MICROWAVE IRRADIATED DURIAN SEED BASED ACTIVATED CARBON FOR CHLORAMPHENICOL REMOVAL

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by

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LIST OF SYMBOLS

A	Arrhenius factor
A_i	Measured absorbance for component, i
A_T	Temkin isotherm constant (L/g)
A^2	Quadratic effect of radiation power
b_c	Path length of the cell
b_T	Temkin constant (J/mol)
B_T	Mathematical function of F
B^2	Quadratic effect of radiation time
C	Solute concentration (mg/L)
C_e	Equilibrium concentration of the adsorbate (mg/L)
C_0	Initial concentration of adsorbate solution (mg/L)
E_a	Arrhenius activation energy (kJ/mol)
F	Fraction of adsorbate at time, t
F_{value}	Ratio of mean square to regression to mean square to residual
K_F	Adsorption capacity
K_L	Langmuir adsorption constant (L/mg)
K_T	Temkin isotherm constant (L/mg)
k_1	Pseudo-first order adsorption rate constant (min^{-1})
k_2	Pseudo-second order adsorption rate constant (g/(mg/min))
M_1	Concentration of stock solution (mg/L)
M_2	Concentration of desired adsorbate solution (mg/L)
n	Number of data points
n_F	Heterogeneity factor
q_e	Amount of adsorbate adsorbed per unit mass of adsorbent (mg/g)
q_m	The utmost monolayer adsorption capacity of the adsorbent (mg/g)
q_t	Amount of adsorbate in the adsorbent at time, t (min)
$q_{t,calc}$	Calculated amount of adsorbate adsorbed at time, t
$q_{t,exp}$	Measured amount of adsorbate adsorbed at time, t
R	Universal gas constant (J/mol.K)
R_L	Separation factor
R^2	Coefficient of correlation

t	Time (min)
T	Absolute temperature (K)
V_1	Volume of stock solution (mL)
V_2	Volume of desired adsorbed solution (mL)
W	Watt
W_c	Dry weight of AC (g)
W_0	Dry weight of precursor (g)
$\underline{Y}$	Average observed value
Y_i	Observed value at ith observation
ε_λ	Molar absorptivity coefficient of solute at wavelength λ (nm)
λ	Wavelength (nm)
$\Delta H°$	Enthalpy change (kJ/mol)
$\Delta G°$	Gibbs free energy (kJ/mol)
Δq_t	Normalized standard deviation
$\Delta S°$	Entropy change (kJ/mol)
1/n	Adsorption intensity

LIST OF ABBREVIATIONS

A	Radiation power
AC	Activated carbon
AP	Adequate precision
ANOVA	Analysis of variance
B	Radiation time
CAP	Chloramphenicol
CCD	Central composite design
CNTs	Carbon nanotubes
CO	Carbon monoxide
CO_2	Carbon dioxide
DS	Durian seed
DSAC	Durian seed activated carbon
H	Hydrogen
HCl	Hydrochloric acid
HPLC	High-performance liquid chromatography
H_2O	Water
H_2SO_4	Sulphuric acid
IR	Infrared
IUPAC	International Union of Pure and Applied Chemistry
KOH	Potassium hydroxide
M	Medium
MH	Medium high
ML	Medium low
N	Nitrogen
N	Total number of observation
N_2	Nitrogen
NaOH	Sodium hydroxide
O	Oxygen
P	Total number of regressor
PSD	Pore size distribution
RSM	Response surface methodology

S	Sulphur
SSE	Sum of square of error
SSR	Sum of square to regression
SST	Sum of squares
STD	Standard deviation
UV-Vis	Ultraviolet-Visible
Y_{AC}	AC yield
Y_{CAP}	CAP removal

MICROWAVE IRRADIATED DURIAN SEED BASED ACTIVATED CARBON FOR CHLORAMPHENICOL REMOVAL

ABSTRAK

Kajian ini bertujuan mensistensis karbon teraktif (AC) yang berasal daripada biji buah durian (DS) bagi tujuan menyerap kloramfenikol (CAP) dari larutan akuas AC ini dihasilkan melalui kaedah pengaktifan fizikal dengan aliran gas karbon dioksida (CO_2) berterusan sebagai agen pengaktif dengan teknik penyinaran gelombang mikro. Dua parameter dipertimbangkan dalam penyediaan AC yang mana daya radiasi gelombang mikro (Watt) dan juga waktu radiasi (min) pada kecekapan penyingkiran CAP dan hasil AC dioptimumkan dengan menggunakan metodologi permukaan sambutan (RSM). Keadaan penyediaan optimum untuk CAP-DSAC ditentukan pada 364 W dan 6 minit, dengan 50.82% penyingkiran CAP dan 45.82% hasilan DSAC.

