

**ADSORPTION AND DESORPTION OF OXYTETRACYCLINE
HYDROCHLORIDE ON MODIFIED ACTIVATED CARBON**

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by

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LIST OF SYMBOLS

Symbol		Unit
C_e	Equilibrium concentration of adsorbate	mg L^{-1}
C_o	Highest initial adsorbate concentration	mg L^{-1}
C_t	Antibiotic concentration at time, t	mg L^{-1}
C_{de}	Concentration of antibiotics being desorbed	mg L^{-1}
E_a	Arrhenius activation energy of adsorption	kJ mol^{-1}
k_1	Adsorption rate constant for the pseudo-first-order kinetic	hr^{-1}
k_2	Adsorption rate constant for the pseudo-second-order	$\text{g mg}^{-1} \cdot \text{hr}^{-1}$
K_F	Freundlich isotherm constant	$\text{mg g}^{-1} (\text{L mg}^{-1})^{1/n}$
K_L	Langmuir adsorption constant	L mg^{-1}
W	Mass of adsorbent	g
n_f	Constant for Freundlich isotherm	-
q_e	Amount of adsorbate adsorbed at equilibrium	mg g^{-1}
q_m	Adsorption capacity of Langmuir isotherm	mg g^{-1}
q_t	Amount of adsorbate adsorbed at time, t	mg g^{-1}
R	Universal gas constant	$8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
R^2	Correlation coefficient	-
t	Time	min
T	Absolute temperature	K
V	Solution volume	L
ΔG°	Changes in standard Gibbs free energy	kJ mol^{-1}
ΔH°	Changes in standard enthalpy	kJ mol^{-1}
ΔS°	Changes in standard entropy	kJ mol^{-1}
λ	Wavelength	nm

LIST OF ABBREVIATIONS

AC	Activated carbon
BET	Brunauer-Emmett-Teller
FTIR	Fourier Transform Infrared
GAC	Granular activated carbon
IUPAC	International Union of Pure and Applied Chemistry
OTC-HCl	Oxytetracycline hydrochloride
KCl	Potassium chloride
M.AC	Modified activated carbon
PAC	Powder activated carbon
rpm	Rotation per minute
TGA	Thermal gravimetric analysis

**PENJERAPAN DAN NYAH PENJERAPAN TERHADAP OXYTETRACYCLIN
HIDROKLORIDA MENGGUNAKAN KARBON TERAKTIF YANG
DIUBAHSUAI**

ABSTRAK

Penjerapan Oxytetracycline hidrokksida (OTC-HCl) menggunakan karbon teraktif komersial (M.AC) yang terubah suai dengan menggunakan $\text{Cu}(\text{NO}_2)_3$ telah dikaji melalui penjerapan proses kelompok. Karbon teraktif yang diubahsuai menunjukkan prestasi yang optimum pada 1 wt%. Kesan pelbagai parameter, seperti pH pada 4 kepekatan awal dari 5 sehingga 25 mg L^{-1} dan suhu (30,40 dan 50) °C. Kapasiti penjerapan menunjukkan penurunan apabila suhu meningkat. Kapasiti penjerapan tertinggi adalah pada $T = 30^\circ\text{C}$ pada kepekatan 25 mg L^{-1} . Model sesuhu Langmuir dan sesuhu Freundlich digunakan untuk menganalisis data pada suhu yang berbeza. Model sesuhu Langmuir hampir sama dengan data eksperimen di mana R^2 lebih besar daripada 0.9. Data kinetik penjerapan telah dianalisis dengan menggunakan pseudo-tertib pertama dan pseudo-tertib kedua. Keputusan menunjukkan, penjerapan terbaik dengan menggunakan kinetik pseudo-tertib kedua. Termodinamik penjerapan dikaji untuk memperoleh parameter termodinamik. Sampel penjerapan yang memberikan keadaan optimum dianalisis menggunakan Fourier transformed infrared. Sementara itu bagi karbon teraktif yang diubah suai dianalisis menggunakan Brunauer-Emmett-Teller dan Thermal gravimetric analysis. Ujian proses penjerapan-nyah jerapan dengan menggunakan M.AC untuk beberapa kitaran berjaya dijalankan sebelum kadar prestasi berkurang.

ADSORPTION AND DESORPTION OF OXYTETRACYCLINE HYDROCHLORIDE ON MODIFIED ACTIVATED CARBON

ABSTRACT

Adsorption of Oxytetracycline hydrochloride (OTC-HCl) onto commercialize activated carbon that been modified by using $\text{Cu}(\text{NO}_2)_3$ was investigated through batch adsorption process. The modified activated carbon (M.AC) shown the optimum performance at 1.00 Wt %. The effects of the various parameters, such as pH, initial concentration from 5 to 25 mg L^{-1} and temperature (30,40 and 50) $^\circ\text{C}$ was investigated. From the result the adsorption capacity is decreased when increasing the temperature. The highest adsorption capacity was at $T=30^\circ\text{C}$ at concentration 25 mg L^{-1} . Langmuir and Freundlich isotherms were used to analyzed data at different temperatures. Its shown that, the Langmuir isotherms almost fits with the experimental data with R^2 almost greater than 0.9. Adsorption kinetics data were analyzed using pseudo-first-order and pseudo-second-order. As a result, the adsorption was best fitted by pseudo-second-order kinetics. The adsorption thermodynamics studied was be done to obtained thermodynamics parameters. The sample of adsorption that give optimum condition were characterized using Fourier transformed infrared meanwhile for the modified activated carbon were characterized using Brunauer-Emmett-Teller and Thermal gravimetric analysis. The reusability study of M.AC as adsorbent revealed that it can be reused for several cycles for adsorption-desorption process before the performance of the process reduced below than out targeted.

