ADSORPTION OF CHLORAMPHENICOL BY ORDERED MESOPOROUS CARBONS USING ASPEN SIMULATION

MUHAMMAD ALIF AIMAN BIN MOHAMMAD NASRUDDIN

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by

MUHAMMAD ALIF AIMAN BIN MOHAMMAD NASRUDDIN

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LIST OF ABBREVIATION

Symbol	Description
BA	Bohart-Adams Model
BH	Bed Height
CAP	Chloramphenicol
IP	Isotherm Parameter
OMC	Ordered Mesoporous Carbon
TM/TH	Thomas Model
YN	Yoon-Nelson Model

LIST OF SYMBOLS

Symbol	Description	Unit
D_k	Knudsen diffusion coefficient	$m^2\ s^{-1}$
D_m	Molecular diffusion coefficient	$m^2\ s^{-1}$
D_p	Effective pore diffusivity coefficient	$m^2\ s^{-1}$
d_p	Adsorbent particle diameter	m
M_s	Molecular weight of the solvent	$g\ mol^{-1}$
k_{fi}	External film mass transfer coefficient	$m\ s^{-1}$
IP_1	Maximum adsorption	$mg\ g^{-1}$
IP_2	Energy constant related to the heat of adsorption	$L\ mg^{-1}$
K_i	Global mass transfer coefficient	s^{-1}
k_L	Energy constant related to the heat of adsorption	$L\ mg^{-1}$
q_{max}	Maximum adsorption	$mg\ g^{-1}$
R_p	Adsorbent particle radius	m
r_p	Pore radius	m
T	Solution temperature	K
v_s	Superficial velocity of the solution	$m\ s^{-1}$
V_m	Solute molar volume at its normal boiling point	$cm^3\ mol^{-1}$
ε_p	Adsorbent porosity	-
ε_b	Bed porosity	-
τ	Tortuosity factor	-
ρ_{sol}	Solution density	$kg\ m^{-3}$
η_{sol}	Dynamic viscosity of the solution	$kg\ m^{-1}\ s^{-1}$
η_s	dynamic viscosity of the solvent	$kg\ m^{-1}\ s^{-1}$
α_A	Association factor of solvent	-

PENJERAPAN KLORAMFENIKOL DENGAN KARBON MESOLIANG TERSUSUN (KMT) MEGGUNAKAN SIMULASI ASPEN

ABSTRAK

Kloramfenikol (KAF) banyak ditemui dalam komposisi air rawatan yang boleh meyebabkan bahaya kepada kesihatan manusia jika diguna dan menjejaskan ekosistem. Oleh itu, kajian ini adalah mengenai penjerapan/penyingkiran daripada kloramfenikol dengan karbon mesoliang tersusun (KMT) meggunakan simulasi Penjerapan ASPEN. Pertamanya, parameter tetap perlu dikenal pasti dan dikira secara manual dalam Microsoft Excel. Contoh parameter tetap adalah nilai parameter isoterma, keliangan penjerap dan keliangan katil, tortuositi dan pekali pemindahan jisim global. Kondisi operasi simulasi pertama adalah dengan memanipulasi kepekatan awal CAP (50, 100 & 200 mg/L) dengan menetap nilai tinggi ketinggian lapisan (2 sm) dan kadar aliran (10 mL/min). Pada kepekatan awal 50 mg/L menunjukkan masa penembusan terpanjang (925 minit) dan masa kelesuan (1600 minit). Untuk perubahan pada kadar aliran (10, 20 & 30 mL/min), masa penembusan dan kelesuan terpanjang adalah pada 10 mL/min yang masing-masing 925 minit dan 1600 minit. Sebaliknya untuk kesan ketinggian katil (2, 4 & 6 sm) pada penjerapan, yang menunjukkan penembusan terpanjang (2700 minit) dan masa keletihan (4500 minit) pada 6 sm. Dalam kajian penjerapan kolum simulasi, model Thomas dan Yoon-Nelson menunjukkan nilai R^2 tertinggi (0.999) berbanding model Bohart-Adams (0.950-0.99).