Penjerapan CAP pada DSAC yang dioptimumkan mengikuti model garis sesuhu Freundlich dengan kapasiti penjerapan masing-masing adalah 1.253, 1.359 dan 1.414 pada 30°C, 45°C dan 60°C. Kajian kinetik menunjukkan bahawa penjerapan CAP ke atas DSAC mengikuti model kinetik pseudo-tertib pertama sementara kajian mekanisma menunjukkan bahawa proses penjerapan CAP ke DSAC dikendalikan oleh mekanisma resapan filem. Hal ini demikian kerana, kajian termodinamik mengesahkan bahawa sistem yang dikaji bersifat eksotemik.

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MICROWAVE IRRADIATED DURIAN SEED BASED ACTIVATED CARBON FOR CHLORAMPHENICOL REMOVAL

ABSTRACT

This study aims to synthesis activated carbon (AC) derived from durian seed (DS) to adsorb chloramphenicol (CAP) from an aqueous solution. DSAC was produced via the physical activation method with a continuous flow of carbon dioxide (CO_2) gas as an activating agent with microwave irradiation technique. By using response surface methodology (RSM), it was revealed that the optimum preparation conditions of DSAC were 364 W and 6 min for radiation power and radiation time, respectively, which resulted in 50.82% of CAP removal and 45.82% of yield.

The adsorption of CAP onto optimized DSAC followed Freundlich isotherm with the adsorption capacities of 1.253, 1.359 and 1.414 at 30°C, 45°C and 60°C respectively. The kinetic studies revealed that the adsorption of CAP onto DSAC followed the pseudo-first order kinetic model while mechanism studies revealed that the adsorption process of CAP onto AC was controlled by the film diffusion mechanism. However, thermodynamic studies confirmed that the studied system was exothermic in nature.

CHAPTER 1

INTRODUCTION

1.1 Research Background

1.1.1 Durian fruit

Durian, king of fruit is a dicotyledonous tropical seasonal plant species belong to the family Bombacaccease. Major producers of durian are Indonesia, Thailand, Malaysia, Philippines, Laos, Vietnam, Cambodia, Myanmar, Sri Lanka, India, Hawaii, Florida, Papua New Guinea and Northern Australia (Ahmad et al., 2015a). There is a conventional desserts-like *dodol*, made of durian pulp cooked with sugar, *lempok* and *tempoyak*. These desserts use the method of preserved the durian flesh with brown sugar, boil and fry and also the addition of prawn paste to salt it. Based on the local community eating lifestyles, massive generations of durian shells, rinds, seeds and peels occurred. The roots and leaves of the durian tree can be used as a traditional medicine to treat fever and jaundice.

1.1.2 Chloramphenicol

Pharmaceuticals are one of the new types of contaminants that can be found in water and wastewater. From the observations in previous studies, hospitals and pharmaceuticals factories contributed to the highest concentrations of pharmaceuticals presence in municipal wastewater. In the 1950s, chloramphenicol (CAP) are employed in human and veterinary medicines (Tahrani et al., 2016). With the presence of this antibiotic in surface water and also in potable, the effect on human health and therefore the environment were highly dangerous yet because it has mutagenic properties which end in the emergence of super-bacteria immune to all antibiotics (Lach & Ociepa-Kubicka, 2017). Several methods were studied within the removal of assorted contaminants through adsorption on activated carbon which permits different types of antibiotics were effectively removed either organic and inorganic matter from waste and wastewater (Lach & Ociepa-Kubicka, 2017).

Chloramphenicol was categorized as antibiotics for humans and veterinary used from bacterium Streptomyces Venezuela in the year 1947. This antibiotic was prescribed in mass in the USA in 1947 due to an outburst of enteric fever. However, it is found to be extremely useful and active against various types of pathogens including bacteria, spirochaetes, rickettsia and etc. (Shukla et al., 2011). CAP was similar to other inhibitors as the High-performance liquid chromatography (HPLC) analysis revealed that the biotransformation of CAP takes place by oxidation, reduction and conjugation. In contrast, every human has different types of reactions to this chemical. The drawbacks of after-used this chemical might bring harm toward health and our physical states. From the literature review, CAP has not suggested if the person has a family history of ‘dyscrasias’, a condition which can cause bruising, tiredness and increased risk of infections. Meanwhile, CAP has detected presence in groundwater, in wastewater, surface water and also in drinking water. The prolonged presence of low concentration antibiotics in human food gave negative effects on health which reduced immunity, carcinogenic, teratogenic and mutagenic effects plus disturbing the physiological function by acting as hormones in our body.

1.2 Problem Statement

CAP had adverse effects on human health and also the environment. One of the disadvantages of CAP is its mutagenic property where it can cause negative effects on human health such as reduction in human immunity and cancer. From the literature review, the most effective one for CAP removal is the adsorption process because of its simplicity and eco-friendliness. It is proven to be an effective method for antibiotics removal (Li et al., 2018).