CHAPTER ONE

INTRODUCTION

1.1 Adverse effects of antibiotics in water stream

Antibiotics may enter the water cycle from a variety of sources, including discharges from hospitals, domestic sewage and pharmaceutical industry. Many kinds of antibiotics are used in the farming of livestock and fish. These include antibiotics, hormone drugs, insecticides, nutrition promoters, antiseptics, and anaesthetics. Among these, antibiotics are usually employed to prevent a disease rather than to cure a disease (Choi et al., 2008). The antibiotic we used is Oxytetracycline hydrochloride (OTC-HCl), as a worldwide used pharmaceutical in human and vet medicine, is an important member of tetracycline which are reported to be toxic to the ecosystem (Ferreira et al., 2007). In the last few years, as more and more pharmaceuticals had been detected in the environment, the antibiotics in the environment emerged as a hot research topic. For example, residues of tetracycline antibiotics have been detected not only in effluents from discharges of pharmaceutical manufacturers, hospitals and municipal wastewater treatments but also from runoff and reservoirs that may be important resources for drinking and irrigation water around the world (Heberer, 2002; Batt et al., 2007; Mompelat et al., 2009; Radjenović et al., 2009). The occurrence of these chemicals is recognized as emerging pollutants in water sources and has been reported all over the world. Recently, the adverse effects of antibiotics in water on the ecosystem and on the human health have been recognized. This means that wastewater treatment plants should take special actions to treat the antibiotics wastewater. The removal of drugs such as pharmaceuticals, antibiotics etc. with adsorption is characterized as one of

the most promising techniques, due to its convenience once applied into current water treatment processes (Kyzas and Deliyanni, 2015). Among existing wastewater treatment technologies, adsorption is extensively used for handling a wide variety of wastewaters. Therefore, the researchers turn their interests on using adsorbents, which will be both effective and of low-cost, reducing drastically the synthesis cost (Kyzas and Deliyanni, 2015).

Nowadays, activated carbon (AC) is widely used in many fields such as in medical, textiles industries, fuel storage and others. Activated carbons have two forms which are granular activated carbon (GAC) and powdered activated carbons (PAC) are common adsorbents used for the removal of undesirable odor, color, taste, and other organic from domestic and industrial wastewater. However, it is ineffective for microbial contaminants, metals, nitrates and other inorganic contaminants. Recently, AC has a good potential to develop and produced because it is simplest such a method for adsorption process because the cost to produce are cheap and the material to produce it is readily available in a market. The raw materials that been use for producing AC are mainly from organic materials with have higher carbon contents. For instance, it is usually made up from coal, woods, coconut shells, peanut husk, egg shells and other organic materials. The carbon-based material is converted to AC by thermal decomposition in a furnace using a controlled atmosphere and heat. This process usually been done at higher temperature. Furthermore, chemical treatment should be done to enhance adsorption properties. As a result, it will give the AC surface with functional group. With the presence of functional group on their surface it would gave better adsorption properties of AC.

Basically, there are two steps to produce AC. First steps are physical activation and the second steps are chemical activation. In the first step the raw materials are

developed into activated carbon using either one or both steps process and for the first process is carbonization. Carbonization is the process of taking a carbon-rich piece of material and converting it to pure carbon through heating. The material with carbon content will undergo pyrolysis which is at the higher range of temperature 400-900 °C in absence of oxygen (Encyclopedia, 2016). It has usually been done at inert atmosphere with a supply of nitrogen gas another process is activation or oxidation. The carbonized material is exposed to oxidizing atmospheres (oxygen) at a temperature above than 250 °C. The second step is chemical activation. This process is mostly done after carbonization. The raw material is impregnated with certain chemicals. The chemical is usually from acid, strong base or salt. The raw material is carbonized at lower temperature. Chemical activation is preferred over physical activation owing to lower temperature and shorter time needed for activating materials (Encyclopedia, 2016).

The description of the adsorption phenomena requires some definitions. In an adsorption system, the solid carbon which adheres molecules on its internal surface area and thus adsorbs them is called an adsorbent. Molecules in the gas or vapor or the solute molecules in the solution which should be adsorbed by the activated carbon are called adsorptive. The concentration of the substance in the boundary between the substance and the solid surface than in the bulk of the substance. During the adsorption process, a layer (film) of the adsorbate molecules or atoms is created on the surface of the adsorbent. This process is a surface phenomenon, which is caused by surface energy (Shabanzadeh, 2012). The large internal surface area of carbon has several attractive forces that work to attract other molecules. These forces manifest in a similar manner as gravitational force therefore, contaminants in water are adsorbed to the surface of carbon from a solution as a result of differences in

adsorbate concentration in the solution and in the carbon pores (John, 2016). Physical adsorption occurs because all molecules exert attractive forces, especially molecules at the surface of a solid (pore walls of carbon), and these surface molecules seek to adhere to other molecules. The dissolved adsorbate migrates from the solution through the pore channels to reach the area where the strongest attractive forces are located. Contaminants adsorb because the attraction of the carbon surface for them is stronger than the attractive forces that keep them dissolved in solution. Those compounds that exhibit this preference to adsorb are able to do so when there is enough energy on the surface of the carbon to overcome the energy needed to adsorb the contaminant (John, 2016). Contaminants that are organic, have high molecular weights, and are neutral, or non-polar, in their chemical nature are readily adsorbed on activated carbon. For water adsorbate to become physically adsorbed onto activated carbon, they must both be dissolved in water so that they are smaller than the size of the carbon pore openings and can pass through the carbon pores and accumulate (John, 2016). Figure 1.1 below illustrated numerous pores in activated carbon.

