

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

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ACTIVATED CARBON**

by

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LIST OF SYMBOLS

	Symbol	Unit
<i>A</i>	Arrhenius factor	-
<i>C</i>	Boundary layer	-
<i>C_e</i>	Equilibrium concentration of adsorbate	mg/L
<i>C_o</i>	Highest initial adsorbate concentration	mg/L
<i>C_t</i>	Adsorbate concentration at time, t	mg/L
<i>E</i>	Mean free energy	J/mol
<i>E_a</i>	Arrhenius activation energy of adsorption	kJ/mol
<i>k₁</i>	Adsorption rate constant for the pseudo-first-order kinetic	1/hr
<i>k₂</i>	Adsorption rate constant for the pseudo-second-order	g/mg.hr
<i>K_F</i>	Freundlich isotherm constant	mg/g (L/mg) ^{1/n}
<i>K_L</i>	Langmuir adsorption constant	L/mg
<i>W</i>	Mass of adsorbent	g
<i>n_f</i>	Constant for Freundlich isotherm	-
<i>q_e</i>	Amount of adsorbate adsorbed at equilibrium	mg/g
<i>q_m</i>	Adsorption capacity of Langmuir isotherm	mg/g
<i>q_t</i>	Amount of adsorbate adsorbed at time, t	mg/g
<i>R</i>	Universal gas constant	8.314 J/mol K
<i>R²</i>	Correlation coefficient	-
<i>R_L</i>	Separation factor	-
<i>T</i>	Time	Min
<i>T</i>	Absolute temperature	K
<i>V</i>	Solution volume	L
ΔG^\square	Changes in standard Gibbs free energy	kJ/mol
ΔH^\square	Changes in standard enthalpy	kJ/mol
ΔS^\square	Changes in standard entropy	kJ/mol
λ	Wavelength	Nm

LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
FTIR	Fourier Transform Infrared
HCL	Hydrochloric Acid
IUPAC	International Union of Pure and Applied Chemistry
KCl	Potassium Chloride
NaOH	Sodium Hydroxide
OTC HCl	Oxytetracycline Hydrochloride
ppm	Parts Per Million
rpm	Rotation Per Minute
TGA	Thermogravimetric
UV	Ultraviolet
WPAC	Wood-based Powdered Activated Carbon

PENJERAPAN DAN NYAHPENJERAPAN OXYTETRACYCLINE HYDROCHLORIDE OLEH KARBON TERAKTIF

ABSTRAK

Penjerapan dan nyahpenjerapan Oxytetracycline Hydrochloride (OTC HCl) atas karbon teraktif telah dikaji dalam eksperimen keseimbangan kelompok. Pelbagai parameter eksperimen dikaji termasuk permulaan kepekatan OTC HCl (5-25 ppm), Ph bagi larutan (3-7) dan suhu (30-50°C). Data data eksperimen dianalisa menggunakan model-model garis lengkung sesuhu Langmuir dan Freundlich. Kebaikan bersesuaian telah diperiksa menggunakan pekali regresi lurus (R^2). Ia adalah didapati model lengkung sesuhu Langmuir sangat sesuai untuk keseluruhan sistem yang telah dikaji. Model kinetik pseudo tertib pertama dan pseudo tertib kedua digunakan untuk menganalisa data kinetik. Walaubagaimanapun, model kinetik pseudo kedua sangat sesuai untuk keseluruhan system yang dikaji. Pelbagai parameter termodinamik seperti tenaga bebas Gibbs (ΔG), perubahan entalpi (ΔH), dan perubahan entropi (ΔS) dikira, di mana ianya menunjukkan system tersebut adalah tidak spontan dan merupakan proses serap haba untuk OTC HCl. Berdasarkan nilai tenaga pengaktifan, ia juga didapati mekanisma penjerapan bukan hanya terhad untuk penjerapan fizikal tetapi juga penjerapan kimia untuk beberapa suhu yang berbeza. Penjerapan OTC HCl pada karbon teraktif ini boleh dikekalkan melebihi 80% di seluruh 5 kitaran penjerapan-nyahpenjerapan dan kalium klorida telah digunakan sebagai medium nyahpenjerapan. Karbon teraktif ini telah dicirikan dengan menggunakan FTIR, TGA, dan penganalisa kawasan permukaan. Selain daripada itu, pH_{pzc} bagi karbon teraktif ini juga telah dikenal pasti dalam eksperimen ini