However, commercial activated carbon (AC) used such as mesoporous silica and carbon nanotubes (CNTs) are often categorized as expensive due to the use of non-renewable raw materials for the adsorbents (Li et al., 2018). In this study, durian seed was introduced as the precursor where it was easily available, low cost, highly effective and also eco-friendly types of adsorbent (Chaidir et al., 2015). The significance of using durian seed activated carbon (DSAC) as adsorbent material is due to the larger surface area and total pore volume which relatively highly enhanced the adsorption process and adsorption capacity (Ahmad et al., 2015a).

High energy consumption was generated in conventional heating (Ahmad et al., 2015a). So these studies used microwave heating due to the energy savings and shortened processing time can be achieved as it allows the microwave-induced reaction to proceed quickly and effectively operated at low bulk temperatures (Ahmad et al., 2015a).

As for the traditional approaches for optimization is time-consuming. So this study used response surface methodology (RSM) to determine the optimum prepared conditions as it ensures better results reproducibility and process optimization as well as a fine viewpoint for the development of predictive models (Kumari & Gupta, 2019).

1.3 Objectives

The objectives for this study are as follows:

i. To synthesis AC from durian seed via microwave heating under the flow of CO_2 gas to treat CAP from an aqueous solution.
ii. To optimize the preparation conditions (radiation power and radiation time) of DSAC to achieve optimum CAP's removal and DSAC's yield using response surface methodology (RSM).
iii. To evaluate the effect of initial concentration, solution temperature and solution pH on CAP removal through batch adsorption studies.
iv. To investigate the nature of CAP-DSAC adsorption system via isotherm, kinetics, mechanism and thermodynamic studies.

CHAPTER 2

LITERATURE REVIEW

2.1 CAP common removal technique

2.1.1 Adsorption process

It is proven that adsorption onto AC is the most efficient technique in terms of efficiency and economically. Due to its tremendous attractiveness, AC is preferred as an adsorbent due to its ability to adsorb a wide range of pollutants and having high flexibility (Khasri et al., 2019). In addition, the high applicability of AC has related to its high porosity rapid adsorption and thermal stability (Zhang et al., 2014). On the other hand, the modification method of AC with ozone does influence the adsorption capacities (Lach & Ociepa-Kubicka, 2017). Generally, the preparation of AC by introducing heat consists of two options either by a convective or conductive heating system. However, recent studies are based on microwave irradiation techniques in the preparation of AC (Khasri et al., 2019). The advantages of using this new method include fast, selective, uniform and volumetric heating, instant and accurate control, which provides the non-contact between the heating source and heating materials compared to the conventional heating (Ao et al., 2018). Furthermore, microwave heating is cost and energy saving compared to conventional heating (Khasri et al., 2019).

2.2 Activated carbon

Activated carbon (AC) is an efficient adsorbent because it is a highly porous material and provides an outsized area to which contaminants may be adsorbed. Removal of various contaminants through adsorption on AC are often used for a good sort of application. It is capable of removing inorganic and organic contaminants from water and wastewater (Lach & Ociepa-Kubicka, 2017). Differing types of antibiotics are often effectively removed by this method such as CAP which has been selected in this project to be studied. The physical characteristics of an AC such as surface area and bulk density, and chemical properties such as pH, ash content and conductivity, can affect the utilization of such substance and render its suitability for specific applications (M. J. Ahmed & Theydan, 2012). The characteristics of AC depend upon the physical and chemical properties of the precursor and the activation method imposed on the precursor. AC features a very large internal surface area up to 1500 m^2/g which makes it highly suitable for the adsorption process. ACs are often impregnated with certain chemicals to boost their properties for certain applications.

2.3 Preparing of AC

Several methods involve in the preparation of AC such as carbonization and activation processes. The activation process can be further categorized into physical activation, chemical activation and also physicochemical activation.

2.3.1 Carbonization process

Carbonization is that the process of converting a carbon-based material to high-carbon materials through heating. This heating process, called pyrolysis comes from an ancient technique for creating charcoal. Very dense carbonaceous material is employed in the beginning and the end result is extra porous material known as AC. Another definition of carbonization is a process of heating biomass feedstock in a kiln at a temperature around 400°C (generally between 300 and 900°C) in the absence of air. The produced biochar is additionally referred to as charcoal, which may be a porous, carbon-enriched, greyish black solid (Marsh et al., 2019).

2.3.2 Activation process

As mention before, the activation process consists of physical, chemical and physicochemical.

2.3.2(a) Physical activation

Physical activation involves carbonization of carbonaceous material at elevated temperature (500 - 900°C) (M. J. Ahmed & Theydan, 2012) in an inert atmosphere followed by activation of the resulting char within the presence of activating agents such as carbon dioxide (CO_2) or steam or some combination of these agents (Zhou et al., 2018).