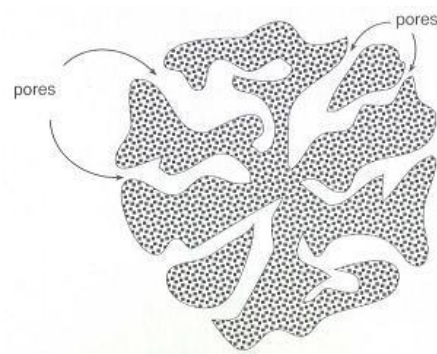


Figure 1.1: Typical carbon particle has numerous pores that provide a large surface area.

1.2 Problem statement

Nowadays water pollution scenario becomes worsen. Based on Figure 1.2 describes that from 2005 to 2013 the clear water shown decreasing trends. There are several factors that caused to this problem such as blooming of industry effluent textiles, pharmaceutical, paints and many more. These will cause harmful to the environment especially when we discharged into the river, sea pond and many more. Besides that, pharmaceutical is one of the major factor that contributing to this problem through discharging of antibiotics before a proper treatment.

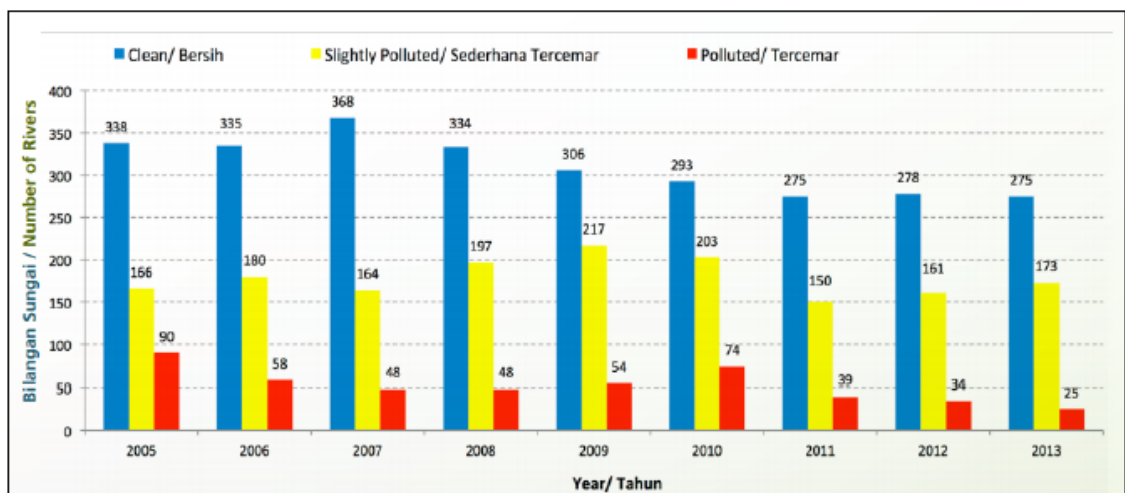


Figure 1.2: River water quality trend (2005-2013) (Huang, Ang et al. 2015)

To remove antibiotics which is refer to Oxytetracycline hydrochloride in the water we may applied adsorption technique. Due to adsorption is low cost and one of the effective technique compared to other such as ion exchange, coagulation etc. However, there is limited information about using this technique to adsorb Oxytetracycline hydrochloride and the kinetics data and the isotherm. Therefore, this work aims to evaluating the use and the performance of modified activated carbons to remove Oxytetracycline hydrochloride from the aqueous solutions. Hence, this

will reveal adsorption equilibriums and isotherms, thermodynamics, kinetic modelling and adsorption capacity studies of the batch adsorption system.

1.3 Research objectives

This research aims:

- i. To performed batch adsorption experiment on Oxytetracycline hydrochloride using modified activated carbon.
- ii. To evaluate the isotherms, thermodynamics and kinetics of antibiotic removal process.
- iii. To study the reusability of the respective modified activated carbon on targeted molecule.

1.4 Scope of work

The scopes of the research were presented in order to achieve the three outlined objectives above:

- i. Oxytetracycline hydrochloride was chosen as model antibiotics in this study. The isotherms and kinetics of antibiotic adsorption will be carried out using batch adsorption procedure.
- ii. Several adsorption parameters such as pH, initial concentration of antibiotic & temperature was studied. Isotherms data of antibiotics adsorption was analysed using the existing equilibrium models such as Langmuir and Freundlich. On the other hand, kinetics data will be analysed using pseudo-first order model and pseudo-second order model.
- iii. In this part, we studied the regeneration and the performance of adsorbent to adsorbed Oxytetracycline hydrochloride.

CHAPTER TWO

LITERATURE REVIEW

2.1 Oxytetracycline hydrochloride

In a 1945, Benjamin Duggar had discovered antibiotics namely as Tetracycline. It is come under broad-spectrum antibiotics. The physical properties are as follows, it is a yellow, highly soluble in water with half-life of 6 to 12 hours (Priya and Radha, 2014). Oxytetracycline hydrochloride (OTC-HCl), as a kind of tetracycline antibiotics, is widely used as antimicrobial additive because of its broad-spectrum antimicrobial activity. The purposed is used against several bacterial infections in human veterinary and use for agricultural. The Table 2.1 below shown the bioavailability of Oxytetracycline hydrochloride.

