PALM SHELL BASED ACTIVATED CARBON MODIFIED BY CuFe LAYERED FOR AMOXICILLIN REMOVAL FROM AQUEOUS SOLUTION

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by

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LIST OF SYMBOLS

		Unit
A_{KC}	Koble-Corrigan constant	-
A_T	Temkin equilibrium binding constant	L/g
b_T	Temkin constant	J/mol
B_{KC}	Koble-Corrigan constant	-
B_t	Mathematical function of the fraction of soute adsorbed at time, t	-
C_e	Equilibrium concentration of adsorbate	mg/L
C_0	Adsorbate initial concentration	mg/L
E_a	Arrhenius activation energy of adsorption	kJ/mol
EC_{50}	Half maximal effective concentration	mol/L
F	Fraction of solute adsorbed at time, t	-
IC_{50}	Half maximal inhibitory concentration	mol/L
k	Rate constant of adsorption	1/min
K_a	Adsorption equilibrium constant	-
K_F	Freundlich constant	-
K_L	Langmuir adsorption constant related to the free energy adsorption	L/mg
LC_{50}	Median lethal concentration	ppm
n	Number of the data points	-
n_{KC}	Koble-Corrigan constant	-
n_F	Adsorption intensity	-
q_c	Amount of soluted sorbate sorbed at time, t	mg/g

q_e	Amount of adsorbate adsorbed at equilibrium	mg/g
q_m	Monolayer adsorption capacity of the adsorbent	mg/g
q_t	Adsorption capacity at time, t	mg/g
$q_{t,exp}$	Experimental adsorbate adsorbed at time, t	mg/g
$q_{t,cal}$	Calculated adsorbate adsorbed at time, t	mg/g
R	Universal gas constant	8.314 J/mol K
R_L	Separation factor	-
t	Time	h
T	Absolute temperature	K
V	Volume of solution	L
W	Weight of PSAC-CuFe composite	g
x	Adsorption capacities at time	mg/g
X	Adsorption capacities at equilibrium	mg/g
	Greek letters	
$\Delta G°$	Changes in standard free energy	kJ/mol
$\Delta H°$	Changes in standard enthalpy	kJ/mol
$\Delta S°$	Changes in standard entropy	J/mol K

LIST OF ABBREVIATIONS

AC	Activated carbon
ANOVA	Analysis of variance
BET	Brunauer-Emmett-Teller
CCD	Central composite design
FTIR	Fourier Transform Infrared
HPLC	High-performance liquid chromatography
KC	Koble-Corrigan isotherm
LDH	Layered double hydroxides
MO	Mixed-order
MW	Microwave
PS	Palm shell
PSAC	Palm shell based activated carbon
PSAC-CuFe	Palm shell based activated carbon modified by CuFe layered
PFO	Pseudo-first-order kinetic model
PSO	Pseudo-second-order kinetic model
RSM	Response surface methodology
RMSE	Root mean square error
SEM	Scanning electron microscopy
STA	Simultaneous thermogravimetric analyser
TPV	Total pore volume
WHO	World Health Organization

TEMPURUNG KELAPA SAWIT BERASASKAN KARBON TERAKTIF DIUBAH SUAI OLEH LAPISAN CuFe UNTUK PENYINGKIRAN AMOKSISILIN DARI LARUTAN AKUAS

ABSTRAK

Dalam kajian ini, karbon teraktif berasaskan cengkerang kelapa sawit (CSKT) telah disediakan untuk penyingkiran amoksisilin dalam larutan akuas. Reka bentuk eksperimen telah menentukan prestasi penjerapan CSKT untuk penyingkiran amoksisilin sangat dipengaruhi oleh nisbah impregnasi CuFe (NI). Hasil CSKT dipengaruhi oleh kuasa pengaktifan dan masa pengaktifan. Berdasarkan analisis Perisian Pakar Reka Bentuk, kuasa sinaran optimum dan masa sinaran untuk penyediaan CSKT ialah 421.34 Watt dan 12.58 minit masing-masing untuk mencapai pengambilan amoksisilin sebanyak 19.54 mg/g dan hasil CSKT sebanyak 38 % dengan menggunakan metodologi permukaan tindak balas. CSKT yang dioptimumkan menunjukkan sifat mesopori dengan struktur liang jenis heterogen. Dalam kajian penjerapan secara berkelompok, pengambilan amoksisilin oleh CSKT-CuFe yang dioptimumkan telah meningkat apabila kepekatan awal amoksisilin dan masa sentuhan meningkat. Pada pH 3, peratusan penyingkiran amoksisilin adalah yang tertinggi. Model garis sesuhu Langmuir ialah model yang paling sesuai untuk mewakili sistem penjerapan yang dikaji. Untuk kajian kinetik, penjerapan amoksisilin oleh CSKT-CuFe mengikuti model kinetik pseudo-tertib pertama. Sistem penjerapan CSKT-CuFe - amoksisilin menunjukkan sifat endotermik.