ADSORPTION OF CHLORAMPHENICOL

BY ORDERED MESOPOROUS CARBONS (OMC) USING ASPEN

SIMULATION

ABSTRACT

Chloramphenicol (CAP) is found abundance in composition of water that hazardous and cause harmful to human health if consume and to ecosystem. Therefore this study is about the adsorption/removal of chloramphenicol by ordered mesoporous carbons (OMC) using the Aspen Adsorption® simulation. First and foremost in the simulation, the constant parameters need to be identified and manual calculated in the Microsoft Excel such as isotherm parameters (IP) values, adsorbent and bed porosity, tortuosity and the global mass transfer coefficient (MTC). The first simulation operation condition are manipulating the initial CAP concentration (50, 100 & 200 mg/L) and constant the bed height (2cm) and flowrate (10 mL/min). At 50 mg/L initial concentration show the longest breakthrough (925 minutes) and exhaustion time (1600 minutes). For the changing in the flowrate (10, 20 & 30 mL/min), the longest breakthrough and exhaustion time is at 10 mL/min which 925 minutes and 1600 minutes respectively. Vice versa for the effect of the bed height (2, 4 & 6 cm) on adsorption, which show the longest breakthrough (2700 minutes) and exhaustion time (4500 minutes) at 6 cm. In the simulation column adsorption studies, Thomas and Yoon-Nelson model shows the highest R^2 value (0.999) compared to Bohart-Adams model (0.950-0.99).

CHAPTER 1

INTRODUCTION

This chapter shows the overview of my research about the adsorption of chloramphenicol on antibiotics using ordered mesoporous carbons. In the research background, the usage of antibiotics either to human or animal or plant are been discuss in this chapter. The information about antibiotics usage in daily life proof that my research will help in removing the chloramphenicol in pharmaceutical antibiotics.

1.1 Background

Pharmaceutical antibiotic greatly used in treatment purposes to prevent microorganisms and bacterial infections. The antibiotic act as medicine either for human or animal while for plant it act as growth promoter. The first invention of antibiotic is in 1928 which is penicillin discovered by Alexander Fleming (Varley, Sule and Absalom, 2009). The antibiotic can prevent further growth of bacteria and soon will kill them by destroy the bacteria cell wall or its cell composition. Although it is beneficial to treat human, it can cause several side effects such are diarrhoea, nausea, upset stomach and vomiting (Heta and Robo, 2018). The intake of antibiotic must be prescribed by certified doctor or pharmacist to prevent these side effects. The usage of antibiotic toward plant growth is currently been used in agriculture industries but in proper dosage which is less than 0.5% (McManus et al., 2002). Meanwhile for animal livestock in Malaysia, the usage of antibiotic has been used to promote growth or prevent disease.

Chloramphenicol is one of the antibiotic class that can treat infections due to bacteria such as Bacteroides, H. influenza, Neisseria meningitides, Salmonella and Rickettsia (Khairuzzaman, 2016). The chemical structure of chloramphenicol is shown in Figure

1.1. It is a white or greyish-white or yellowish-white crystalline powder and soluble in water and alcohol (Profile, 2017). Since it is soluble in water therefore it cannot been seen inside the water sources that may cause harm to human and animal health. The chloramphenicol is already prohibited for application on food-animal due it can cause harmful effects to human health. Bone marrow depression and fatal blood dycrasias is the most serious adverse effect of chloramphenicol (Dinos et al., 2016).

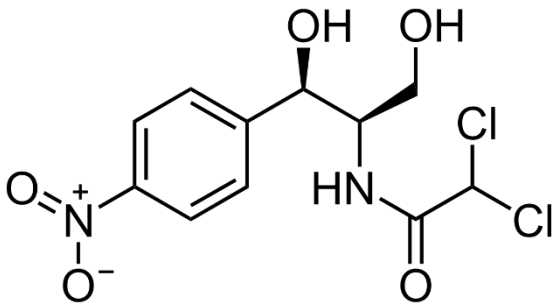

Figure 1.1 Chemical structure of chloramphenicol

1.1.1 Consumption of Antibiotics to Human

In this current situation, the most common medicine used in our daily life is antibiotics which use to fight bacterial infections. Even though it will cure some disease caused by bacteria, it will cause harmful effect if we over dosage the consumption of antibiotics. Based on Klein et al. (2018) article about global antibiotic consumption through year 2000 to 2015 show an increase of 39% consumption antibiotics rate. In 2015, the country that used highest amount of antibiotics is Turkey and Tunisia which are 48 defined daily doses (DDDs) per 1000 person. For Malaysia the amount antibiotic usage is about 18 DDDs per 1000 person which almost the same with our neighbouring country Singapore (19 DDDs). This article also expected that the consumption of antibiotics in the future will further increase which will continue to growth around 50

DDDs in 2020 and 125 DDDs in 2030. This is acceptable growth curve since human population will also continue to increase.