ADSORPTION AND DESORPTION OF OXYTETRACYCLINE HYDROCHLORIDE ON ACTIVATED CARBON

ABSTRACT

The adsorption and desorption of Oxytetracycline hydrochloride (OTC HCl) onto wood-based powdered activated carbon was studied in batch equilibrium experiments. Various experimental parameters were studied including initial OTC HCl concentration (5-25 ppm), pH of the solution (3-7) and temperature of the solution (30-50°C). The experimental data were analysed using Langmuir and Freundlich isotherm model and the goodness of fits were checked by using linear regression coefficients (R^2). It was found that, Langmuir isotherm model best represented the equilibrium data. Pseudo-first-order and pseudo-second-order kinetic model were used to analyse the kinetic data. It was found that the best fitting corresponded to the pseudo-second-order kinetic model. Various thermodynamics parameters, such as Gibbs energy, enthalpy change and entropy change, were calculated, which indicated that the present system was unspontaneous and endothermic process for OTC HCl. Based on the value of activation energy, it is also found that the adsorption mechanism was not only limited to physical adsorption but also chemisorption too for several different temperatures. The adsorption of OTC HCl on this activated carbon can be maintained above 80% across the 5 adsorption-desorption cycles and potassium chloride had been used as a desorption medium. The activated carbon was characterized by using FTIR, TGA, and surface area analyser. Other than that, the pH_{pzc} of the activated carbon also had been identified in this experiment.

CHAPTER ONE

INTRODUCTION

1.1 Pharmaceutical industry and the antibiotic molecule effluents

Many kinds of pharmaceuticals 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) and antibiotics were more frequently detected than others. They are difficult to remove through common biological treatment methods (Awartani and Jodeh, 2011). Most of the pharmaceuticals entry route to the environment is from the domestic sewage. But, we also must consider the effluents of pharmaceutical and chemical-pharmaceutical industries, rural effluents, and the presence of drugs in animal manure used for soil fertilization and improper disposal of expired products or unwanted drugs (Focazio et al., 2007).

Only a fraction of medication is completely absorbed by the body, and the excess is excreted as unchanged compounds or processed metabolites. With septic systems, pharmaceutical compounds leach directly into ground water (Yamamoto et al., 2009). Because of this, variety of antibiotics were detected in various water samples including hospital wastewater, municipal wastewater, effluent of wastewater treatment plants, antibiotics industry wastewater, livestock farm mud and wastewater, surface water, underground water, and drinking water. Once residual antibiotics enter the environment, the fate of these antibiotics depends on the nature and physical and chemical properties of the antibiotics (Rama Pulicharla, 2014). Biodegradable antibiotics get ultimately mineralized to carbon dioxide and water or metabolizes to

a more hydrophilic molecule that passes through the wastewater treatment plant and ends up in the water reservoir. However, nonbiodegradable antibiotics do not degrade readily and are partially retained in the sedimentation sludge. (Martinez, 2009)

The persistence of residual pharmaceuticals in the environment constitutes a serious environmental problem because they may impose serious toxic effects on humans and other living organisms. It has been found that several bacteria, including pathogenic, display antibiotic resistance. This resistance partially might be due to the residues of antibiotics in the environment. Bacteria have become resistant to antimicrobial agents because of chromosomal changes or the exchange of genetic material via plasmids and transposons (Neu, 1992). This study chooses Oxytetracycline Hydrochloride (OTC HCl) as an example of antibiotics that are released into the environment since the average consumption in both human and veterinary sectors reached 4.5 tons of OTC HCl in the last two years (Awartani and Jodeh, 2011). In this research, complementary studies of OTC HCl adsorption have been reported with emphasis on adsorption mechanism, equilibrium, and kinetics.

1.2 Problem Statement

The major removal pathways of antibiotics in wastewater treatment processes include adsorption, biodegradation, disinfection as well as membrane separation. Other removal pathways, such as hydrolysis, photolysis and volatilization may be ruled out due to their minor role for antibiotics reduction in wastewater treatment processes (Tong Zhang, 2011). Biological treatments are not able to deplete completely all the pharmaceuticals present in wastewaters. Current wastewater treatment processes always involve biological technologies, the activated sludge system is the most common one (de Cazes et al., 2014).

It is based on aeration and agitation of wastewater, which contains a very large spectra biomass population. Some bacteria can assimilate and transform pharmaceutical micropollutants, if the conditions are favourable for biomass growth. In fact, pharmaceutical micropollutants are highly biologically active molecules, and they could have a negative impact on the metabolism of microorganisms. (de Cazes et al., 2014). Chemical treatment like disinfection method, ozone, iodine, or chlorine will be used to remove and deactivate the antibiotics, but then, the high cost of initial start-up and the electricity consumption always become the challenge to apply this method in wastewater treatment.

Physical treatment such as ion exchange, reverse osmosis, precipitation, coagulation, and adsorption techniques. Most of these processes are costly and lead to generation of sludge or formation of by-products. However, among the physical methods, adsorption process is known to be the most efficient methods especially if the adsorbent is inexpensive. Activated carbon adsorbent is one of the best candidates as it did not require any additional pre-treatment before its application. However, its expensive price in market due to the price of coal as precursor has limited its commercial application. For this reason, the activated carbon synthesized from wood was used as an adsorbent.

1.3 Research Objective

The main objectives of this study are:

- i. To perform batch adsorption experiment on Oxytetracycline hydrochloride using activated carbon.
- ii. To evaluate the isotherm., thermodynamics, and kinetics of antibiotic removal process.