PALM SHELL BASED ACTIVATED CARBON MODIFIED BY CuFe LAYERED FOR AMOXICILLIN REMOVAL FROM AQUEOUS SOLUTION

ABSTRACT

In this study, palm shell based activated carbon (PSAC) was prepared for removal of amoxicillin in the aqueous solution. Experimental design has determined the adsorption performance of PSAC for the amoxicillin removal were greatly influence by CuFe impregnation ratio (IR). The yield of PSAC was influence by activation power and activation time. Based on the analysis of Design Expert Software, the optimum radiation power and radiation time for the preparation of PSAC were 421.34 Watt and 12.58 minute, respectively to achieve amoxicillin uptakes of 19.5443 mg/g and PSAC's yield of 38.0025 % by using response surface methodology (RSM). The optimized PSAC shows mesoporous type of pore structures. In the batch adsorption study, the uptake of amoxicillin by the optimized PSAC was increased when the initial amoxicillin concentration and contact time increased. At pH 3, the amoxicillin percentage removal was the highest. Langmuir isotherm model was the most suitable isotherm model for the amoxicillin – PSAC adsorption system. For the kinetics study, the adsorption of amoxicillin onto PSAC followed pseudo-first-order kinetic model. Amoxicillin - PSAC adsorption system showed an endothermic nature.

CHAPTER 1

INTRODUCTION

1.1 Antibiotic in aqueous solution

Antibiotics are a class of ionizable pharmaceuticals that have been widely used to treat and prevent microbial infection. The excessive consumption of antibiotics has brought adverse effects to the environment and human health. However, the antibiotics are frequently detected in the aquatic environment, and they are still active after entering the environment. The inappropriate disposal of medical effluent is leading to changes in the microbial community and finally leads to the occurrence of antibiotic resistance genes in bacteria.

Antibiotic resistance is the ability of a certain bacterium to survive in the presence of an antibiotic that was originally used to treat the infections caused by that bacterium or the gaining of a resistance mechanism against that specific antibiotic (Magiorakos, 2012). Inappropriate disposal of medicinal effluents, unused antibiotics and overuse of antibiotics in the agriculture sector have contributed to the antibiotic resistance of bacteria. Past and recent data have shown the increasing population of bacteria have become resistant to certain antibiotics. This situation is worrying because it will eventually cause the common disease to become untreatable since antibiotics are useless to kill the harmful bacteria. The World Health Organization (WHO) said antimicrobial resistance will be the main threat to global public health. WHO has agreed to ‘One Health’, a global action plan in 2015 for resistance containment in the environment (World Health Organization, 2015).

Amoxicillin is an acid stable, partially synthetic antibiotic which is under the Penicillin. It provides a broad spectrum of activity against Gram-positive and Gram-negative bacteria in both human and animals. It is usually used to demonstrate antibacterial effectiveness against various infections through the inhibition of biosynthesis of cell wall mucopeptide during binary fission. Also, it is useful to treat the infections including the middle ear, tonsils, throat, larynx, pharynx, lungs, bronchi, urinary tract, and skin. Amoxicillin is white colour powder with slight sulphurous odour and it is very soluble in water (Kaur et al., 2021).

Amoxicillin is a moderate-spectrum, semisynthetic β-lactam which is usually used for oral adsorption. It provides a broad spectrum of activity against Gram-positive and Gram-negative bacteria (Salvo et al., 2009). It is usually used to demonstrate antibacterial effectiveness against various infections, including liver, lungs, prostate, middle ear effusions, maxillary sinus secretions, bone, gallbladder, bile, and into ascitic and synovial fluids but has poor penetration into cerebrospinal fluid (Huttner et al., 2020). However, the discharge of amoxicillin to the environment will lead to the development of antibiotic resistance among bacteria. Amoxicillin induces direct biotoxic effect to a wide range of organism and altering species distributions in the harmful ways for the ecosystem (Wang et al., 2019). In short, amoxicillin has a significant ecological risk and suggesting the discharge of amoxicillin will affect the aquatic environment.

Nowadays, amoxicillin antibiotics removal from aqueous solution technologies have been developed and improved such as hydrolysis, adsorption, photolysis, oxidation-reduction and so on (Sodhi et al., 2021). However, adsorption and advanced oxidation processes have received more attention since they are more environmentally friendly compared to other methods. Advanced oxidation processes depend on the photocatalytic degradation of organic compounds and convert amoxicillin into CO_2 and H_2O (Kanakaraju et al., 2018). Adsorption method allows amoxicillin in fluid phase to adhere to the solid surface and it is a simple and low-cost process.

The materials used for adsorption of amoxicillin are synthesized zinc oxide and graphene oxide nanoparticles. Although these materials can perform highly effective on adsorption of antibiotics, they are not environmentally friendly in large scale applications (Xue-jiaoTong, 2011).

Activated carbon (AC) is a carbonaceous solid that has large surface area and good porous structure (Ogungbenro et al., 2020). In general, the AC can be produced from organic biomass that has high fixed carbon composition. The synthesis of AC from biomass waste has two methods which are chemical and physical activation. Physical activation requires high activation temperature to increase the porosity of carbon with big surface area. Chemical activation is usually chosen due to its good porous structure, shorter activation time, low operating temperature and simplicity. Recently, microwave (MW) activation is proven to have good performance in preparation of AC. This is due to the advantages in faster temperature rise, energy savings and high yield (Ao, et al., 2018).