According to Fatokun (2014) study about antibiotics consumption and practices in Malaysian community which he conducted a survey from 250 different person. The result of the survey show most Malaysian has consume antibiotics which in the year of study about 36.4% while other are about 1 to 2 year before. In the last 12 months all surveyor has consume antibiotics about 66.3% in total compared to 33.2% not consume any antibiotics. Majority of surveyor are aware of the function of antibiotics and bacterial resistance due to consumption of this medicine. All surveyor are getting the antibiotics from the right and proper sources which from hospital, pharmacy and clinics. This shows that all surveyor are getting the right prescription usage for the antibiotics and not from the improper antibiotics sources. But the way of expired and leftover antibiotics are dispose in the wrong method for most surveyor which throw to rubbish bin and flush to water sources. Both of this method will cause harmful effect to our environment. Only 6.4% surveyor are use the proper way to dispose the medicine which sent it back to pharmacist or doctor which they will throw the antibiotics in the proper manner.

1.1.2 Consumption of Antibiotics to Animal

In this current era, antibiotic are vastly used in animal food to increase their immune system, for health treatment and also act as growth promoter. From some research shown that about 80% of total amount of antibiotic has been given annually as to promote the animal growth. As the increase use of antibiotic in food animal industry, it will cause antimicrobial resistance (AMR) which cause bacteria to evolve and make the infections more harmful and hard to be treated and may also cause high contagious disease. Based on the global trend antibiotic consumption in food animals it is expected

to growth about 67% from 63,151 tons (2010) to 105,596 tons (2030) (Van Boeckel et al., 2015).

According to Hassali et al., (2018) article are discussing about the use of antibiotic in food animals based in Malaysia. Antibiotic can be categorized into two different types which are bacteriocidal antibiotics and bacteriostatic antibiotics. Bacteriocidal antibiotics is the antibiotics that kill the bacteria such as aminoglycosides, beta lactams, fluoroquinolones, glycopeptides, lipopeptides, nitroimidazoles and nitro furans. For the bacteriostatic antibiotic is the one that inhibit the growth of bacteria example are plycylcyclines, lincosamides, macrolides, oxazolidinones, streptogramins and sulphonamides. Food animal are defined as the farm animal that are raised to obtain food for human such as eggs, milk and meat. These animal are usually chickens, ducks, beef cows, dairy cows, goat, sheep, pigs and deer. The usage of antibiotic in food animal are as to treat infectious animal disease, to increase the animal weight and as metaphylaxis is to minimize the risk of contagious disease outbreak. The antibiotics consumption in producing one kilogram of meat are based on different livestock which are 45mg of antibiotic use in beef, 148mg of antibiotic use in chicken and 172mg of antibiotic use in pork. The evolving of bacterial resistance toward antibiotic are being reported as the increase of antibiotic usage will increase the antibiotic resistance. From the table 1.1 shows the of antibiotic resistance in foods which show about 87.5% from imported chicken are resistance to ampicillin while 25.0% resist to chloramphenicol. The resistance for other antibiotics are been shown in the table for domestic and imported chicken and imported beef.

Table 1.1 Antibiotic resistance in food animal obtain by (Hassali *et al.*, 2018)

Antibiotic type	Domestic chicken (%)	Imported chicken (%)	Imported beef (%)
Ampicillin	54.5	87.5	10.5
Chloramphenicol	45.5	25	0
Ciprofloxacin	9	25	5.3
Gentamicin	40	25	5.9
Nalidixic acid	36.4	75	10.5
Streptomycin	27.3	50	0
Sulphonamide	63.6	50	5.3
Tetracycline	54.5	25	15.8
Trimethoprim	45.5	37.5	10.5
Trimethoprim + Sulfamethoxazole	36.4	25	0

The bacterial infections can be reduce by cooking the food, clean the cooking environment which clean the utensil or cutting board and chill the food in the refrigerator at 4℃. This may help to reduce the infection of disease to human as eating the food animal products. The quote obtained from Antibiotic use in food animals: Malaysia overview (Hassali et al., 2018). "USFDA's Import Alert 16-136 dated 18 April 2016, shown that from October 1 2014 through September 2015, it detected an increase of chloramphenicol content in shrimp products from Peninsular Malaysia. Out of 138 shrimp samples, 45 sample detected contain chloramphenicol."

Based on Ma et al., (2020) study amount of antibiotic residues in animal manure after been the food animal consume the antibiotics. The highest amount of norfloxacin was found has highest residue in animal manure which around 225.45 mg/kg. Table 1.2 shows the other antibiotic found in animal manure.