Table 2.1: Bioavailability of Oxytetracycline hydrochloride
(Priya and Radha, 2014)

%	Consuming
100	via intravenous route
50	via oral route
50-80	get excreted through feces and urine

For veterinary purposes, it depends on weight of the animal. For example, the more the body weight, the more drug were applied to animals. The widely use of antibiotics has led to spreading of antibiotic-resistance among bacterial populations and reducing the effectiveness of antibiotics itself. It can persist for a long period time in the environment if sunlight is not present. The consequences from this activity, it is disturbing our ecosystem functions. This is because antibiotics are partially eliminated in wastewater treatment plant. Thus, the reuse of wastewater may result in occurrence of antibiotics residue in soil, ground, surface water etc. Moreover, the biggest concern is the potential toxicity of these compounds to aquatic

organisms and humans through drinking water or the consumption of vegetables and crops irrigated by polluted water.

2.2 Adsorption

There are several techniques been studied by researcher to remove Oxytetracycline hydrochloride in wastewater. These technologies usually divided into two which are physical and chemical treatment. Table 2.2 and Table 2.3 is simplified for the advantages and disadvantages of antibiotics removal practiced in wastewater and the removal of Oxytetracycline hydrochloride using different treatment processes respectively.

Table 2.2: Advantages and disadvantages of antibiotics removal method (Daghrir and Drogui, 2013)

Method	Advantages	Disadvantages
Physical Treatment		
Adsorption	Simple, effective and not produce any further metabolites.	Cost and the difficulties of regenerations.
Membrane filtration	Good permeate qualities	Presence of higher levels of these compounds in water could cause fouling to the membrane.
Chemical Treatment		
Photolysis using UV- radiation	Simple, clean and less expensive	The maintenance and the electrical energy costs are also some limiting factors.
Ozonation	Strong oxidant it capable to act direct or indirectly with pollutants	Mass transfer limitations.
Electrochemical oxidation	Clean & flexible,	Higher energy consumptions

Table 2.3: Removal of Oxytetracycline hydrochloride antibiotics using different treatment processes (Daghrir and Drogui, 2013)

Type of treatments	Operating conditions	Results and comments
Reverse osmosis	NTR-7450 membrane; NTR-7459 membrane Area = 155 cm ² , T = 21–23°C, Pressure = 1.8 MPa	Reduced from 1,000 mg/L to 80 mg/L (87.5 % removal)
Ultrafiltration	Stirred cell; 3, 10, 30,50 kDa cut-off membranes Operational pressure = 0.30 MPa	Recovery ratio was higher than 60 %, the purity higher than 80 %
Gamma radiation	Temperature = 25 C ± 1.0°C, Temperature = 25 C ± 1.0°C, pH = 2–10, radiation dose = 1.66–3.83 Gy/min	Toxicity inhibition: surface water 47.2 % Oxytetracycline Ground water: 44.4 % of Oxytetracycline
Adsorption with activated carbon	Contact time 5 min, 10l g/L For adsorption process, granular activated carbon carbon filtration: Calgon F400 and coconut-based carbon	Synthetic water: 43–94 % removal of the drug River water: 44–67 % removal of the drugs
Oxidation/reduction	pH = 7.0 ± 0.1, 5 mM phosphate buffer, T = 22.0 ± 1.0°C, X _e arc lamp (172 nm) [TOC] = 13l g/L, electron pulse radiolysis (472 nm, G = 5.2 9 10 ⁻⁴ m ² /J	The efficiencies for OH reaction = 32–60 % The efficiencies for e ⁻ reaction = 15–29 %,

Adsorption is the process of capturing molecules of dissolved solids, liquids or gases on the surface of certain active solids. In other word adsorption is based on a theory that a solid surface in contact with a solution tends to accumulate a surface layer of solute molecules caused by imbalance of surface forces. From a Table 2.4 below adsorption can be classified into two, physisorption and chemisorption based on the nature of forces involved.

Table 2.4: Nature of forces

Adsorption	Nature of forces
Physisorption	London, van der Waals and electrostatic forces
Chemisorption	Covalent bonding, ionic bonding

In a liquid phases, molecules, ions or atoms in a liquid is diffused to the surface of a solid, where they bond with the solid surface through physical attractive forces, ion exchange, and chemical binding.

2.3 Activated carbon

Activated carbon have been widely used to remove organic contaminants from water and wastewater in industrial scale applications and more recently in removing pharmaceuticals from sewage effluent. It is a form of carbon that has been treated by thermal decomposition in a furnace under controlled of heat. This method helps to produce a highly porous carbon with large surface area per unit volume up to $>500 \text{ m}^2 \text{ g}^{-1}$ (Yin et al., 2007). High degree of micro porosity, well developed surface area, and high adsorption capacity are the key features for both granular and powdered that make them suitable as adsorbent for the removal of organic contaminants. A 90% removal efficiency of Oxytetracycline hydrochloride was obtained by using activated carbon from powder activated carbon. Basically, the pore

structure of activated carbon is classified into three major groups as shown in table by International Union of Pure and Applied Chemistry (IUPAC)