Many studies have demonstrated that AC supported with layered double hydroxides (LDH) showed better adsorption performance as compared to using single AC only. LDH is represented by the metal with the chemical formula of $[M^{2+}{}_{1-x}\,M_x^{3+}(OH)_2]^{x+}(A^{n-})_{x/m}.mH_2O$, where x is the molar ratio of M^{3+}, M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively while A^{n-} is the interlayer anion with charge (Zubair, et al., 2018). LDH can provide layered structure, better surface characteristics and low toxicity with good anion exchange capability (Jarrah, et al., 2019). The AC modified with LDH has been proved that it can improves the physicochemical characteristics of AC modified by LDH such as functionality, surface area and amoxicillin removal efficiency in the aqueous solution (Muaazu, et al., 2020).

In this research study, the study of adsorption capability of palm shell based activated carbon (PSAC) modified by CuFe layered (PSAC-CuFe) to amoxicillin as adsorbate. During the experiment, the chemical and physical characteristic such as BET surface area, thermal stability, porosity and polymetric of the adsorbent are investigated and analysed.

1.2 Problem Statement

In this research study, PSAC-CuFe was proposed to remove amoxicillin from aqueous solution. Amoxicillin is an antibiotic used by humans to treat or prevent microbial infection. The disposal of amoxicillin antibiotics to the environment from the pharmaceutical industry will alter the microbial environment and lead to antibiotic resistance. The layered double hydroxides (LDH) containing CuFe is produced to modify activated carbon to study the performance on amoxicillin removal. This proposed research shall provide a good opportunity to reduce the cost of antibiotic removal and increase the process sustainability due to the employment of renewable biomass, which is palm shell as raw material for adsorption. The proposed solution contributes to cost effective, sustainable, and environmentally friendly. Apart from that, CuFe LDH can provide high adsorption and good reusability performance for the amoxicillin removal compared to conventional methods.

1.3 Objectives

a) To prepare PSAC-CuFe adsorbent for amoxicillin removal.

b) To optimize PSAC preparation conditions in term of radiation power and radiation time by using RSM

c) To characterize the physical and chemical properties of PSAC-CuFe in term of surface area, pore characteristic, surface morphology, surface chemistry and elemental analysis.

d) To investigate the effects of amoxicillin initial concentration, contact time, solution temperature, solution pH for the adsorption of amoxicillin on PSAC-CuFe.

e) To perform equilibrium, kinetic and thermodynamics study.

CHAPTER 2

LITERATURE REVIEW

2.1 Adsorption of contaminants in aqueous solution

Adsorption is the process that allows the adsorbate to adhere to the surface of adsorbent to separate the adsorbate from the aqueous solution. Adsorbents should have high selectivity to adsorb the selected components from a mixture solution on its surface. Therefore, adsorption is usually used in wastewater treatment process to adsorb the pollutants from wastewater. Adsorption capacity, adsorbent selectivity, regenerability, kinetics and compatibility are important parameters to choose a suitable adsorbent. There are two types of adsorbents which are inorganic such as aluminas, silicas and zeolites and organic adsorbents such as activated carbon and polymers.

Adsorption of liquid mixture is very important for the separation and purification of industrial liquid mixtures but also the treatment of environmental wastewater. The more the components exist in the aqueous solution, the more complicated parameters we need to determine and investigate. For example, for a two-component solution at constant operating condition, the parameters of this adsorption process are molecular interactions in the bulk phase, surface phase, between bulk and surface phases and between solid and solution interface (Da, 2001).

There are many adsorption kinetic models have been developed to describe the adsorption kinetic process such as pseudo-first-order (PFO), pseudo-second-order (PSO), the mixed-order (MO), the Ritchie’s equation, the Elovich model and the phenomenological mass transfer. However, some of the kinetic models cannot be used to calculate mass transfer since they are lacking physical information (Wang & Guo, 2020).

2.2 Amoxicillin

Amoxicillin is an amino-penicillin antibiotic and usually used in the primary care setting. It is a common antibiotic which is created by adding an extra amino group to penicillin and used to fight with the bacteria infection. Amoxicillin demonstrates antibacterial efficacy against aerobic gram-positive and gram-negative organisms and moderate activity against bacteria.

Amoxicillin is a β-lactam antibiotic drug which under the group of penicillin drugs. The most sensitive emission wavelength of amoxicillin is 274, 231 and 205 nm. Thin-layer chromatography, reverse-phase liquid chromatography, reverse-phase liquid chromatography and high-performance liquid chromatography (HPLC) can be used to determine amoxicillin in the aqueous solution.

The antibiotics disposed in the aquatic environment has raised the concerns due to their potential hazards to the natural ecosystem and human health. The global antibiotic market for β-lactam antibiotics is over 65% (Pourakbar et al., 2016).

Amoxicillin is usually detected in the wastewater and surface water as it has low biodegradability. Even a low concentration of amoxicillin present in the water from ng/L to µg/L, the unexpected risks can be caused by amoxicillin to the environment, eco-system and human exposure because of its adverse long-term effects. The toxicity of amoxicillin on the different aquatic organism is summarized in **Table 2.1** (Sodhi, et al., 2021).