- iii. To study the desorption and the reversibility of the respective activated carbon on targeted molecule.

1.4 Scope of study

The scope of study of this study includes the characterization, study of adsorption process parameters and regeneration of the adsorbents of the OTC HCl adsorption. Commercially available Wood-based Powdered Activated Carbon (WPAC) was selected to be used in this study due to its good performance in adsorption and its stable properties. The WPAC was characterized in terms of surface area, surface morphology, proximate content, elemental content, and surface chemistry by using surface area analyzer, TGA analyzer and FTIR, respectively.

The equilibrium, kinetic, thermodynamic, and the reusability were studied to obtain the best condition for OTC HCl adsorption. Finally, the results will help to realize the OTC HCl adsorption performance of the adsorbents and determine the optimum condition for OTC HCl. To carry out the analysis, batch adsorption study was done by examined the effect of adsorbate initial concentration (5-25 ppm), pH of the solution (3-7), solution temperature (30-50°C) for adsorption of OTC HCl onto the WPAC.

CHAPTER TWO

LITERATURE REVIEW

2.1 Antibiotics

Antibiotic use plays a major role in the emerging public health crisis of antibiotic resistance. Although most antibiotic use occurs in agricultural settings, relatively little attention or concern has been paid to how antibiotic use in farm animals and eventually contributes to the overall problem of antibiotic resistance (Landers et al., 2012). This study chooses group of an antibiotics known as Tetracycline, Oxytetracycline or Oxytetracycline Hydrochloride (OTC HCl) is one of this group. Tetracyclines are the third most consumed antibiotic, after penicillin and quinolones, and due to this, it has been detected an increasing number of bacteria resilient to tetracyclines. (Borghi and Palma, 2014)

Tetracyclines constitute a large group of broad spectrum antibiotics obtained by fermentation of a specific bacteria and produce tetracycline, chlortetracycline and oxytetracycline (Borghi and Palma, 2014). Oxytetracycline is present as either the amphoteric base compound, the hydrochloride salt or as a quaternary ammonium salt complex. Oxytetracycline in the form of hydrochloride salt or Oxytetracycline Hydrochloride is the common form in parenteral and water soluble animal health product. It is yellow crystalline compound that is odourless and slightly bitter in taste. It is very soluble in water with 1 g/ml maximum solubility and organic solvent. (Meeting et al., 1997)

Tetracycline is an antibiotic that is widely used as a prophylactic and therapeutic treatment in livestock animals, and it is also used as a growth promoter due to its broad antibacterial spectrum and low cost (Cheng et al., 2014). It has a

strong inhibitory effect on most microorganisms in the biological wastewater treatment process, and it is added in fodder for quick growth and disease resistance.

Animals metabolize only small part of tetracycline, as most tetracycline is discharged as waste; thus, discharged tetracycline is contained in wastewater. The environmental influence of tetracycline has aroused a great deal of concern (Cheng et al., 2014). For this reason, the environmental behaviour of tetracycline has been investigated in different environments such as sewage treatment plants (Miao et al., 2004), soils (Hamscher et al., 2002), and marine sediments (Smith and Samuelsen, 1996). Figure 1 shows the path of tetracycline to the environment, after consumed by the human and animal. The final route shows that both animal and human will be affected and suffered from this antibiotic.

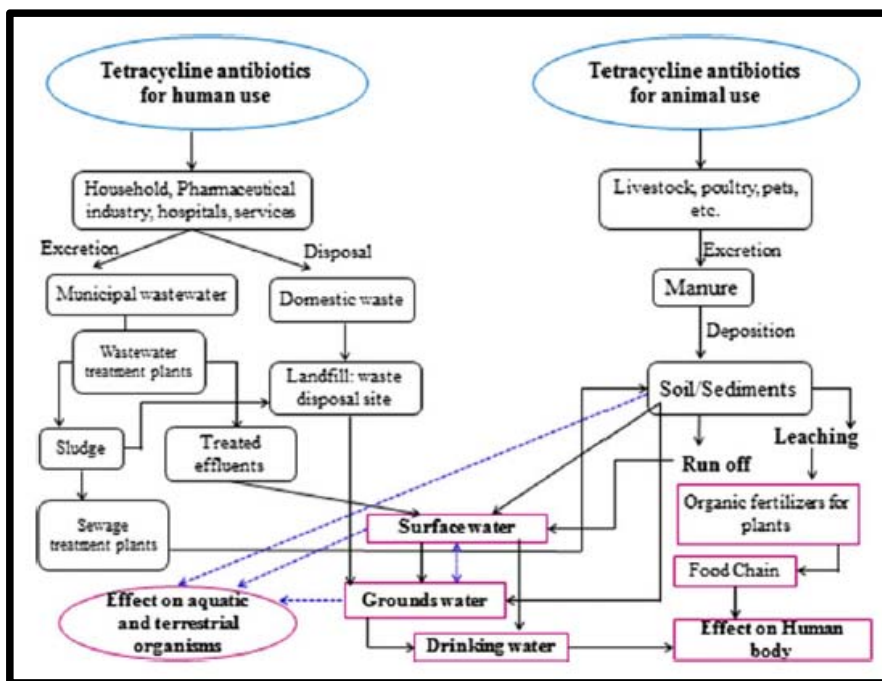


Figure 2.1: Possible sources and pathways for the occurrence of tetracycline antibiotics in the environment (Daghrir and Drogui, 2013)