2.3.2(b) Chemical activation

In chemical activation, the precursor is impregnated with a chemical activator such as $ZnCl_2$, H_3PO_4, KOH, etc. The impregnated material is heated in an inert atmosphere. Chemical activation is preferred over physical activation due to higher yield, simplicity, lower temperature and shorter activation time, and good development of the porous structure (M. J. Ahmed & Theydan, 2012). The chemical activation process has been widely utilized by many researchers for the preparation of AC from different agricultural wastes by various chemical activators (Zhou et al., 2018).

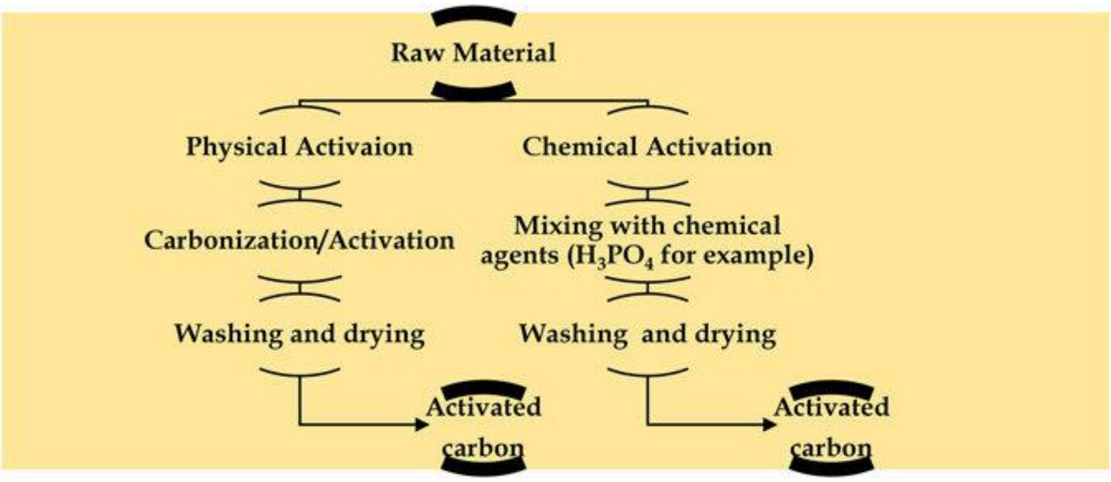


Figure 2.1 Schematic diagram of the process of producing of activated carbons

2.3.2(c) Physicochemical activation

This process is often administered by increasing the adsorbent temperature above the thermal stability of the surface chemical groups on the AC. During this way, the oxygenated groups are converted to CO_2 and CO (Bernal et al., 2018). The thermal stability of most oxygen groups are between 200 K and 1500 K (Zhou et al., 2018). The physicochemical properties of the adsorbate and adsorbent influence the effectiveness of the adsorption process. In fact, factors such as pore size, area and surface chemistry are relevant if the method is allotted in AC. Below is the summary of the description, advantages and disadvantages between the physical, chemical and physicochemical activation.

Table 2.1 Conventional activation methods (Ao et al., 2018)

Conventional methods	Description	Advantages	Disadvantages
Physical activation	One-step or two-step; carbonization/pyrolysis and activation; CO_2, steam or oxygen as oxidizing agents.	Environmentally friendly and there are not any specific requirements for the development materials.	High activation temperature, long activation low carbon yield, inferiority of AC's (e.g. low specific surface areas), and enormous energy consumption.
Chemical activation	One-step or two-step, precursor materials are impregnated with chemical reagents and heated in an inert or oxidizing gas atmosphere. Steam is typically preferred due to mainly to smaller molecules and larger diffusion rate. Main activation reagents are alkali metals (e.g. KOH, K_2CO_3, NaOH and Na_2CO_3), metallic elements (e.g. $AlCl_3$, $FeCl_3$ and $ZnCl_3$) and a few acids (e.g. H_3PO_3, and H_2SO_4).	Lower carbonization and activation temperatures, shorter carbonization and activation times, thus requiring smaller energy consumption. Activation reagents promote pyrolytic decomposition, inhibit tar formation and increase carbon yields.	Severe corrosion to the equipment, strict requirements for washing to get rid of excessive residues of activation reagents, and adverse effects on the environment and public health.
Physicochemical activation	Combination of physical and chemical activation: 1) Carbonization with chemical impregnation onto the raw precursors followed by physical activation; 2) Carbonization and activation of impregnated char in oxidizing gas or inert gas atmosphere.	Applied when chemical reagents were not fully eliminated even after washing, promoting pore formation; development of unique textural and chemical characteristics of activated carbon.	More complex process and better investment.