Table 1.2 Antibiotic residues in animal manure from (Ma *et al.*, 2020)

Antibiotic	Animal	Residues (mg/kg)
Fleroxacin	Chicken	99.43
Norfloxacin	Chicken	225.45
Ciprofloxin	Swine/ chicken/ cattle	33.98/ 45.59/ 29.59
Enrofloxacin	Swine/ chicken/ cattle	33.26/ 1,420.76/ 46.70
Oxytetracycline	Swine/ cattle	59.06/ 59.59
Chlortetracycline	Swine/ cattle	21.06/ 27.59
Tetracycline	Swine	34.58
Sulfonamides	Swine, chicken, cattle	0.17
Macrolides	Swine	4.8
Nitro furans	Swine, chicken, cattle	0.085

In the Action, Asia and Network (2013), study about the antibiotic can be a threat to human and animal health. This study are proposed the encouragement to monitor the usage of antibiotics in animal feed due to its microbial resistance. It also encourage to enforce laws on the prescription for the consumption of antibiotic to animal.

1.2 Problem Statement

The toxic pharmaceutical waste like chloramphenicol need to be removed from the water stream to prevent the harmful effect toward human health. The Malaysia health government has already prohibited the usage of the chloramphenicol toward food-animal industries. The effect of chloramphenicol toward human, animal and environment has been further studies in this research. Adsorption of chloramphenicol via ordered mesoporous carbon must be done to remove the drug waste from the water. Research in removing the chloramphenicol in the water has been getting attention in this recent years due to its dangerous side effect toward human health. Most of the research in removing chloramphenicol has used activated carbon as adsorbent due to its simplicity and low-cost material (Johnson, 2014), (Reimerink, 1999). With this current situation due to COVID-19, the experiment results cannot be done therefore the adsorption of chloramphenicol has been done using Aspen simulation. Using the Aspen

simulation, the parameters affecting the removal of chloramphenicol can also been studied. We will need to observe the column adsorption studies toward adsorption by manipulating the initial concentration, flowrate and bed height.

1.3 Objectives

The objective of this study are as follows:

i. To study the effect of flowrate, bed height of adsorption column and initial concentration of chloramphenicol toward adsorption of chloramphenicol using Aspen Adsorption software.
ii. To analyse the fixed bed adsorption data with the dynamic model.

CHAPTER 2

LITERATURE REVIEW

This chapter explain about removal of chloramphenicol using mesoporous carbons through adsorption process. Some previous articles and reviews from scientific sources were obtained to be used in understanding the knowledge related to this research. This chapter also explain more about adsorption, type of adsorbent used and adsorption isotherm.

2.1 Adsorption

Adsorption is define as a process of collecting molecules by the surface of the solids such as the activated charcoal is used to collect harmful gasses. Adsorption on mesoporous carbons can remove the pharmaceutical waste such as chloramphenicol based on this studies. Figure 2.1 show the basic concept of adsorption process. Most of pharmaceutical waste can be found in the river or water sources. This may due to irresponsible of some industries that dump the waste to nearby water stream to reduce the capital cost or maybe some leakage waste that the company does not aware. To remove these waste, the adsorption on the activated carbon has been studied and applied in current industries. Based on some studies the heavy metals from industrial wastewaters is been remove through adsorption using activated carbon reported by Kadirvelu, Thamaraiselvi and Namasivayam (2001). The colour of wastewater can also been removed using activated carbon adsorption according to Singh et al. (2003).

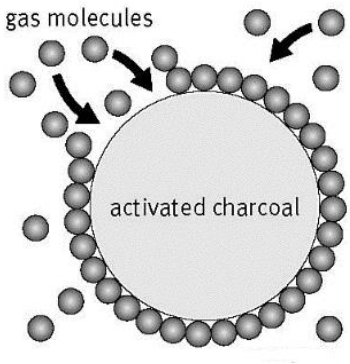

Figure 2.1 Adsorption process mechanism

Adsorption can be divided into two types which are physical adsorption (physisorption) and chemical adsorption (chemisorption). Physical adsorption is also known as van der Waals adsorption which only occur when have the inter-molecular interaction between adsorbent and adsorbate based on Wikipedia. Based on Xia et al., (2019) which study the mercury removal using physisorption concept. The activated carbon, mesoporous silica and zeolite are under same porous adsorbent structure that can remove the mercury from the liquid. The preparation of making the porous structure is using from agriculture waste such as rice husk, sugarcane bagasse, wood dust and etc. The preparation of this structure are bio-friendly, simple to obtain and cheap in operation and production. Table 2.1 shows the various type of adsorbent used in physisorption will affect the removal efficiency. The highest removal efficiency is using ZSM-5 zeolite as adsorbent which is 96.3%.