2.2 Adsorption

In the previous couple of decades, many strategies have been developed to find an economic and efficient way to treat the antibiotics polluted effluent. These technologies usually composed of physical, chemical, and biological treatment. Table 2.1 shows the various technique to treat or degrade the oxytetracycline.

Adsorption happens when there is a natural tendency for components of liquid or a gas to collect often as a monolayer but sometimes as a multilayer at the surface of a solid material (Humphrey and Keller, 1997). In an adsorption process, molecules, atoms, or ions in a gas or liquid diffuse to the surface of a solid and form bonds with the solid surface or are held there by weak intermolecular forces. Adsorbate are the components being adsorbed and the solid material is the adsorbent (Seader and Henley, 1998).

Adsorption may be grouped as physical adsorption or chemical adsorption depending upon the types of forces between the fluid molecules and the molecules of the solid (Seader and Henley, 1998). Physical adsorption or known as van der Waals adsorption, a readily reversible phenomenon, is a result of intermolecular forces of attraction between molecules of the solid and the substance adsorbed. Chemisorption, or activated adsorption, is the result of chemical interaction between the solid and the adsorbed substance. The strength of the chemical bond may vary considerably, and identifiable chemical compounds in the usual sense may not actually form, but the adhesive force is generally much greater than that found in physical adsorption (Treybal, 1980).

Table 2.1: Various method to treat Oxytetracycline from other researchers

Methods	Result and Comment
Ultrafiltration and Reverse Osmosis	The oxytetracycline recovery ratio was higher than 60 %, the purity higher than 80 %
(Li et al., 2004)	The organic content in the permeate was decreased from 10,000 mg COD/L to 200 mg COD/L (98 % removal); oxytetracycline was reduced from 1,000 mg/L to 80 mg/L (87.5 % removal)
Ozonation	100 % oxytetracycline degradation after 20 min; BOD5/COD was higher than 0.3 biodegradable effluent; By-products were more toxic than parent compounds
(Li et al., 2008)	
Direct Photolysis	90 % oxytetracycline degradation, 14 % total organic carbon removal, 47 % of inhibition rate after 240 min of irradiation.
(Jiao et al., 2008)	
Electrochemical Oxidation	Rate constants: $9.9 \times 10^{-5}/s$ (pH 2.10), $1.9 \times 10^{-4}/s$ (pH 5.45) Complete loss of the antimicrobial activity of oxytetracycline after 120 min of electrolysis time and at 5 mA/cm ²
(Rossi et al., 2009)	
Adsorption	For concentrations higher than 70 mg/L ⁻¹ , mass transfer became rapid and the chemical reaction at the surface of the solid phase was the rate-limiting step. The results showed that the pseudo-second-order model accurately described the adsorption reaction.
(Djedouani et al., 2013)	

By comparing all those technique to treat or degrade the oxytetracycline, adsorption technique has been found to be prominent method for treating pollutants due to their efficiency, simplicity of design, ease of operation and also cost effective (Crini, 2006).

2.3 Desorption

Desorption is a process that opposite the adsorption. This phenomenon occur whereby a substance is released from or through a surface. Activated carbons and synthetic adsorbents have been used for liquid purification and wastewater treatment. The feasibility of an adsorption process greatly depends on the cost of regeneration of spent adsorbents. Although the adsorption capacity of activated carbons is generally larger than that of synthetic adsorbents, they are disadvantageous for certain applications because of their difficult regeneration. Hence, desorption characteristics are very important for selecting a suitable adsorbent for the adsorption process (Tamon and Okazaki, 1996). The reuse ability of WPAC will be discussed later in this study.

2.4 Adsorbent

Solids have been known to be able to adsorb gaseous and liquids. But, only a few solids have the high adsorption capacity and sufficient selectivity to make them feasible as commercial adsorbents. The most important factor is a large specific surface area (area per unit volume), which can be achieved by adsorbent manufacturing techniques that results in solids with a microporous structure. There are many types of adsorbents available commercially such as activated carbon, activated alumina, silica gel, molecular sieve carbon, zeolite, and polymeric based adsorbent (Seader and Henley, 1998). The surface properties of adsorbents such as porous

structure, pore size distribution, specific surface area, and hydrophilic-hydrophobic properties play important roles in the adsorption capacity (Wang et al., 2011)

Among these commercial adsorbents, activated carbon is the most widely used adsorbent since this activated carbon can be synthesized from any carbonaceous material and of course this will reduce the cost. Over the last few decades, adsorption systems involving activated carbon have gained importance in purification and separation processes on an industrial scale. It is now considered as one of the best available technologies in removing both organic and inorganic contaminants (Girgis and El-Hendawy, 2002).