Table 2.1 Toxicity of amoxicillin on the aquatic organism

Aquatic organisms	Endpoint and duration of exposure	Concentration
Daphnia magna	EC_{50} (15 min)	>1000 mg/L
Moina macrocopa	EC_{50} (15 min)	>1000 mg/L
Oryzias latipes	LC_{50} (15 min)	>1000 mg/L
Vibrio fischeri	IC_{50} (15 min)	3597 mg/L
Microcystis aeruginosa	EC_{50} (7 days)	0.0037 mg/L
Synechococcus leopoliensis	LC_{50} (4 days)	1.56 µg/L
Danio rerio	EC_{50} (2 days)	132.4 mg/L
Spirodela polyrhiza	IC_{50} (7 days)	0.089 µg/L

2.3 Amoxicillin Removal Techniques

Generally, there are two main methods for the removal of amoxicillin which are adsorption and degradation process. Adsorption is a popular wastewater treatment practice due to cost-effective and environmentally friendly. There are various types of techniques for adsorption process such as batch, continuous moving bed, continuous fixed bed, continuous fluidized bed and pulsed bed adsorption. For adsorption, there are many types of adsorbents used to remove amoxicillin which are biochar-based adsorbents, biomass-based adsorbents, carbon-based adsorbents, polysaccharide-based adsorbents and miscellaneous adsorbents. It is suggested that carbon-based adsorbents could provide the highest efficiency for amoxicillin removal.

For the degradation method, there are photocatalytic degradation, sonophotocatalytic degradation, catalytic degradation, Fenton oxidation, electrochemical degradation, and biological degradation. However, it is reported that Fenton oxidation will generate large amount of ferrous sludge and partially degraded antibiotic compounds that may be harmful to the environment.

2.4 Activated carbon

The researchers found that activated carbon produced from the biomass waste is one of the best ways as an adsorbent to treat the wastewater due to cost effectiveness, affordable, environmentally friendly, and high adsorption affinity, and capacity. In Malaysia, the amount of palm shell waste is very high. Therefore, palm shell waste is chosen to treat amoxicillin from aqueous solution due to highly accessibility. The maximum adsorption capacity of AC based palm shell is 100.38 mg/g only (Darweesh & Ahmed, 2017).

2.5 CuFe layered doubled hydroxides

To have good adsorption capacity, low cost and environmentally friendly adsorbent, the modification on the AC based palm shell is needed. To modify the AC based palm shell, CuFe is chosen due to it provides high adsorption capacity, compared to other LDH such as CoFe, NiFe, ZnFe and NiMgAl. The adsorption capacity of CuFe to EBT dye is 250 mg/g (Zubair, 2021). In this project, the adsorption capacity of AC/CuFe is studied by analysing the chemical and physical characteristic of this adsorbent. The modification method is microwave irradiation. The AC is a good microwave adsorber since it can receive microwave energy directly through dipole rotation and ionic conduction and bulk temperature will increase rapidly (Wang, et al., 2012). In this study, different radiation power and retention time are investigated to determine the optimum operating condition of microwave irradiation method.

2.6 Chemical and physical activation

Basically, the conventional AC preparation methods are mainly chemical activation and physical activation. For chemical activation, the precursor materials are impregnated with chemical agents and heated in an inert or oxidizing gas environment. The advantages of chemical activation are low energy consumption and low amount of tar formation. However, the chemical agent may cause serious corrosion to the equipment and a stricter procedure must be taken during the washing step to removing the excessive residues of chemical agents.

For physical activation, CO_2 and O_2 stream are used as oxidizing gases in the carbonization and pyrolysis activation. Physical activation is an attractive method since it is environmentally friendly and simple in operation. However, it requires high activation temperature and long activation time, causing high energy consumption and not cost effective.

The adsorption parameters of chemical activation and physical activation are compared in **Table 2.2** (Kabbashi et al., 2021).

Table 2.2 Comparison between chemical activation and physical activation

Parameters	Chemical Activation	Physical Activation
Activation temperature	Low	High
Yield	High	Low
Surface area	High	Low

2.7 Adsorption isotherm

Adsorption isotherms are used to describe the phenomenon of adsorption equilibrium when the adsorbate concentration in the bulk solution and interface are in dynamic balance as an adsorbate has been contacted with the adsorbent for sufficient time. The adsorption isotherms that are usually used for antibiotics adsorption are Langmuir isotherm, Freundlich isotherm, Temkin isotherm, and Koble-Corrigan isotherm.

2.7.1 Langmuir isotherm

Langmuir isotherm is developed to describe the gas-solid-phase adsorption onto activated carbon and quantify the amount of adsorbate adsorbed on an adsorbent as a function of partial pressure or concentration at constant temperature. Langmuir isotherm explains the relationship between the decrease of the intermolecular attractive forces and the increase of distance. The Langmuir isotherm can be represented as follow: (Langmuir, 1918)

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{2.1}$$

where q_e is the amount of adsorbate adsorbed at equilibrium (mg/g); q_m is maximum monolayer adsorption capacity of the adsorbent (mg/g); C_e is equilibrium concentration of adsorbate (mg/L) and K_L is Langmuir adsorption constant related to the free energy adsorption (L/mg). A graph of plot of C_e/q_e against C_e gives a straight line with the slope of $1/q_e$ and intercept of $1/K_L q_m$. A further analysis of the Langmuir equation can be made on separation factor, R_L given by the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \tag{2.2}$$

where K_L (L/mg) is the Langmuir constant, C_0 (mg/L) indicates the adsorbate initial concentration and R_L is the adsorption nature. If $R_L > 1$, the adsorption is unfavourable. If $R_L = 1$, it is linear adsorption. If $0 < R_L < 1$, it is favourable adsorption. If $R_L = 0$, the adsorption is irreversible.