Table 2.1 Physisorption with different adsorbents from (Xia et al., 2019)

Adsorbents	BET surface area (m2/g)	Mercury removal efficiency (%)	Adsorption capacity (mg/g)
Activated carbon	1690	82	0.869
Porous carbon	780	95	151.5
Activated carbon	555	60-80	128
ZSM-5 zeolite	189	96.3	51.54
Activated carbon fibre (ACF)	848-1259	-	290-710

The second type of adsorption is chemisorption which define as an adsorption process that involves chemical reaction between surface and adsorbate based on Wikipedia. Thus in contrast from physisorption, chemisorption is involving transfer of electrons between the surface of substances and adsorbent. According to (Van Tran et al., 2019) article is discussing the synthesis of mesoporous carbons from $Fe_3O(BDC)_3$ for removal of chloramphenicol in antibiotics. The optimal conditions of chemisorption process is at pH 6, 10mg/L CAP concentration and 0.5 g/L adsorbent dosage in getting the removal CAP efficiency almost 100% after 4 hours. Table 2.2 shows the various type of adsorbents used in chemisorption will affect the maximum adsorption capacity and CAP removal efficiency.

Table 2.2 Chemisorption with various type of adsorbents from (Zhang *et al.*, 2013; Samanidou *et al.*, 2016; Tran *et al.*, 2017; Van Tran *et al.*, 2019)

Adsorbents	BET surface area (m2/g)	CAP removal efficiency (%)	Adsorption capacity (mg/g)
MPC700	224.7	~100	96.3
Fe3O(BDC)3	7.6	25.6	24.1
Sol-gel MIP	167.3	-	23
Bamboo charcoal	67.8	70.3	8.1
Plasma modified StS	4.5617	87.1	3.167
Raw StS	2.7179	86.4	2.92
BSA/ Fe2O3	-	93	147.83

2.2 Type of Adsorbents

Adsorbent is a solid substances that used to extract the solute molecules from liquid or gas by attracting solute particle to its surface. The most common adsorbent used in the adsorption of CAP are activated carbons, agriculture charcoal such as bamboo charcoal and mesoporous carbons. The production of mesoporous carbons have been studied by (Van Tran et al., 2019) which the mesoporous carbons structure will depend on

pyrolysis temperature. In this study, the best adsorption capacity for adsorbent is at temperature of 700℃ (MPC700) which has capacity about 40.6 mg/g. Based on Figure 2.2 shows the MPC pyrolysis temperature will affect the CAP adsorbed capacity. MPC700 has nearly 100% been removed from the wastewater with 96.3 mg/g maximum adsorption capacity with CAP concentration 0.5 mg/L at pH 4.

The adsorbents using agriculture waste such as bamboo charcoal also been used based on literature Liao et al. (2013), in the study of adsorption of tetracycline and chloramphenicol in aqueous solutions by bamboo charcoal: A batch and fixed-bed column study. The highest antibiotics removal efficiency of CAP is about 70.3% and the lowest is 40.1%.

The last common adsorbents used in industry adsorption is activated carbons which have a lot of studies such as Lach (2019) and Ociepa-Kubicka (2017), these articles are using three type of adsorbent which are WG-12, ROW 08 and F-300. The type of adsorbent used will based on the pH solution such as the highest removal efficiency at pH 2 is ROW 08 while at pH 7 is F-300. Based on Lach article (2019), as the amount of activated carbon dosage increase, the adsorption efficiency will also increase. It shown that at 1 g/L dose the adsorption efficiency is about 36% while at 8 g/L dose have over 99% removal efficiency.