2.3.3 Microwave irradiation

Microwave irradiation has attracted the attention of researchers as a tool for activation because of its capability of molecular-level heating. The microwave irradiation technique offers many advantages over conventional treatment such as increasing AC's adsorption capacity. Microwave heating exhibits a faster activation rate and a better carbon yield compared with the traditional thermal process (Alslaibi et al., 2013).

Table 2.2 Common activation method and activating agents for preparation of activated carbon (Alslaibi et al., 2013)

Activation method	Activation agent	Reference
Physical activation	Steam	(Petrov et al., 2008)
	Pure steam	(Zhou et al., 2018)
	Steam (H_2SO_4 pre-treatment)	(Alslaibi et al., 2013)
	Steam, CO_2	(Saleem et al., 2019)
	CO_2	(Ganan et al., 2006)
Chemical activation	CO_2/N_2	(Liu et al., 2014)
	Phosphoric acid (H_3PO_4)	(Salman & Hameed, 2010)
	Potassium hydroxide (KOH)	
	Potassium carbonate (K_2CO_3)	
	Sodium hydroxide (NaOH)	(Wu & Tseng, 2008)
	Sulphuric acid (H_2SO_4)	(Guo et al., 2005)
Physicochemical activation	Potassium hydroxide (KOH)/CO_2	

Table 2.3 Comparison between conventional and microwave heating methods in AC production (Alslaibi et al., 2013)

Parameter	Conventional heating	Microwave heating
Thermal time	The thermal process may take several hours, even up to a week to achieve the specified level of activation in order that process incurs extra operating costs.	The treatment time are considerably reduced, which in many cases represent a reduction in energy consumption.
Heating process	- Surface heating - A thermal gradient is generated from the new surface of the char particle to its interior, which results in difficulties in caloric transport. - The surface heating from the fireside wall of the furnace does not ensure a homogeneous temperature for various shapes and sized of samples. This generates a thermal gradient from the new surface of the sample particle to its interior and impedes the effective removal of gaseous products to its surroundings, thereby leading to a detrimental effect on the standard of AC's prepared.	- Both internal and volumetric heating. - An incredible thermal gradient from the inside of the char particle to its cool surface allows the microwave-induced reaction to proceed quickly and effectively at an occasional bulk temperature. - The adsorbed microwave readily transform into heat inside the particles by dipole rotation and ionic conduction, which provides the benefits of uniform heating, rapid temperature rise, and energy saving.
Gas consumption	High consumption of the gases employed in the treatment process.	Consumption of gases are often reduced by microwave because of short treatment time.
Equipment size	The large size of conventional furnaces.	Microwave furnaces are normally smaller than conventional furnaces. In comparison with conventional electric tube heating.
AC preparation conditions	The ranges of optimum experimental condition to prepare AC from agricultural by-products were 400 – 800 °C of activation temperature, 1- 3 h of activation time and 0.5 – 2 of IR.	The ranges of optimum experimental conditions to prepare AC from agricultural by-products were 350 – 700 W of microwave radiation power, 5 – 15 minutes of microwave radiation time and 0.5 – 2 of IR.
AC surface area	The high surface area of produced AC.	Microwave results in the event of relatively higher surface areas of produced AC for an equivalent precursor than conventional heating.

2.4 Factor affecting AC's adsorption performance and AC's yield

For the microwave irradiation technique, two main factors that influence the AC's adsorption performance and AC's yield are the radiation power and radiation time.

2.4.1 Effect of radiation power

Theoretically, the AC yields heavily rely on the properties of AC precursors, interactions between AC precursors and chemical reagents, and secondary pyrolysis (Deng et al., 2009). Higher microwave heating power leads to larger energy input to the sample, thus more active sites and pores were generated on the samples. When microwave power reaches a particular level, overfull energy could make some quantity of carbon to be burnt, and therefore the structure of pores is destroyed (Foo & Hameed, 2011). Effects of microwave power on the adsorption capacity and yield of ACs were closely associated with the kind of AC precursors, activation time, gas atmosphere (e.g. steam), additives added (e.g. chemical activation reagents) and impregnation ratios (Foo & Hameed, 2011).

2.4.2 Effect of radiation time

Radiation time is another factor that influences AC's properties. The longer the radiation time is, the more energy is transferred to the precursor (Deng et al., 2009). More active sites and pores occur on the surface of samples when microwave radiation time is extended. As a result, AC's adsorption capacity rises. However, when the microwave radiation time exceeds a certain value, some carbon is burned off, potentially lowering the adsorption capacity and lowering the AC yield (Sriprom et al., 2021). Due to the unique properties posed by microwave heating, this method significantly reduces activation time and energy consumption (Gao et al., 2013).