2.5 Activated Carbon

Activated carbons are the oldest adsorbents known (Hassler, 1963) as they had been used started 3750 years before century. At that time, charcoal was used for reduction of copper, zinc, and tin ores for bronze manufacturing. As the time pass by, activated carbon has found new ways in various applications. It has been used for medicinal purposes to adsorb odorous vapours from putrefactive wounds, decolourization agent of sugar syrup and later during World War I, activated carbon was used in the protective breathing apparatus to stop soldiers from inhaling toxic gases (Dabrowski, 2001).

Activated carbon encompasses a broad range of amorphous carbon-based materials having high degrees of porosity and extensive surface areas and are available in variety forms and particle sizes mainly powder, granular, pellet and bead. Powdered activated carbon is comprised of fine particles, less than about 0.2 mm in diameter, and thus presents large external surface area and small diffusion resistance. Hence the rate of adsorption is very high.

Activated carbons concern many industries as diverse as food processing, pharmaceuticals, chemical, petroleum, nuclear and automobile, because of their adsorptive properties due to high available surface area which is presented in their extensive internal pore structure. The high porosity of activated carbons is a function of both the precursor as well as the scheme of activation. Activated carbons are now frequently used in environmental processes for removing toxic gases and in wastewater as well as potable water treatments (El-Hendawy, 2005)

Activated carbon can be prepared from a wide variety of raw materials which should be abundant and cheap, with high carbon content and low inorganic content. In addition, raw materials should be easily activated and should have low degradation by aging (Dabrowski, 2001). Practically any carbonaceous materials, natural or synthetic, rich in carbon and low in ash are theoretically feasible for activated carbon production (Attia et al., 2008). Coal, lignite, and wood are examples of material which are rich in carbon

2.6 Adsorption Isotherm

The process of adsorption is usually studied through graphs known as adsorption isotherm. In this study, it is the graph between the amounts of OTC HCl adsorbed on the surface of WPAC and pressure at constant temperature. From this graph, the interactions between OTC HCl and WPAC together with the surface properties and capacities of the WPAC can be determined. Data is fitted into different isotherm models in order to establish the most appropriate correlations for the equilibrium data in each system (Tsai et al., 2001). There are two adsorption isotherms namely Langmuir and Freundlich were conducted in this study. Linear regression is frequently used to determine the best-fitting isotherm. The linear least-squares method with

linearly transformed isotherm equations has also been widely applied to confirm experimental data and isotherms using coefficients of determination (Ho, 2006)

2.6.1 Langmuir Isotherm

Langmuir model (Langmuir, 1918) has been widely applied to some process of molecules sorption. The basic assumption of the Langmuir theory is that uptake of molecules occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed molecules that is all the adsorption sites have equal adsorbate affinity and that the adsorption at one site does not affect the adsorption at an adjoining site. So, the Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The Langmuir adsorption isotherm model is given by equation (2.1) (Treybal, 1980)

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

which can then be further rearranged to equation (2.2):

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

where,

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

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

q_m = Monolayer adsorption capacity of the adsorbent (mg/g),

K_L = Langmuir adsorption constant (L/mg).

The linear plot of Langmuir adsorption isotherm (C_e/q_e vs. C_e) demonstrated the applicability of Langmuir adsorption isotherm. It will give a straight line with the slope of $1/q_m$ and intercept of $1/K_L q_m$. The adsorption coefficient can be determined from the slope and intercept of the straight line.

2.6.2 Freundlich isotherm

The Freundlich isotherm theory said that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentration of the solute in the solution is not constant at different concentrations. It can be used for non-ideal sorption that involves heterogeneous adsorption. The heat of adsorption decreases in magnitude with increasing the extent of adsorption (Agrawal et al., 2004). The model of Freundlich adsorption isotherm, which is an indicative of surface heterogeneity of the sorbent, is given by equation (2.3).

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

which can then be further rearranged to: equation (2.4)

$$\ln q_e = \frac{1}{n_F} \ln C_e + \ln K_F \quad (2.4)$$

where,

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

$1/n_F$ = Adsorption intensity,

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

K_F = Freundlich isotherm constant (mg/g (L/mg)^{1/n}).

A graph of $\ln q_e$ against $\ln C_e$ gives a straight line with the slope of $1/n_F$ and intercept of $\ln K_F$. From the slope of graph, the value of $1/n_F$ can be obtained which measures the adsorption intensity or surface heterogeneity. Additionally, from the intercept of graph, the value of K_F can be determined which is a constant related to the bonding energy of a system. It is the adsorption or distribution coefficient that represents the quantity of adsorbate adsorbed onto adsorbents for a unit equilibrium concentration.