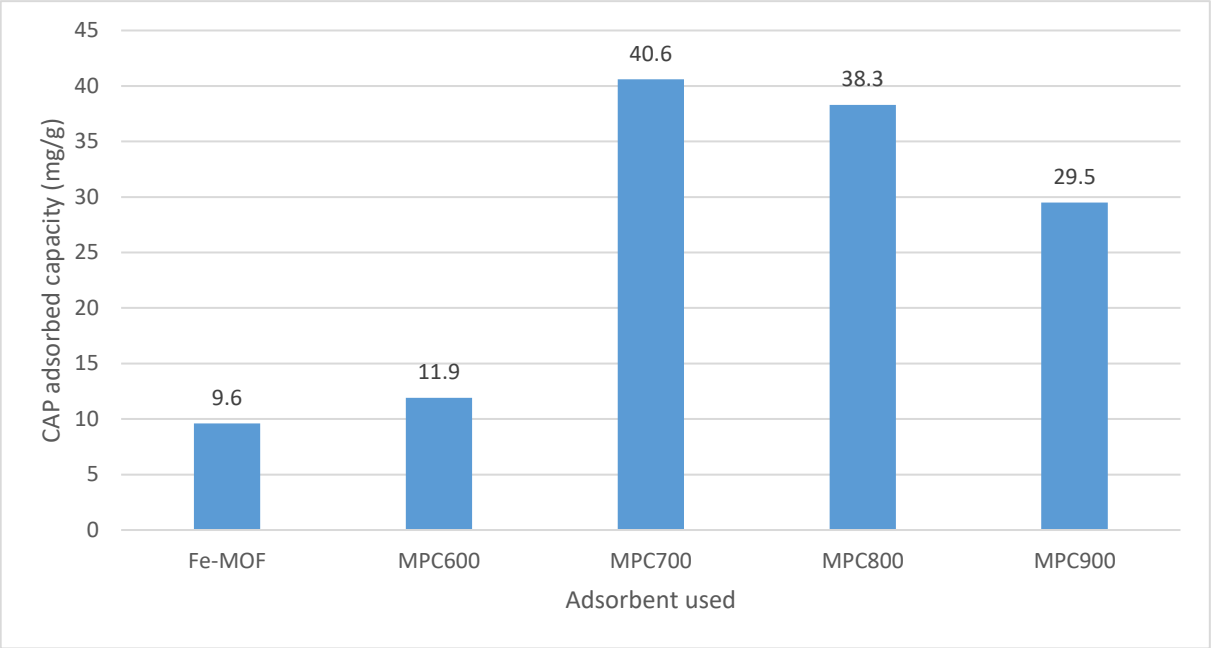

Figure 2.2 MPC structure against CAP adsorbed capacity from (Van Tran *et al.*, 2019)

2.3 Dynamic column adsorption studies

For this column study, the analysis of breakthrough curves are studied by changing the initial concentration of CAP, bed height and flowrate. These parameter were studied by using breakthrough curve. Breakthrough curve designate the dynamic response of adsorbent system. Breakthrough curve were plot between C_e/C_0 against breakthrough time. Breakthrough time is define as the time taken to chemical imbued completely through the material. Breakthrough time usually time at 5 % of adsorption happen while saturation time at 95 % of total process which explain by Zhou et al. studies (2011).

The dynamic response of adsorption were been studied through some adsorption models such as Thomas model, Yoon-Nelson model and Bohart-Adams model. These model are the mostly used model to validate the continuous adsorption system.

2.3.1 Thomas Model (TM)

According to Sazali, Harun and Sazali (2020), Thomas model is also designated as bed-depth service time (BDST) and further simplified into Bohart-Adams irreversible isotherm model. The assumption made by Thomas model is that is no mass transfer resistance between fluid film and intra-particle. Hence the adsorption rate can be manipulate by surface reaction between ion molecules and unoccupied sites. Based on Biswas and Mishra (2015), q_0 value will increased as the influent concentration and pH increase. However q_0 will decrease with increase of flowrate. In vice versa for k_{TH} as it decrease with increase of initial concentration and bed height but increase with increase of flowrate.

The expression of Thomas model can be obtained in the equation 20.

$$\frac{C}{C_0} = \frac{1}{1 + \exp\left(\frac{k_{TH} q_0 m_{adsorbent}}{Q} - k_{TH} C_0 t\right)} \quad (20)$$

Linearizing the Thomas model expression, (21)

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{k_{TH} q_0 m_{adsorbent}}{Q} - k_{TH} C_0 t \quad (21)$$

Where,

C_0 is the influent concentration of solution (mg/L),

C is the effluent concentration of solution (mL/min),

q_0 is the adsorption capacity (mg/g),

Q is the volumetric flowrate (mL/min),

$m_{adsorbent}$ is the adsorbent mass (g),

k_{TH} is the kinetic coefficient or Thomas model rate constant (mL min^{-1} mg^{-1})

In obtaining the k_{TH} and q_0, the graph of ln [(C_0/C)-1] against time were plotted that can be assumed its initial guess value. The R^2 value of the graph need to be obtained higher to ensure the data experiment and simulation is fitted well.

2.3.2 Yoon-Nelson Model (YN)

According to Sazali, Harun and Sazali (2020), Yoon-Nelson model are almost similar to Thomas model. This model illustrated that the adsorption rate will decrease as pollutant increase. The τ will increase with increased in bed height while decrease with increased of initial concentration and flowrate. k_{YN} will increased with increase of initial concentration and flowrate. As increased in bed height, the rate constant k_{YN} will decreased.

The expression of Yoon-Nelson model can be obtained in the equation 22.

$$\frac{C}{C_0} = \frac{\exp(k_{YN}t - \tau k_{YN})}{1 + \exp(k_{YN}t - \tau k_{YN})} \quad (22)$$

Linearizing the Yoon-Nelson model expression, (23)

$$\ln\left(\frac{C_0}{C - C_0}\right) = k_{YN}t - \tau k_{YN} \quad (23)$$

Where,

τ is the time required for 0.5 adsorbate breakthrough (min),

k_{YN} is the kinetic coefficient or Yoon-Nelson rate constant (mL min^{-1} mg^{-1})

The R^2 (0.57 – 0.99) value of the graph need to be obtained higher to ensure the data experiment and simulation is fitted well.