2.5 Response surface methodology as optimization tool

In the response surface methodology (RSM) method, the experiment should be carried administered to verify the reliability of the theoretically determined models under optimum conditions (de Oliveira et al., 2018). The chi-square test and t-tests are most ordinarily accustomed to determining the difference between experimental and predicted values. Besides, it ensures better results reproducibility and process optimization as well as a fine viewpoint for the development of predictive models (Kumari & Gupta, 2019). Another method to gauge the validation of the model is to calculate the experimental error between theoretical and experimental values. The interaction of one behaviour of one factor could also rely on the extent of another factor, which could be determined too (de Oliveira et al., 2018). It also requires less time and energy. Because of these advantages, RSM is widely used in other areas of research field such as food science.

2.6 Adsorption isotherms

In this research, three isotherms with two parameters have been studied on the adsorption process which is Langmuir, Freundlich and Temkin isotherms. The values of correlation, R^2 were studied based on the equilibrium data provided from the literature review studies with the suitability and the applicability of the isotherms equation (Ahmad et al., 2015a).

2.6.1 Langmuir isotherm

Langmuir equation are often written within the following linear form (Ahmad et al., 2015a):

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (2.1)$$

where,

C_e = equilibrium concentration of the adsorbate (mg/L),

q_e = amount of adsorbate adsorbed per unit mass of adsorbent (mg/g),

q_m = the utmost monolayer adsorption capacity of the adsorbent (mg/g), and

K_L = Langmuir adsorption constant related to the free energy adsorption (L/mg).

The essential characteristics of Langmuir equation is expressed of dimensionless separation factor, R_L (Ahmad et al., 2015a):

$$R_L = \frac{1}{(1 + K_L C_0)} \qquad (2.2)$$

where,

C_0 is the highest initial solute concentration and R_L value implies the adsorption is favourable $(R_L > 1)$, linear $(R_L = 1)$, favourable $(0 < R_L < 1)$, or irreversible $(R_L = 0)$.

2.6.2 Freundlich isotherm

Freundlich isotherm equation is expressed as follow (Ahmad et al., 2015a):

$$log q_e = log K_F + \left(\frac{1}{n}\right) log C_e \qquad (2.3)$$

where,

q_e = the amount of adsorbate adsorbed at equilibrium (mg/g),

C_e = the equilibrium concentration of adsorbate (mg/L),

K_F = adsorption capacity (L/mg) and,

$\frac{1}{n}$ = adsorption intensity

It indicates the relative distribution of the energy and therefore, the heterogeneity of the adsorbate sites (Ayawei et al., 2017).

The assumption was that the binding strength decrease with the increasing degree of site occupation (Ahmad et al., 2015a). The adsorption intensity is measured by plotting the graph of ($log\ q_e$) against ($log\ C_e$) because the slope of the graph is $\frac{1}{n}$ ranging between 0 and 1. As the value gets closer to 0, it is becoming more heterogeneous.

2.6.3 Temkin isotherm

Linear form of Temkin isotherm is written as follow:

$$q_e = \frac{RT}{b_T} ln\ K_T + \frac{RT}{b_T}\ ln\ C_e \qquad (2.4)$$

Rearrange the equation and it becomes:

$$q_e = B\ lnA_T + B\ lnC_e \qquad (2.5)$$

where,

q_e = amount of adsorbate adsorbed at equilibrium (mg/g),

C_e = equilibrium concentration of adsorbate (mg/L),

T = absolute temperature (K),

R = universal gas constant (8.314 J/mol.K),

b_T = Temkin constant which related to the heat of sorption (J/mol), and

A_T = Temkin isotherm constant (L/g) (Ayawei et al., 2017).

This model has taken into account the adsorbent-adsorbate interactions. Due to these interactions, it is assumed that the heat of adsorption of all the molecules in the layer would decrease linearly with the increased surface recovery (Ahmad et al., 2015a) (Ayawei et al., 2017). However, the validity of this isotherm is only for an intermediate range of ion concentrations.

2.7 Adsorption kinetics

To study the adsorption kinetics, pseudo-first order and pseudo-second order kinetic model were used to identify the adsorption mechanism of CAP and the main rate-limiting steps.

2.7.1 Pseudo-first order kinetic model

The equation for pseudo-first order equation is as follow:

$$ln\,(q_e - q_t) = lnq_e - k_1 t \qquad (2.6)$$

where,

q_e = the amounts of the adsorbate in the adsorbent at equilibrium (mg/g),

q_t = the amount of the adsorbate in the adsorbent at time t (min), and

k_1 = pseudo-first order adsorption rate constant (min^{-1})

2.7.2 Pseudo-second order kinetic model

Pseudo-second order equation is expressed as follow:

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

where,

q_e = the amounts of the adsorbate in the adsorbent at equilibrium (mg/g),

q_t = the amount of the adsorbate in the adsorbent at time t (min), and

k_2 = pseudo-second order adsorption rate constant (g/(mg.min))

2.8 Adsorption diffusion mechanism

The adsorption mechanism on the CAP removal was studied using the intraparticle diffusion mechanism model and Boyd plot (Ahmad et al., 2015a).