When the value of $1/n_F$ is close to 0, it indicates that the system become more heterogeneous (Haghseresht and Lu, 1998). Meanwhile, with the value lower than 1, it shows a normal Langmuir isotherm. Meanwhile, if the value above 1, it shows that the system is from cooperative adsorption (Fytianos et al., 2000).

2.7 Adsorption Kinetics

The kinetic investigations are important for the adsorption studies because it can predict the rate at which an adsorbate molecule is removed from aqueous solutions and provides valuable data for understanding the mechanism of adsorption reactions by determining how the adsorption capacity and adsorbent in term of kinetic can affect the adsorption rate. In this study, two kinetic models are used which includes the pseudo-first-order and pseudo-second-order models.

2.7.1 Pseudo-First-Order

The adsorption rate of adsorbate on the adsorbent is based on the adsorption capacity. It followed a pseudo-first-order equation which is often used for estimating k_1 considered as mass transfer coefficient in the design calculations. equation (2.5) described the non-linear form of the pseudo-first-order equation.

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (2.5)$$

where,

- q_t = Amount of adsorbate adsorbed at time t (mg/g),
- k_1 = Pseudo-first-order rate constant of adsorption (1/hr),
- q_e = Amount of adsorbate adsorbed at equilibrium (mg/g).

By integrating the above equation with boundary layer condition of $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, a linear equation can be obtained as equation (2.6)

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

. Values of k_1 are calculated from the plots of $\log (q_e - q_t)$ versus t . This model assumes that the rate of change of solute uptake with time is directly proportional to the difference in saturation concentration and the amount of solid uptake with time.

2.7.2 Pseudo-Second-Order

Pseudo-second-order model is based on the adsorption capacity onto a solid phase, which is used to predict the behaviour over the entire studied range. It involves the valence forces through sharing or exchange of electrons during the adsorption process (Ho and McKay, 1999). The second-order kinetics equation is described as equation (2.7)

$$\frac{dq_t}{dt} = k_2 (q_e - q)^2 \quad (2.7)$$

where,

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

k_2 = Pseudo-second-order rate constant of adsorption (g/mg.h),

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

which can then be further rearranged to equation (2.8)

$$\frac{dq_t}{(q_e - q_t)^2} = k_2 dt \quad (2.8)$$

By integrating the above equation with boundary layer condition of $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, a linear equation can be obtained as equation (2.9)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2.9)$$

A graph of t/q_t against t gives a straight line with the slope of $1/q_e$ and intercept of $1/k_2q_e^2$.

2.8 Adsorption Thermodynamic

Energy transformation in an adsorption process can be determined by thermodynamic parameters. It is assumed that entropy change is the driving force in an isolated system (Kumar and Kumaran, 2005). Thermodynamic parameters are used to characterize the adsorption process due to the transfer unit mole of solute from solution onto the solid-liquid interface. They include: (i) standard enthalpy change (ΔH°); (ii) standard entropy change (ΔS°); and (iii) standard free energy change (ΔG°).

The value of ΔH° and ΔS° can be calculated by using the equation (2.10):

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

where,

- k_L = Langmuir adsorption constant (L/g),
- ΔS° = Changes in standard entropy (kJ/mol K),
- R = Universal gas constant (8.314 J/mol K),
- ΔH° = Changes in standard enthalpy (kJ/mol),
- T = Absolute solution temperature (K).

Then, the values of both ΔH° and ΔS° from the slope and intercept of the graph can be determined by plotting a graph of $\ln k_2$ against $1/T$. Theoretically, a positive ΔH° value indicates that an adsorption process is endothermic in nature while a negative value represents exothermic reaction. As for ΔS° , a positive value shows the increment in randomness at the solid/solution interface that occurs in the adsorption process besides reflecting the affinity of the adsorbent toward the adsorbate (Bello et

al., 2015). Additionally, the change in standard Gibbs energy, ΔG° can be calculated using the following relation as equation (2.11) with a negative ΔG° value indicates that an adsorption process is a spontaneous process at the study temperature and vice versa.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2.11)$$

The magnitude of activation energy, E_a , can determine the nature of adsorption. Arrhenius equation has been applied to determine either the process is physical or chemical. Physisorption process has activation energy ranging from 5 to 40kJ/mol and chemisorption process has activation energy in range from 40 to 800 kJ/mol (Nollet et al., 2003). As shown in the following relationship, Arrhenius equation can be represented by the equation (2.12):

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad (2.12)$$

where,

k_2 = Rate constant obtained from pseudo-second-order kinetic model (g/mg h)

A = Arrhenius factor,

E_a = Arrhenius activation energy of adsorption (kJ/mol),

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

T = Absolute temperature (K).

Therefore, by plotting a graph of $\ln k_2$ against $1/T$, the values of E_a from the slope of the graph, $-E_a/R$ can be determined.