2.3.3 Bohart-Adams Model (BA)

According to Sazali, Harun and Sazali (2020), Bohart-Adams were derived from Thomas model adsorption isotherm. Based on Biswas and Mishra, (2015) N_0 value will increased as the bed height increase. However N_0 will decrease with increase of flowrate and initial concentration. In vice versa for k_{BA} as it decrease with increase of bed height only but increase with increase of flowrate and initial concentration.

The expression of Bohart-Adams model can be obtained in the equation 20.

$$\frac{C}{C_0} = \frac{1}{1 + \exp\left(\frac{k_{BA}N_0L}{u} - k_{BA}C_0t\right)} \tag{24}$$

Linearizing the Bohart-Adams model expression, (21)

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{k_{BA}N_0L}{u} - k_{BA}C_0t \tag{25}$$

Where,

N_0 is the saturation concentration of solution (mg/L),

L is the depth of fixed-bed column (cm),

u is the superficial velocity (cm/min),

k_{BA} is the kinetic coefficient or Bohart-Adams rate constant (mL min^{-1} mg^{-1})

In obtaining the k_{BA} and N_0, the graph of ln [(C_0/C)-1] against time were plotted that can be assumed its initial guess value. The R^2 value of the graph need to be obtained higher to ensure the data experiment and simulation is fitted well.

Table below shows the summary of column adsorption model and various operation parameters with assume increasing model rate constant coefficient. (Patel, no date)

Table 2.3 Summary table for column adsorption model

Column Adsorption Model	Model Rate Constant	Operation Parameters			
		Initial Concentration	Flowrate	Bed Height	Temperature
Thomas model	k_{TH}	Decreased	Increased	Decreased	Decreased
	q_0	Increased	Decreased	Increased	Increased
Yoon-Nelson model	k_{YN}	Increased	Increased	Decreased	N.A
	τ	Decreased	Decreased	Increased	N.A
Bohart-Adams model	k_{BA}	Increased	Increased	Decreased	Decreased
	N_0	Decreased	Decreased	Increased	Increased
Bed depth service time model (BDST)	k_{BDST}	Increased	Increased	N.A	Increased
	N_0	Increased	Increased	N.A	Increased
Clark model	A	Decreased	Decreased	Increased	Increased
	R	Increased	Increased	Decreased	Decreased
Wolborska model	B	Decreased	Increased	Decreased	Decreased
	N_0	Increased	Decreased	Increased	Increased
Modified dose response model (MDRM)	A	Decreased	Increased	Increased	N.A
	B	Increased	Increased	Increased	N.A

2.4 Effect of Initial CAP Concentration on Adsorption

Based on Li, Zhang and Liu (2018) article represent the effect of initial concentration on CAP adsorption. Based on Figure 2.3 shows the adsorption capacity against CAP concentration as the adsorption capacity tend to increase with increasing of CAP

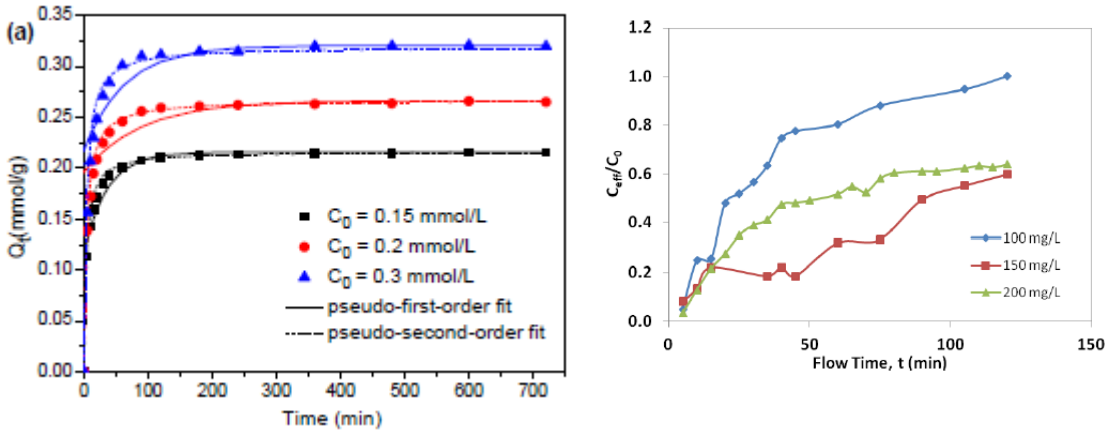

Figure 2.3 Adsorption kinetics and breakthrough curve at different initial concentration