2.7.2 Freundlich isotherm

The Freundlich isotherm is proposed to describe the gas phase adsorption and solute adsorption at constant temperature (Freundlich, 1906). Freundlich isotherm can be represented:

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

The equation can be linearized and the temperature dependent constants K_f and 1/n by taking the logarithmic of both sides:

$$\log q_e = \frac{1}{n_F} \log C_e + \log K_F \tag{2.4}$$

where, K_F and n_F are the Freundlich constants which indicate the adsorption capacity and adsorption intensity, respectively while q_e is the amount of adsorbate adsorbed at equilibrium (mg/g). The graph can be plotted as log q_e is y-axis and log C_e is x-axis. The n_F value means the degree of nonlinearity between solution concentration. If $n_F = 1$, the adsorption is linear. If $n_F < 1$, the adsorption is a chemical process but if $n_F > 1$, the adsorption is a physical process.

2.7.3 Temkin isotherm

Temkin isotherm describes how the adsorbate interaction affects the adsorbent based on the uniformly distributed binding energies (Hameed et al., 2009). Temkin isotherm is expressed as:

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \tag{2.5}$$

The equation is usually expressed in a linear form and is expressed as:

$$q_e = B_T \ln A_T + B_T \ln C_e \tag{2.6}$$

Where $B_T = RT/b$, b is the Temkin constant (J/mol) related to heat of sorption, q_e (mg/g) is the amount of adsorbate adsorbed at equilibrium. A_T (L/g) is the Temkin equilibrium binding constant, R (8.314 J/mol K) is the gas constant and T (K) is the absolute temperature. A graph of q_e versus $\ln C_e$ can be plotted with a slope, B_T and intercept, A_T.

2.7.5 Koble-Corrigan isotherm

Koble-Corrigan isotherm is the combination of Langmuir and Freundlich isotherm type models and representing the equilibrium adsorption data (Han et al., 2005). The isotherm is expressed as:

$$q_e = \frac{A_{KC} c_e^{n_{KC}}}{1 + B_{KC} c_e^{n_{KC}}} \tag{2.7}$$

where, A_{KC}, B_{KC} and n_{KC} are the Koble-Corrigan parameters.

The three isotherm constants also can be expressed in linear plot and using trial and error optimization method:

$$\frac{1}{q_e} = \frac{1}{A_{KC}} \times \frac{1}{c_e^{n_{KC}}} + \frac{B_{KC}}{A_{KC}} \tag{2.8}$$

where, q_e (mg/g) is the adsorbed at equilibrium state, C_e (mg/L) is the adsorbate equilibrium concentration (mg/L). If n is close to 1, it indicates the isotherm is closer to Langmuir form. This model is valid only when $B > 1$.

2.8 Adsorption kinetic

Adsorption kinetic is an important analysis determining the adsorption performance and efficiency through establishing the solute uptake rate, which determines the residence time required for completion of adsorption process. The most used kinetic models are pseudo-first order and pseudo-second order.

2.8.1 Pseudo-first-order kinetic model

Lagergren has been proposed pseudo-first-order kinetic model which is widely used for the adsorption of an adsorbate from an aqueous solution (Ho, 2004). The pseudo-first order rate equation:

$$\frac{dx}{dt} = k(X - x) \tag{2.9}$$

Where, X and x (mg g^{-1}) are the adsorption capacities at equilibrium and at time, t (min), respectively. k (min^{-1}) is the rate constant of adsorption.

Equation 2.16 is integrated with the boundary conditions at $t = 0$ to $t = t$ and $x = 0$ to $x = x$:

$$\ln\left(\frac{X}{X - x}\right) = kt \tag{2.10}$$

Rearrange it:

$$x = X(1 - e^{-kt}) \tag{2.11}$$

Rearrange the equation to linear form:

$$\log(X - x) = \log(X) - \frac{k}{2.303}t \tag{2.12}$$

Simplified to:

$$\log(q_e - q_t) = \log(q_e) - \frac{k}{2.303}t \tag{2.13}$$

Where, q_e (mg/g) is the adsorption capacity at equilibrium while q_t (mg/g) is the adsorption capacity at time t. k (min^{-1}) is the rate constant of pseudo-first order adsorption.

2.8.2 Pseudo-second-order kinetic model

Pseudo-second-order model is proposed by (Ho & Mckay, 1999) and provides better correlation coefficient on reaction rate. It is expressed as:

$$\frac{dq_t}{dt} = k(q_c - q_t)^2 \tag{2.14}$$

Equation 2.21 is integrated with the boundary conditions at $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$:

$$\frac{1}{(q_c - q_t)} = \frac{1}{q_c} + kt \tag{2.15}$$

Rearrange it:

$$\frac{t}{q_t} = \frac{1}{{q_c}^2 k_2} + \frac{1}{q_c}t \tag{2.16}$$

Where, q_t and q_c (mg g^{-1}) are the amount of soluted sorbate sorbed at time, t and at equilibrium, respectively. k (g/mg min) is the rate constant of adsorption.