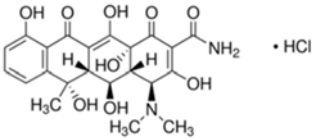
CHAPTER THREE

MATERIALS AND METHOD

3.1 Materials

In this research, activated carbon which synthesise from wood is used to act as an adsorbent. Oxytetracycline Hydrochloride (OTC HCl) as an adsorbate. It was supplied by Sigma-Aldrich (M) Sdn. Bhd, Malaysia. OTC HCl properties was summarized in Tables 3.1.

Table 3.1 Properties of OTC HCl (PUBCHEM)

Properties	
Common name	Oxytetracycline Hydrochloride (OTC HCl)
IUPAC name	(4S,4aR,5S,5aR,6S,12aR)-4-(dimethylamino)-1,5,6,10,11,12a-hexahydroxy-6-methyl-3,12-dioxo-4,4a,5,5a-tetrahydrotetracene-2-carboxamide; hydrochloride
Other name	5-Hydroxytetracycline hydrochloric
Molecular formula	C ₂₂ H ₂₄ N ₂ O ₉ · HCl
Molecular weight	496.9 g/mol
CAS number	2058-46-0
Maximum wavelength, λ_{\max}	273.3 nm
Chemical structure	

During the study effect of pH, the Hydrochloric Acid (HCl) and Sodium Hydroxide (NaOH) had been used to adjust the pH of the Oxytetracycline Hydrochloride solution. Both are diluted to 0.1 M by using distilled water. Desorption was conducted by using Potassium Chloride (KCl) at various weight percentage (1-9 %)

3.2 Equipment and instrumentation

3.2.1 Characterization system

The samples are to be characterized by various techniques to study their characteristics that affected the performance of Wood-based Powdered Activated Carbon. The samples were analysed by using surface area analyzers and thermogravimetric analyzers (TGA) to determine its chemical and physical characteristic. From surface area analyser and analysing the adsorption profile, the BET surface area, micro pore volume, total pore volume and pore size distribution can be obtained. Proximate analysis is performed in the TGA to determine the amounts of moisture, volatile matter, fixed carbon, and ash content in activated carbons. The chemical functionality of wood-based powdered activated carbon was qualitatively identified by Fourier Transform Infrared Spectroscopy (FTIR).

3.2.2 Batch adsorption-desorption

Adsorption experiments were carried out by adding a fixed amount of WPAC (0.10 g) to a series of 250mL conical flasks filled with 100mL diluted solutions (5-25 ppm). Each solution was adjusted to optimum pH. The pH meter was used to determine the pH of the solution. The conical flasks were then sealed and placed in a water-bath shaker and shaken at 50rpm with a required time at 30, 40 and 50 min. The flasks were then removed from the shaker, and the final concentration of OTC HCl in the solution was measured at maximum wavelengths of OTC HCl (273.3 nm) using a double beam UV/vis spectrophotometer (Shimadzu UV/vis1601 Spectrophotometer, Japan).

For the study of desorption, first, the adsorption experiment need to be repeated, but, by changing the initial concentration of OTC HCl to 250 ppm for every conical flask, and left for 24 hours. The amount adsorbed was determined from the difference in the initial and residual concentrations of the adsorbates in the liquid phase. After the adsorption step, the WPAC were filtered by using the filter paper and ceramic filter funnel. Then, the WPAC will be left for desorption in the KCl solution with vary weight percentage (1-9%) in the water bath shaker for optimum time duration and temperature to study the effect of KCl. In the study of reuse ability, the optimum KCl weight percentage will be the constant for each cycle.

3.3 Experimental Procedure

3.3.1 Preparation of stock and OTC HCl solution

100 ppm of OTC HCl solution was prepared by dissolving 0.1 g of OTC HCl powder in 1000 ml of distilled water. A range of dilutions, ranging from 5 to 25 mg/L were then prepared by using distilled water.

3.3.2 Sample and statistical analysis

By using 3 ml of disposable syringe and a filter, the sample was collected at every time interval. The respective OTC HCl concentration was determined by using UV-visible spectrometer. For OTC HCl, the wavelength was set at 273.3 nm. Calibration Curve for OTC HCl had been presented in the appendix A. The linear relationship between absorbance of the OTC HCl onto WPAC and concentration was plotted in graph of absorbance versus concentration of the OTC HCl solutions.

Statistic is a mathematical science pertaining to the collection, analysis, interpretation or explanation, and presentation of data. A common goal for a statically research project is to investigate causality, and to draw a conclusion on the effect of changes in the values of predictors or independent variables on dependent variable or response.

