology (RSM) with Central Composite Design (CCD) was applied to optimize the ASAC preparation conditions. The factors studied in this research work were microwave radiation power ( $x_1$ ) and activation time ( $x_2$ ). The ranges and the levels (coded -1 to 1) of the factors are tabulated in Table 3.2.

Table 3.2 Independent variables and their coded levels for CCD.

Variable (factor)	Code	Units	Coded Values		
			-1	0	+1
Radiation power	$x_1$	W	364	490	616
Activation time	$x_2$	min	2	4	6

Four factorial points, four axial points and five replicates at the central points were used for the CCD design in this study. The total set of experiment required for two independent variables is determined by using the equation below:

$$N = 2^n + 2n + n_c \quad (3.1)$$

$$N = 2^2 + 2(2) + 5$$

$$N = 13 \text{ runs}$$

where

N = Total number of experiment required

n = Total number of variables

n<sub>c</sub> = Centre runs

To analyse the pure error, a total of 13 trials were conducted for the two factors, consisting of 9 experiments and five replicate parameters.

The goal of the experimental design was to optimize the response variables (Y), which are the CAP removal efficiency and obtained yield in this study. The experimental run was randomized in order to minimize the error and effect of the uncontrolled factors (Behera et al., 2018). The corresponding model is expressed by:

$$Y = \beta_o + \sum_{i=1}^n \beta_i X_i + \sum_{i=1}^n \beta_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \beta_{ij} X_i X_j + e_i \quad (3.2)$$

where

Y = Predicted response

$\beta_o$  = Constant coefficient

$\beta_i$  = Linear coefficient

$\beta_{ii}$  = Quadratic coefficient

$\beta_{ij}$  = Interaction coefficient

$X_i, X_j$  = Coded values of the AC preparation factors

$e_i$  = Error

Design Expert Software (version 6.0.7) was used for further analyse the regression, variance (ANOVA), and response surfaces.

A complete design matrix for ASAC preparation has been obtained and tabulated in Table 3.3.

Run	ASAC preparation parameters	
	Radiation power, $x_1$ (W)	Activation time, $x_2$ (min)
1	490 (0)	2 (-1)
2	490 (0)	4 (0)
3	490 (0)	6 (+1)
4	490 (0)	4 (0)
5	616 (+1)	6 (+1)
6	616 (+1)	4 (0)
7	490 (0)	4 (0)
8	490 (0)	4 (0)
9	364 (-1)	2 (-1)
10	364 (-1)	6 (+1)
11	490 (0)	4 (0)
12	616 (+1)	2 (-1)
13	364 (-1)	4 (0)

Table 3.3 Experimental design matrixes.

### 3.5 Experimental procedures

In this section. the experimental procedure such as preparation of ASAC, stock and sample solution and batch adsorption studies of CAP onto ASAC, including the equilibrium, kinetic and mechanism studies were outlined.

#### 3.5.1 Preparation of ASAC

Almond with shell that bought from online were first shelled in order to obtain the AS. The obtained AS were then dried in a drying oven at 100 °C for 24 hours. After that, the activation process was conducted with the aid of a modified microwave at different radiation powers: 364, 490 and 616 W, and various activation times: 2, 4, and 6 min. A continuous flow of CO<sub>2</sub> gas at 150 cm<sup>3</sup>/min was supplied throughout the activation of ASAC. After activation, the sample were cooled to room temperature with the continuous supply of CO<sub>2</sub>.