2.8.3 Boyd kinetic model

Boyd kinetic model is used to determine the actual rate-controlling step in the adsorption process (Tavlieva et al., 2013). The Boyd kinetic equation can be expressed:

$$F = 1 - \left(\frac{6}{\pi^2}\right) \exp\left(-B_t\right) \tag{2.17}$$

where, B_t is a mathematical function of F while F is the fraction of solute adsorbed at different times, t:

$$F = \frac{q_t}{q_{eq}} \tag{2.18}$$

where, q_t (mg/g) and q_e (mg/g) is the amount of adsorbate adsorbed at time, t (min) and at equilibrium.

$$B_t = -0.4977 - \ln(1 - F) \tag{2.19}$$

The graph can be plotted as B_t is y-axis and t is the x-axis. The external diffusion is the rate limiting process if the plot does not pass through the origin.

2.10 Adsorption thermodynamics

The thermodynamic study provides more details about the inherent energetic changes related with adsorption process. There are three parameters can be analysed in thermodynamic study which are enthalpy of adsorption (ΔH°), free Gibbs energy (ΔG°) and change of entropy (ΔS°) as one mole of solute from the solution is transferred onto solid-liquid interface (Hong et al., 2009).

The Gibbs free energy equation can be expressed:

$$\Delta G^{\circ} = -RT \ln K_a \tag{2.20}$$

where, ΔG° (J/mol) is standard free energy charge, R is universal gas constant (8.314 J/mol K), T (K) is the absolute temperature and K_a is the adsorption equilibrium constant. If ΔG° is negative value, the reaction occurs spontaneously at the given temperature. In the differential form, change in equilibrium constant with temperature can be obtained as follows:

$$\frac{d \ln K_a}{dT} = \frac{\Delta H^{\circ}}{RT^2} \tag{2.21}$$

After integration, the equation becomes:

$$\ln K_a = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \tag{2.22}$$

Rearrange the equation and Gibbs free energy equation then becomes:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{2.23}$$

Arrhenius equation can be applied to evaluate the activation energy of adsorption.

The equation is shown below:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \tag{2.24}$$

Where k_2 (g/mg h) is the rate constant obtained in pseudo-second-order kinetic model, E_a (kJ/mol) is the Arrhenius activation energy of adsorption, R is universal gas constant (8.314 J/mol K) and T (K) is absolute temperature. The graph of $\ln k_2$ versus $1/T$ can be plotted in a straight line to determine the slope -E_a/R and y-intercept of $\ln A$.

CHAPTER 3

RESEARCH METHODOLOGY

Figure 3.1 shows the schematic diagram of the research flow.