The coefficient of determination is used to analyse the data from this experiment since it represents the percentage of variability in the dependent variable that has been explained by the regression line. The value of the coefficient of determination, calculated from eq, may vary from 0-1

3.3.3 Adsorption batch equilibrium, kinetics, and thermodynamics studies

Adsorption experiments were carried out by adding a fixed amount of WPAC (0.10 g) to a series of 250mL conical flasks filled with 100mL diluted solutions (5–25 ppm). Each solution pH will be adjusted to the optimum pH. The conical flasks were then sealed and placed in a water-bath shaker and shaken at 50rpm with a required time at 30, 40 and 50□. For every fixed time interval, the solution samples were then withdrawn and the concentrations were measured using UV-Vis spectrometer based on the wavelength of maximum adsorption. These measurement steps were repeated until a steady state was reached. For equilibrium studies, the amount of adsorption at equilibrium, q_e can be determined by using the following equation (3.1)

$$q_e = \frac{(C_o - C_e)V}{w} \quad (3.1)$$

where, C_o = Liquid-phase adsorbate concentrations at initial stage (mg/L),

C_e = Liquid-phase concentrations of adsorbate at equilibrium stage (mg/L),

V = Volume of OTC HCl solution (L),

W = Mass of WPAC used (g).

Meanwhile, the percentage of OTC HCl removal, % C can be calculated by using the equation (3.2):

$$\% C = \frac{(C_o - C_t)}{C_o} \times 100 \quad (3.2)$$

where C_t is liquid-phase OTC HCl concentrations at time.

Langmuir and Freundlich were used to fit the experimental data. The best-fitted isotherm can be determined through the value of correlation coefficient; R^2 which is closest to the unity. Meanwhile, for the kinetics studies, the amount of adsorption at time t , q_t (mg/g), was calculated by using equation (3.3):

$$q_t = \frac{(C_o - C_t)V}{W} \quad (3.3)$$

where,

C_o = Liquid-phase OTC HCl concentrations at initial stage (mg/L),

C_e = Liquid-phase concentrations of OTC HCl at equilibrium stage (mg/L),

V = Volume of OTC HCl solution (L),

W = Mass of WPAC used (g).

For kinetic studies, pseudo-first-order and pseudo-second-order models were used in this study. By applying the above models, the correlation coefficient, R^2 can be determined. Likewise, for thermodynamics study, the standard enthalpy, ΔH° , standard entropy, ΔS° and standard free energy, ΔG° were calculated based on the adsorption data. The value of ΔH° and ΔS° can be determined by plotting Van't Hoff graph. Meanwhile, the standard Gibbs energy, ΔG° can be calculated using Equation 2.12 while the Arrhenius activation energy, E_a can be determined by plotting a graph

of $\ln k_2$ against $1/T$. Conjunctionally, the effect of initial OTC HCl concentration, contact time, and solution temperature on the adsorption uptake were investigated.

3.3.4 Effect of solution pH

Effect of solution pH was investigated at pH 3, 4, 5, 6 and 7. 0.10 g sample of WPAC was added to each 100mL volume of OTC HCl solution having an initial concentration of 25 ppm for a constant adsorption time of 24 hours.

3.3.5 Effect of initial concentration

The 0.10 g sample of WPAC was added to each 100mL volume of OTC HCl solution. The initial concentrations of OTC HCl solution tested were 5, 10, 15, 20 and 25 ppm and the experiments were carried out at 30, 40 and 50 °C until the OTC HCl solution reach equilibrium.

3.3.6 Effect of solution temperature

The 0.10 g sample of WPAC was added to each 100mL volume of OTC HCl solution at different initial concentrations the experiments were carried out at 30, 40 and 50 °C until the OTC HCl solution reach equilibrium.

3.3.7 Study of adsorption-desorption

Adsorption experiments were carried out by adding a fixed amount of WPAC (0.10 g) to a series of 250mL conical flasks filled with 100mL diluted solutions 250 ppm OTC HCl. Each solution pH will be adjusted to the optimum pH. The conical flasks were then sealed and placed in a water-bath shaker and shaken at 100 rpm and

at the most optimum adsorption temperature. The sample will be left in water bath shaker for 24 hours, the solution samples were then withdrawn and the concentrations were measured using UV-Vis spectrometer based on the wavelength of maximum adsorption. The amount adsorbed was determined from the difference in the initial and residual concentrations of the adsorbates in the liquid phase. After the adsorption step, the WPAC were filtered and used to study the effect of KCl solution.

3.3.8 Effect of KCl solution

The 0.10 g sample of filtered WPAC was added to each 100mL volume of KCl solution at different weight percentage (1, 3, 5, 7, and 9%) and at the optimum pH. The conical flasks were then sealed and placed in a water-bath shaker and shaken at 100 rpm. The experiments were carried out at optimum desorption temperature for 3 hours.

3.3.9 KCl regeneration of spent WPAC

To investigate the efficiency of KCl regeneration of spent WPAC, the spent WPAC saturated with the adsorbates were filtered and dried. The adsorbates were next desorbed by the optimum KCl weight percentage at optimum desorption temperature for the same time duration as the previous adsorption (3 hours). The regenerated WPAC was filtered and the residual KCl was removed and dried. The regenerated WPAC was again used for adsorption of the same adsorbate. Repeat until 5 cycle.