2.8.1 Intraparticle diffusion mechanism model

This model assumes constant diffusivity in spherical coordinates and may be integrated with appropriate initial and boundary conditions (Song et al., 2016). As mentioned before, the adsorption process consists of bulk diffusion, film diffusion, inter-particle diffusion and intraparticle diffusion and surface adsorption step.

The bulk diffusion can be neglected and therefore the surface adsorption is extremely fast consistent with the well-established fact. For this reason, only film diffusion, inter-particle diffusion and intraparticle diffusion are considered (Describir, 2019). Consistent with the intraparticle diffusion model, (i) the plot of qt versus the square root of time (t^0.5) should be linear if the intraparticle diffusion is involved within the adsorption process, (ii) if the lines go through the origin when the intraparticle diffusion is that the rate-controlling step, and (iii) two or more slopes could occur during a multi-step adsorption process (Pan et al., 2017).

2.8.2 Boyd plot

The Boyd kinetic equation was used to determine the slowest step in the adsorption process. It is written as (Boyd et al., 1947):

$$F = \frac{q_t}{q_e} \qquad (2.8)$$

Rearrange by taking the natural logarithm to obtain the following equation (Ahmad et al., 2015a):

$$B_t = -0.4977 - \ln(1 - F) \qquad (2.9)$$

where,

q_e = the amounts of the adsorbate in the adsorbent at equilibrium (mg/g),

q_t = the amount of the adsorbate in the adsorbent at time t (min),

F = fraction of adsorbate adsorbed at time t, and

B_t = mathematical function of F

To test the linearity of the experimental values, Boyd plot of B_t against t is plotted. Intraparticle diffusion is the slowest step in the adsorption process if the plot is linear and passes through the origin. The slowest step, on the other hand, would be film diffusion if Boyd's plot does not pass through the origin.

2.9 Adsorption thermodynamic parameter

The thermodynamic behaviour of the adsorption process can be evaluated by four important parameters which are enthalpy change ($\Delta H°$), entropy change ($\Delta S°$), Gibbs free energy ($\Delta G°$) as well as the Arrhenius activation energy, E_a. The value of $\Delta H°$ and $\Delta S°$ can be calculated by Vant Hoff Equation as follows (Achmad et al., 2012) (Pan et al., 2017):

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

On the other hand, Gibbs free energy, $\Delta G°$ can be obtained from the following equation:

$$\Delta G° = \Delta H° - T\Delta S° \qquad (2.11)$$

Or using the following equation:

$$\Delta G° = -RT\ lnK_L \qquad (2.12)$$

where,

$\Delta G°$ = Gibbs free energy (kJ/mol),

$\Delta H°$ = enthalpy change (kJ/mol),

$\Delta S°$ = entropy change (kJ/mol),

K_L = Langmuir adsorption constant related to the free energy adsorption (L/mg),

R = universal gas constant (8.314 J/mol.K), and

T = absolute temperature (K)

The positive value of enthalpy ($\Delta H°$) represents endothermic nature while the negative value of $\Delta H°$ corresponds to the exothermic nature. Positive value entropy ($\Delta S°$) is related to an increase in randomness at the solid-liquid interface while a negative value of $\Delta S°$ signifies the decrease in randomness. The negative value of Gibbs free energy ($\Delta G°$) cause that the adsorption process is favourable and spontaneous in nature. The activation energy (E_a) via the Arrhenius equation can be verified as it is the nature of the adsorption process either physic-sorption or chemisorption.

$$ln\ k_2 = ln\ A - \frac{E_a}{RT} \qquad (2.13)$$

where,

k_2 = rate constant from pseudo-second order kinetic model (g/mg.h) and

A = Arrhenius factor

Table 2.4 Methods of obtaining thermodynamics parameters (Achmad et al., 2012)

Parameters	Methods of obtaining
Enthalpy change, $\Delta H°$	Calculated from the slope in Vant Hoff plot on ln K_L against 1/T.
Entropy change, $\Delta S°$	Calculated from the y-intercept in Vant Hoff plot of ln K_L against 1/T.
Gibbs free energy, $\Delta G°$	Calculated by using Equation 2.11 or 2.12
Arrhenius activation energy,E_a	Obtained from the slope of plot ln k_2 against 1/T.
K_L	Calculated from the plot of ln q_e/C_e against q_e at different solution temperature.
k_2	Calculated from the average rate constant obtained from pseudo-second order kinetic model for all initial CAP concentrations at three different solution temperature.