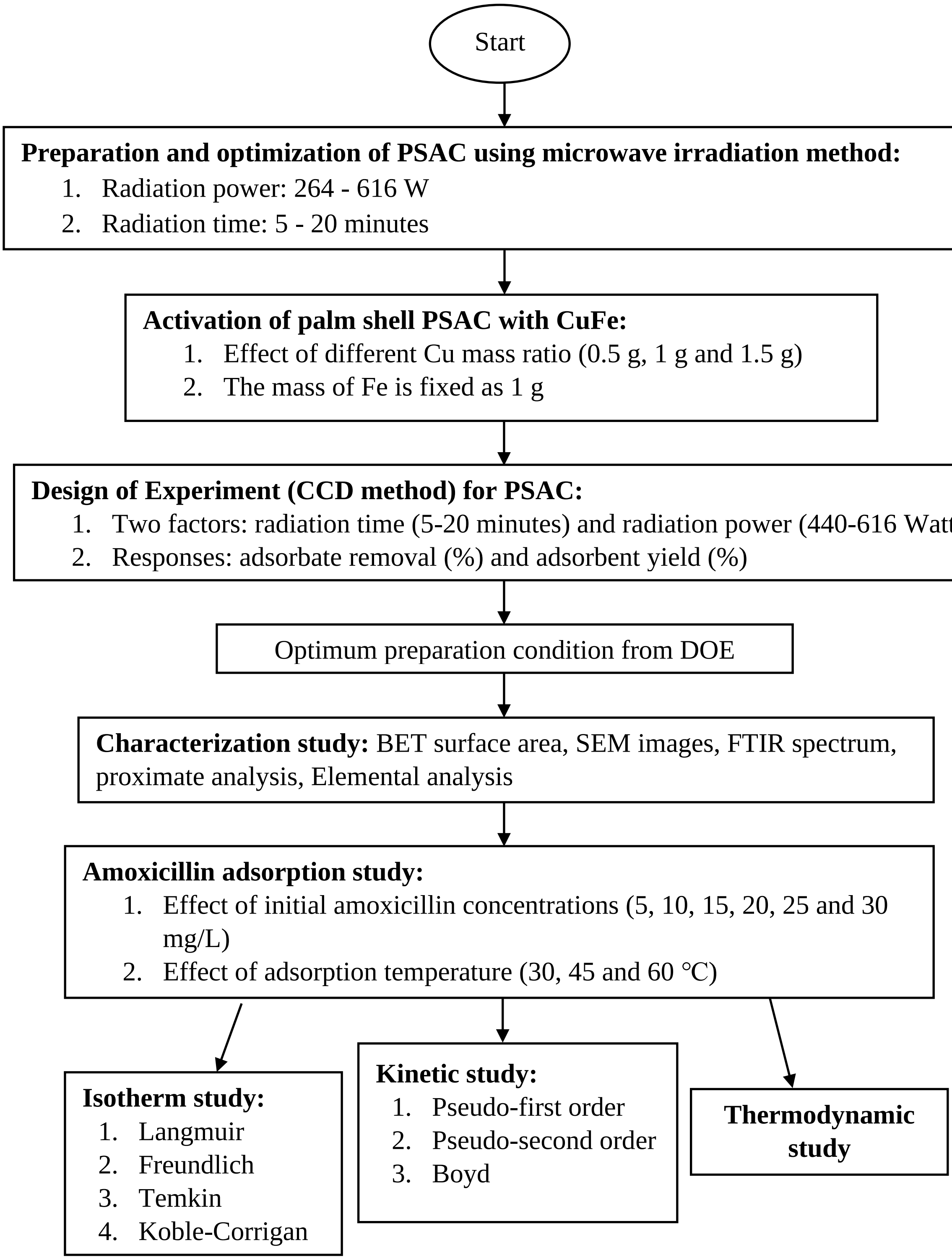

Figure 3.1 Schematic diagram of research flow

3.1 Preparation of Materials

Amoxicillin (>98%) was purchased from Y.S.P. Industries (M) Sdn Bhd and used as received. The palm shells waste was collected from United Oil Palm Industries Sdn. Bhd as shown in **Plate 3.1 (a).** The palm shells are dried, crushed and sieved to a particle size of 2.0-2.8 mm, which are the common size for producing adsorbent as shown in **Plate 3.1 (b)**. The list of chemicals that were used during the experiment lab work are listed in **Table 3.1**.

(a) (b)

Plate 3.1 Palm kernel shell (a) From the industry (b) After dried, crushed, and sieved

Table 3.1 List of chemicals

Chemical	Supplier	Purity (%)	Usage
Hydrochloric acid	Merck, Germany	37	AC wash and pH adjustment
Sodium hydroxide	Essex, UK	99	pH adjustment
Amoxicillin	Y.S.P Industries, Malaysia	99	Adsorbate

3.2 Experimental procedure

The experimental procedure included the AC preparation, AC modified with CuFe layered and followed by batch adsorption studies of amoxicillin onto AC. The batch adsorption studies consisted of equilibrium, kinetic and thermodynamic of the adsorption system.

3.2.1 PSAC preparation

The prepared palm shells (PS) were grinded into small and equal size pieces, then they were filtered to separate the PS and fibres. These precursors were dried in the oven at temperature of 110 °C for 24 hours to remove the moisture content. 20 g of dried precursor was placed in a test tube and then placed in the microwave as shown in **Plate 3.2**. Carbon dioxide gas was purging through the microwave at the flow rate of 100 cm^3/min. The temperature of the microwave at radiation power of 421.34 W and radiation time of 12.58 min. The microwave was cooled down to room temperature under CO_2 gas flow. Finally, PSAC was produced.

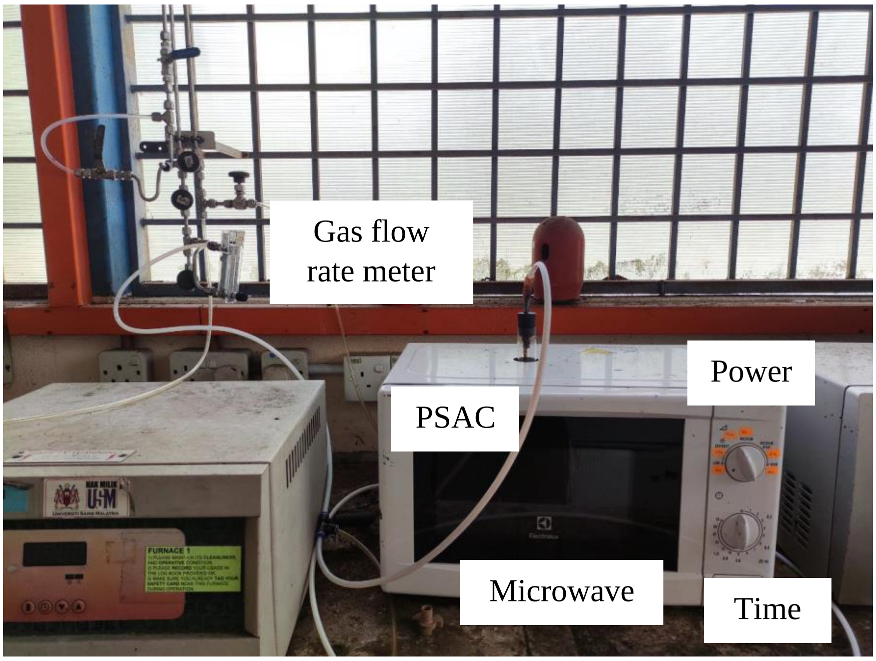

Plate 3.2 Experimental set up for the AC preparation

3.2.2 PSAC-CuFe preparation

1 g of PSAC was added with 1 g of Cu and 1 g of Fe which followed the mass ratio of 1:1 (Cu:Fe). Then, 200 mL of deionized water was added into the mixture and put the mixture in the water bath shaker at the room temperature and rotation speed of 200 rpm for 1 hour.