Table 2.5: Pore structure of activated carbon

Structure	Range of Size
Micropore	< 2 nm
Mesopore	2-50 nm
Macropore	>50 nm

These will provide large surface area for adsorbate to be attached at surface of adsorbent. Physically, activated carbon binds with the adsorbate by Van der Waals force. Adsorption on activated carbon can occur mainly due to the difference in adsorbate concentration in the solution. Moreover, modification and impregnation were used to increase the surface adsorption capacities and the removal rates. It is, therefore, crucial to understand the several factors that influence the adsorption capacity of activated carbon prior to their modification so that it can be matched to their specific physical and chemical characteristics to enhance their affinities toward metal, inorganic or organic species present in wastewater. These factors include specific surface area, pore-size distribution, pore volume and presence of surface functional groups. Referring to the antibiotics we used is Oxytetracycline hydrochloride as adsorbate which is amphoteric molecules. It may exist as a cation, a zwitterion or a negatively charged ion. Thus, we can impregnate the activated carbon with base or acid due to activated carbon surface can display acidic, basic or neutral characteristics depending on the presence of surface functional groups. Table 2.6 shown advantages and disadvantages of modification techniques.

Table 2.6: Advantages and disadvantages of modification (Yin et al., 2007)

Modification	Treatment	Advantages	Disadvantages
Chemical characteristics	Acidic	Increases acidic functional groups on AC surface. Enhances chelation ability with metal species	May decrease BET surface area and pore volume
	Basic	Enhances uptake of organics	May in some cases decrease the uptake of metal ions

2.4 Desorption

Recovery of saturated adsorbent is one of the most important steps in the adsorptive removal of contaminant, as the feasibility of an industrial adsorption process largely depends on the cost of regeneration of spent adsorbents which can be reused subsequently. The adsorbent is mostly produced from agricultural such as biomass, for industrial for example timber and municipal such as sewage or solid waste. Each of preparation process has different reagents and equipment cost. This lead to the process of regeneration of activated carbon in industrial to avoid spent cost on buying adsorbents. Table 2.7 shown the comparison of cost and the limitations type of adsorbents used treated antibiotics in wastewater. After being saturated with contaminants, the regeneration of adsorptive precursors is dependent on the type of adsorbents. Once desorbed, the antibiotic-loaded solvents should be disposed carefully (Ahmed et al., 2015). Due to, eliminate pollution as well as utilizing the energy content of solvents, as otherwise antibiotics will be transferred from water to another phase.

Table 2.7: Comparison of cost and limitations type of adsorbents used in wastewater (Ahmed et al., 2015)

Type of adsorbents	Limitations	Operating cost
Carbon nanotubes, CNT	Not be widely applicable due to their high material cost and in most cases their adsorption is not reversible	High/expensive
Bio char, BC	-	Low (waste material)
Activated carbon, AC	Adsorption of antibiotics is significantly influenced of the physical morphology and functionality	High

In order to, perform desorption process, there are several chemicals was used to make desorption solution. For example, in dyes removal study have proven that the ethanol is the best solution for desorbed dyes compared with acid or base but for antibiotics was referred to Oxytetracycline hydrochloride is vice versa at which base or acid are used for desorption process. According to Özkaya (2006), it was found that when HCl at 0.1 M was used only 2.5% was desorbed compared to NaOH at 0.1 was used, it about 72% was desorbed. Besides that, NaOH can be replaced by other base family. KCl was studied as desorption solution in removal of dyes. Thus, it was observed about 46% is desorbed for dyes (Khattari and Singh, 2009). For this experiment, we try it as a desorption solution to see the percent of adsorbed with respect to antibiotics. If the adsorbed antibiotics on the solid surface can be desorbed by water, then the attachment of the antibiotics on the adsorbent is by weak bonds. If sulphuric acid of 1 M or alkaline water can desorb the antibiotics, then the adsorption is by ion exchange. If organic acids, for example acetic acid, can desorb the antibiotics, then the antibiotics is held by the adsorbent through chemisorption (Namasivayam et al., 1996).

2.5 Adsorption isotherms

2.5.1 Langmuir isotherm

Langmuir model applies to homogeneous adsorption, which each molecule possesses constant enthalpies and sorption activation energy and postulates no transmigration of the adsorbate in the plane of the adsorbent surface. Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface (Tan et al., 2009).

The non-linear expression of the Langmuir model is presented by the following Equation 2.1:

$$q_e = \frac{Q_m k_l c_e}{1 + k_l c_e} \quad (2.1)$$

q_e = amount of adsorbate adsorbed at equilibrium (mg g^{-1})

Q_m = monolayer adsorption capacity (mg g^{-1})

c_e = equilibrium concentration of adsorbate (mg L^{-1})

k_l = Langmuir adsorption constant related to the free energy adsorption (L mg^{-1})

After linearizing Equation 2.1 it given following Equation 2.2:

$$\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{k_l Q_m c_E} \quad (2.2)$$

In the case of the Langmuir model, equivalence of adsorption sites and monolayer of adsorbate coverage is predicted. The amount of solute adsorbed, in mg g^{-1} , is equilibrium concentration in solution in mg L^{-1} , is Langmuir constants. A plot of $\frac{1}{q_e}$ against $\frac{1}{c_E}$ from the linear of Equation 2.2 can be used determined the values of $\frac{1}{Q_m}$

which is intercept and $\frac{1}{Q_m K_l}$ is slope

2.5.2 Freundlich isotherm

Freundlich has a practical application in describing the non-ideal and reversible adsorption of heterogeneous system. Freundlich model is an empirical equation based on sorption on a heterogeneous surfaces or surfaces supporting sites of varied affinities. It is assumed that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation (Tan et al., 2009). This empirical model can be applied to multilayer adsorption, with non-uniform distribution energy on the adsorbent surface.