CHAPTER 3

METHODOLOGY

3.1 Materials

The materials used in this project is divided into precursors, chemicals and gases. Besides that, the methodology that comprised AC samples preparation, experimental design and adsorption studies were also included.

3.1.1 Precursor

Durian fruit was purchased from a local market in Mengkuang, Penang, Malaysia. The fruit was dehusked by cutting along the suture on the back of the locules (Ahmad et al., 2015a). Later, the durian seed was dried in the oven for overnight before undergoes the activation process. Each sample was weighted of 0.2 g and 13 sets of runs were carried out to fulfil the optimization study.

3.1.2 Chemicals

The list of chemicals used in this project is stated in Table 3.2 together with the properties of CAP in Table 3.1.

3.1.2(a) Properties of Chloramphenicol (CAP)

Table 3.1 Physical and chemical properties of CAP

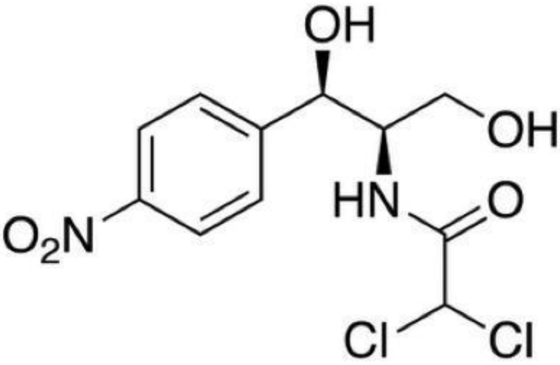
IUPAC Name	2,2-dichloro-N-[(1R,2R)-3-dihydroxy-1-(4-nitrophenyl)propan-2-yl]acetamide (A. Hamoudi & A. Bashir, 2018)
Molecular structure	 Figure 3.1 Structural formula of Chloramphenicol
Molecular formula	$C_{11}H_{12}Cl_2N_2O_5$
Synonyms	Chloramphenicol Chloramycetin 56-5-7 Chlornitromycin Levomycetion
Chemical safety	   Corrosive Irritant Health Hazard
Molecular weight	323.13 g/mol (A. Hamoudi & A. Bashir, 2018)
Physical description	Solid
Colour/form	 Figure 3.2 Chloramphenicol powder • White to greyish white or yellowish-white fine crystalline powder or fine crsytal. • Needles or elongated plates from water or ethylene dichloride.

	 Figure 3.3 Chloramphenicol solution
Taste	Bitter to taste
Boiling point	Sublime at high vacuum
Melting point	150.5°C (A. Hamoudi & A. Bashir, 2018)
Solubility	• Solubility in propylene glycol: 150.8 g/mol • Very soluble in methanol, ethanol, butanol, ester, acetone. • Fairly soluble in ether. • Insoluble in benzene, petroleum ether, vegetables oils. • Solubility in 50% acetamide solution about 5%.
Stability	• Following reconstitution with sterile water for injection, chloramphenicol sodium succinate injection containing 100 mg of chloramphenicol per mL features a pH of 6.4 – 7.0 and is stable for 30 days at room temperature. • Neutral and acid solution are stable on heating. • Chloramphenicol is stable for several years at room temperature. • Exceptionally stable within the presence of high pH, although it is destroyed at pH in more than 10. • Dissolved in distilled water, it can withstand boiling for few hours.
Decomposition	When heated to decomposition, it emits very toxic fumes of nitrogen oxides and chloride.
UV spectra	• UV max: 278 nm • UV: 385 nm (Adsorption spectra in UV and Visible Region, Academic Press, New York)
Hazard classes and categories	• Skin sensitivity: 1 (11.34%) • Eye damage: 1 (40.72%) • Acute toxicity (dermal): 5 • Carcinogenity: 1B • Reproductive toxicity: 1B • Specific organ toxicity: - single exposure (Category 5) • Aspiration hazard: - Category 1 (bone marrow, nervous system, digestive system) - Category 2 (heart)

3.1.3 Gases

Nitrogen gas (N_2) and carbon dioxide gas (CO_2), both with a purity of 99.99% were used in this project. N_2 gas was used to purge through the furnace during the activation process to create an inert atmosphere while CO_2 gas was used as a gasification agent in the preparation of AC in the activation step.

Table 3.2 Lists of chemical

Chemical	Purpose
Hydrochloric acid (HCl)	AC wash and pH adjustment
Sodium hydroxide (NaOH)	pH adjustment
Chloramphenicol (CAP)	Adsorbate

3.2 Experimental activities

To optimize DSAC preparation conditions based on CAP removal efficiency and yield, the experiments were designed by using the Standard Response Surface Methodology (RSM) and Central Composite Design (CCD). Two variables were used which is radiation power (A) and radiation time (B). A total of 13 experiments were generated by RSM. The schematic flow chart of experimental studies is presented in Figure 3.4 as below.