After 1 hour, the pH of the mixture was adjusted to pH 10 by washing it with the 0.1 M of sodium hydroxide (NaOH) solution. The pH value was measured using pH meter (Model Delta 320, Mettler Toledo, China). The pH adjusted mixture was placed in the water bath shaker at the room temperature and rotation speed of 200 rpm for 24 hours.

After 24 hours, the washing process was continued using hydrochloric acid (0.1 M) until the pH of washing solution reached 6.5 – 7. The centrifuge (Labogene Scanspeed1248R, Malaysia) was used in the washing process. The washed sample was kept in the oven at 110 ℃ for 24 hours. The dried sample was PSAC-CuFe. It was stored in an air-tight container for further characterization and adsorption studies.

3.2.3 Experimental design for PSAC preparation

To study the optimum parameter of preparing PSAC, a standard response surface methodology (RSM) design called a central composite design (CCD) was used. In this study, two variables studied for the preparation of PSAC were:

i. x_1, radiation power (W)

ii. x_2, radiation time (min)

Table 3.2 tabulates the coded variable level of the variables investigated in this study.

Table 3.2 The coded levels for CCD of independent variables

Variables (factors)	**Coded variable level**		
	-1	0	+1
Radiation power (W)	264	440	616
Radiation time (min)	5	12.5	20

Table 3.3 Experimental design matrix

Run	**Standard**	**Preparation variables**	
		Radiation power, x_1 (°C)	**Radiation time, x_2 (min)**
1	13	440	12.5
2	10	440	12.5
3	2	616	5
4	8	440	20
5	5	264	12.5
6	1	264	5
7	9	440	12.5
8	12	440	12.5
9	4	616	20
10	7	440	5
11	3	264	20
12	11	440	12.5
13	6	616	12.5

Based on the ranges and the coded level provided, a complete design matrix of the experiments employed in this study is presented in

Table 3.3. Based on the experimental design matrix, there were 13 experiments run at the certain radiation power and radiation temperature. In

Table 3.3, the experimental sequence for every standard was randomized to reduce the effects of the uncontrolled factors. The model was based on the face centered. The center points are used to measure the experimental error and the reproducibility of the data.

3.3 Characterization of PSAC-CuFe

The characterization of samples were identified by using surface area analyzer, scanning electron microscopy (SEM), thermogravimetric analyzer (STA) and Fourier transform infrared spectroscopy (FTIR). Brunauer-Emmett-Teller (BET) surface area, pore size distribution, total pore volume (TPV) and average pore diameter of the PSAC-CuFe are measured by using surface area analyser (Micromeritics, Model ASAP 2020, USA). Textural characteristics are determined by nitrogen adsorption with an accelerated surface area and porosimetry system. The calculations of surface area, TPV and average pore size were carried out by using the software (Microspore version 2.46). The BET equation was also used to calculate the surface area of the PSAC. TPV was estimated by determining the liquid volume of nitrogen at a relative pressure of 0.98.

The analysis of surface morphology was carried out using the SEM analyser (Model Quanta 450 FEG, Netherland). The samples were placed on the aluminium stub and coated with gold for the reflection of electron. Elemental analysis analysis was carried out by using elemental analyzer. For the elemental analysis, the element of carbon (C), hydrogen (H), nitrogen (N), sulphur (S), and other elements can be obtained in term of percentage. FTIR spectroscope (Model IR Prestige 21 Shimadzu, Japan) was used to determine the surface chemistry of the samples. The infrared adsorption bands can identify the specific molecular compounds and functional groups in the samples.

3.4 Measurement of Amoxicillin Adsorption

The adsorption experiments are carried out by adding 20mL amoxicillin solution into a conical flask and mixing it with 0.2 g of PSAC-CuFe. The adsorption kinetics are investigated with different initial concentrations of amoxicillin and different operating temperatures at the same pH value. The mixtures of amoxicillin solution and PSAC-CuFe are shaking for 24 h and filtered through a nylon membrane immediately to check the adsorption performance. UV-VIS Hach Lange spectrophotometer is used to determine the final concentration of amoxicillin at a maximum wavelength of 295 nm.

The adsorption capacity and removal percentage of amoxicillin are calculated using the formula below:

$$Adsorption\ capacity\ (\frac{mg}{g}) = q_e = \frac{(C_0 - C_e)V}{W} \tag{3.1}$$

$$Removal\ percentage\ (\%) = \frac{(C_0 - C_e)}{C_e} \times 100\% \tag{3.2}$$

where, C_0 and C_e are the initial and equilibrium concentration (mg/L) of amoxicillin in the aqueous solution, respectively. W is the weight of PSAC-CuFe composite (g) and V is the volume of solution (L). The adsorption performance was explained by studying the batch equilibrium, batch kinetic and thermodynamics.