The empirical equation of Freundlich is presented by the following Equation 2.3:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (2.3)$$

q_e = amount of adsorbate adsorbed at equilibrium (mg g^{-1})

c_e = equilibrium concentration of adsorbate (mg L^{-1})

K_F = Freundlich constant (L mg^{-1})

$\frac{1}{n}$ = heterogeneity factor

After linearizing Equation 2.3, it given the following Equation 2.4

$$\log q_e = \frac{1}{n} \log c + \log K_F \quad (2.4)$$

In Freundlich model q_e is amount of adsorbate adsorbed at equilibrium (mg g^{-1}), C_e is equilibrium concentration of the adsorbate (mg L^{-1}). As for Freundlich, a plot of $\log q_e$ against $\log C_e$ enables the determination of constant K_F which is intercept and exponent $1/n$ is a slope (Din et al., 2009).

2.6 Kinetics data

2.6.1 Pseudo-first order model

The pseudo-first-order kinetic model has been widely used to predict sorption kinetics. The model given by Langergren and Svenska by following Equation 2.5

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2.5)$$

where q_e and q_t (mg g^{-1}) are the amounts of adsorbate adsorbed at equilibrium and at any time, t (h), respectively and k_1 ($1/\text{h}$) is the adsorption rate constant. The plot of $\ln(q_e - q_t)$ versus t gave the slope of k_1 and intercept of $\ln q_e$ (Tan et al., 2009). The value of k_1 at 30°C

2.6.2 Pseudo-second order model

According to Zawani (2009) suggested that the second-order kinetic model is expressed by following Equation 2.6:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (2.6)$$

Where, k_2 is the pseudo-second-order rate constant of adsorption ($\text{g mg}^{-1}\text{min}^{-1}$). The linearized integrated form for Equation 2.6 represented by Equation 2.7

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

By plotting $\frac{t}{q_t}$ against t . Equation 2.7 will give a linear relationship with $\frac{1}{q_e}$ as a slope and $\frac{1}{k_2 q_e^2}$ as intercept. The pseudo second-order kinetics model has been successfully applied to several biosorption systems (Zawani Z, 2009).

2.7 Thermodynamics data

The thermodynamic parameters that must be considered to determine the adsorption processes were changes in standard enthalpy (ΔH°), standard entropy (ΔS°), standard free energy (ΔG°) due to transfer of unit mole of solute from solution onto the solid–liquid interface, as well activation energy of adsorption (E_a) (Tan et al., 2009). The thermodynamic sorption onto modified activated carbon were evaluated using the following Equation 2.8

$$\ln K_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (2.8)$$

where R ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) is the universal gas constant, T (K) is the absolute solution temperature and K_L (L mg^{-1}) is the Langmuir isotherm constant. ΔG° can then be calculated using the relation presented by Equation 2.9 and Equation 2.10 below

$$\Delta G^\circ = -RT \ln K_L \quad (2.9)$$

$$\Delta G^\circ = \Delta H - T \cdot \Delta S \quad (2.10)$$

Arrhenius equation has been applied to evaluate the activation energy of adsorption representing the minimum energy that reactants must have for the reaction to proceed, as shown by the following relationship represented by Equation 2.11

(Tan et al., 2009):

$$\ln K_2 = \ln A - \frac{E_A}{RT} \quad (2.11)$$

where K_2 ($\text{g mg}^{-1} \text{ h}^{-1}$) is the rate constant obtained from the pseudo second-order kinetic model, E_A (kJ mol^{-1}) is the Arrhenius activation energy of adsorption and A is the Arrhenius factor. When $\ln K_2$ is plotted against $1/T$, a straight line with slope of $-E_A/R$ is obtained.

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction

This chapter elaborate on materials, methods and overall procedure for the whole experiment work conducted in this research study. It is consisted of the materials, chemical and equipment's used to conduct the experiment. Firstly by, preparation of the adsorbent (Oxytetracycline hydrochloride) and preparation of modified activated carbon through impregnation method. Then performed the batch adsorption experiment, study of adsorption isotherm such as Langmuir and Freundlich, thermodynamics, point of zero charged and analysed kinetics data using pseudo-first order model and pseudo-second order model. Lastly, study desorption process and reusability. This research generally conducted in the following step as shown in Figure 3.1 below in order to achieve the research objectives.

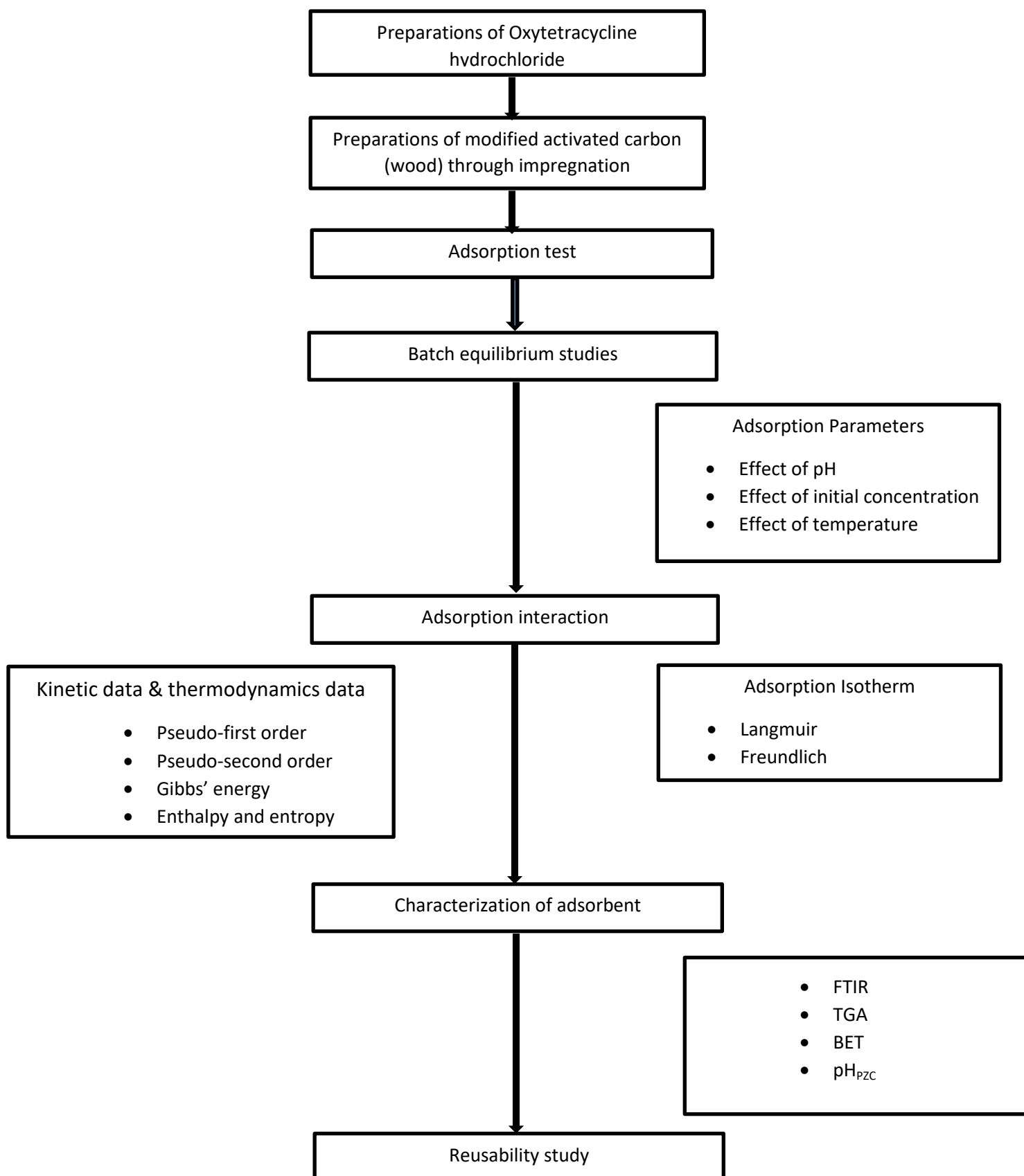
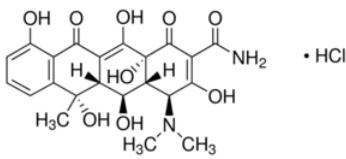


Figure 3.1: Research activities flow chart

3.2 Materials and chemicals

In this study, activated carbon (wood) used as precursor before it used to impregnate with Copper nitrate, $\text{Cu}(\text{NO}_3)_2$. The raw material was obtained from a local supplier. Oxytetracycline hydrochloride (OTC-HCl) used as adsorbate. It was supplied by Calbiochem Sdn. Bhd, Malaysia. OTC-HCl properties was summarized in Tables 3.1.

Table 3.1: Properties of OTC-HCl

Properties	
Common name	Oxytetracycline Hydrochloride (OTC-HCl), Terramycin
IUPAC name	4-(Dimethylamino)-1,4,4a,5,5a,6,11,12a-octahydro-3,5,6,10,12,12a-hexhydroxy-6-methyl-1,11-dioxo-2-naphhtacenecarboxamide hydrochloride.
Molecular formula	$\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_9 \cdot \text{HCl}$
Molecular weight	496.90 g/mol
CAS number	2056-46-0
Maximum wavelength, λ_{max}	234.7 nm
Chemical structure	

The chemical and materials used were listed in Tabel 3.1 and Table 3.2 including their supplier, characteristic and purpose in the experiment and the equipment need to run the experiment smoothly in Table 3.3. All the chemicals used were of analytical grade and were used without further purification.

Table 3.2: List of chemical and materials

Chemical/Material	Chemical Formula	Usage
Oxytetracycline hydrochloride	$C_{22}H_{24}N_2O_9.HCl$	Adsorbate
Activated Carbon (wood)	-	Adsorbent
Sodium hydroxide	NaOH	pH Adjustment
Hydrochloric acid	HCl	pH Adjustment
Copper nitrate	$Cu(NO_3)_2$	Impregnator
Sodium chloride	NaCl	pHpzc Test

3.3 Equipment and instrumentations

Table 3.3: List of equipment used in this experiment

Equipment	Model	Usage
Brunauer-Emmett-Teller (BET)	Autosorb I	Analysis technique for the measurement of the specific surface area of a material.
Fourier Transform Infrared (FTIR)	Shimadzu IR Prestige-21	To identify the presence of certain functional groups in a molecule
Shaker	Water bath shaker Menmert	To provide better distribution of mixture.
Portable pH Meter	Eutech Instrument	To check and adjust pH of solution.
Analytical Balance	HR-250AZ	To weight the sample.
Oven	Menmert universal oven	To dry sample.
UV-Spectrophotometer	Shimadzu UV-1800	To check concentration of the adsorbate.
Filter paper	Qualitative filter paper (12.5 cm)	To filter the sample.

3.4 Method of experiment

3.4.1 Preparation of adsorbate

The stock solution was prepared by diluting 0.1 g Oxytetracycline Hydrochloride (OTC-HCl) powder with 1000 ml distilled water in an appropriate volumetric flask. The stock solution then was diluted to the desired initial concentrations ($5-25 \text{ mg L}^{-1}$). 0.1 mg adsorbent was added into conical flasks filled with 100 mL of Oxytetracycline Hydrochloride (OTC-HCl) solutions. The beaker

were then covered with aluminium foils and placed inside the water bath shaker at 30 °C, 40 °C and 50 °C with shaking speed of 50 rpm (Din et al., 2013).

3.4.2 Calibration curve

From the stock solution, the Oxytetracycline hydrochloride will be diluted into concentration of 5, 10, 15, 20, and 25 mg L⁻¹. For every sample, it must be tested using UV-spectrophotometer to measure the absorbance value. The absorbance value is measured repeated for 3 times and average value is taken for plotting the curve. Figure A1 shown a graph of absorbance against Oxytetracycline hydrochloride concentration is plotted.

3.4.3 Preparation of adsorbent

3.4.3(a) Screening different type of chemical for impregnation

Wood-based activated carbon was used as supports in this study. The supports (5 g ± 0.01 g) and (1 g ± 0.01 g) was impregnated with acid H₂SO₄, HCl, HNO₃ and base Cu(NO₃)₂ and KOH respectively. For the impregnation, it approximately 50 mL of impregnating solution was added into 5 g and 1 g of activated carbon respectively. Then the sample was placed in bath shaker and shaken for 24 h at 30 °C. After that, the sample was filtrated and the adsorbent was dried at room temperature.

3.4.3(b) Screening different weight percent, wt% for impregnation

Wood-based activated carbon was used as supports in this study. The supports (1 g ± 0.01 g) was impregnated with base Cu(NO₃)₂ at varies of Wt% from 1, 3, 5, 7, and 9 %. For the impregnation, it approximately 50 mL of impregnating solution was added into 1 g of activated carbon, and the sample was placed in bath

shaker and shaken for 24 h at 30°C. After that, the sample was filtrated and the adsorbent was dried at room temperature.

3.4.3(c) Preparation of the of the adsorbent at optimum condition

Wood-based activated carbon was used as supports in this study. The supports (8 g ± 0.01 g) was impregnated with 1% Cu(NO₃)₂. For the impregnation, it approximately 50 mL of impregnating solution was added into 8 g of activated carbon. Then the sample was placed in bath shaker and shaken for 24 h at 30°C. After that, the sample was filtrated and the adsorbent was dried at room temperature.

3.5 Adsorption test

The adsorption test was conducted with 3 different parameters which are pH, concentration, and temperature of the OTC-HCl solution. The adsorption of OTC-HCl was performed by shaking the adsorbent and OTC-HCl solution using Menmert water bath shaker for 24-hours. For every 30 minutes, the solution was taken into the UV-Spectrometer equipment to be analyze it. Then the adsorbent will be tested until it reaches it limitation of adsorption process.

3.6 Batch equilibrium studies

For the adsorption test, we add a fix amount of modified activated carbon 0.1 g to a series of 100 ml beaker with 100 ml of diluted solution from 5 - 25 mg L⁻¹ of OTC-HCl. The beaker was covered by using aluminium foil and placed it into water bath shaker and shaken it for 24 hours at rate 50 rpm at various temperature which are 30, 40 and 50 °C. After that, the sample were taken for each 5, 30 and 60 minutes and using shimadzu UV-visible 1601 spectrophotometer at wavelength of OTC-HCl which is 234.7 nm to measure the concentration of adsorbate. Each

experiment was duplicated under identical conditions. The amount of adsorption at equilibrium, q_e (mg g^{-1}), was calculated by following Equation 3.1:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (3.1)$$

where C_0 and C_e (mg L^{-1}) are the liquid-phase concentrations of OTC-HCl at initial and equilibrium, respectively. V is the volume of the solution (L), and W is the mass of dry adsorbent used (g). Then, OTC removal is calculated by using the following equation 3.2

$$\text{Removal percentage} = \frac{c_0 - c_e}{c_0} \times 100\% \quad (3.2)$$

where c_0 and c_e (mg L^{-1}) are the initial and the equilibrium OTC-HCl concentration respectively.

3.6.1 Effect of pH solution

The effect of the pH solution was investigated at pH 2, 3, 4, 5, 6 and 7. The pH of the solution can be adjusted by using 0.1M and 1M hydrochloric acid, HCl to decrease the pH value or 0.1M and 1M NaOH for increase the pH value of the solution. This pH value was measured by Eutech instruments portable pH. It about 0.1 g of modified activated carbon was added into 100 ml of OTC-HCl which has different pH. This experiment was conducted at constant temperature which is 30 °C, at same concentration 25 mg L^{-1} and the same rotation speed of shaker 50 rpm.

3.6.2 Effect of the initial concentration

To study the effect of the initial concentration on the adsorption, 0.1 g of modified activated carbon was added into 100 ml volume of OTC-HCl solution. It will be test with different initial concentration which are 5, 10, 15, 20 and 25 mg L^{-1} and the experiment are being carried out at temperature 30,40 and 50 °C. The pH