concentration. Therefore the breakthrough time in Aspen simulation tend longer for lower initial concentration compared to higher concentration. In this simulation, the initial concentration were varied at 50 ppm, 100 ppm and 200 ppm. Ping Ling, Tan and Lik Pueh Lim (2016) studied that the slope for breakthrough curve were steepest for the lowest inlet concentration. In this study the inlet concentration were changes at 100 mg/L, 150 mg/L and 200 mg/ with constant the bed height and flowrate at 5.5 cm and 3 mL/min.

2.5 Effect of Flowrate on Adsorption

The flowrate of CAP fed would affect the adsorption capacity of adsorbent according to article about the study of fixed-bed column for cadmium adsorption by Ping Ling, Tan and Lik Pueh Lim, (2016). In this study the bed height and initial were kept constant

at 5.5 cm and 200 mg/L. Meanwhile the flowrate were manipulate at 2.0 mL/min, 3.0 mL/min and 5.0 mL/min. Based on Figure 2.4 below it resulted that the flowrate will affect the adsorption efficiency which show the decreasing of breakthrough time as flowrate increase.

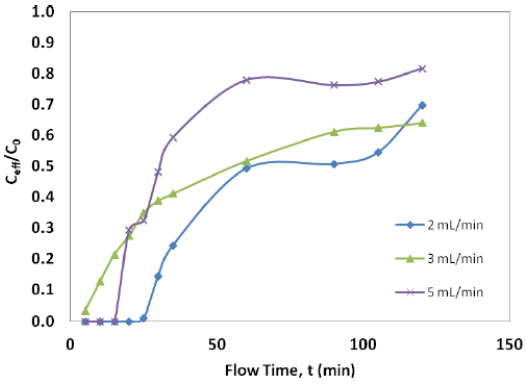

Figure 2.4 Breakthrough curve for adsorption of cadmium at different flowrate.

2.6 Effect of Bed Height on Adsorption

Based on article by Ping Ling, Tan and Lik Pueh Lim (2016), the bed height of the fixed-bed adsorption also play a role affecting the adsorption efficiency. In this study, the manipulating bed height are at 3.0 cm, 4.0 cm and 5.5 cm with constant the initial concentration and flowrate. From the Figure 2.5 it show that the highest bed 5.5 cm has slowest breakthrough period. The highest removal was observed for all bed height 3.0 cm, 4.0 cm and 5.5 cm were 46.16%, 50.59% and 53.71% respectively.

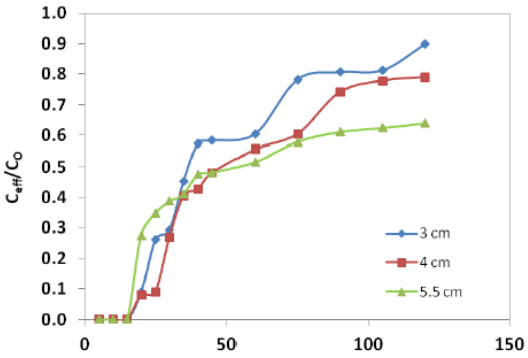

Figure 2.5 Breakthrough curve for adsorption of cadmium at different bed height

CHAPTER 3

METHODOLOGY

This chapter will explain about the methodology research work studies about adsorption of chloramphenicol on antibiotic by ordered mesoporous carbons using Aspen simulation. Firstly, the constant parameter for simulation must identified by manual or Excel calculating such as isotherm parameters, adsorbent properties, bed properties and global mass transfer coefficient. Then all parameter are needed to be inserted in the simulation properties to run the simulation.

3.1 Mathematical Adsorption Modeling of Aspen Simulation

The mathematical calculation for this simulation can be divided into three steps which are determination of isotherm parameters (IP) values, determination of adsorbent and bed properties and finally the global mass transfer coefficient.

3.1.1 Determination of Isotherm Parameters (IP) Value for Aspen Simulation.

The most suitable for adsorption isotherm for the adsorption of CAP is the Langmuir isotherm. Langmuir equation were illustrated in below equation (7) (Juela, 2020):

$$q_e = \frac{q_{max}.k_L.C}{1 + k_L C} \qquad w_i = \frac{IP_1.IP_2.C}{1 + IP_2.C} \tag{7}$$

The left expression is main and common expression of Langmuir isotherm, while on the right side is the Langmuir isotherm in the Aspen Adsorption simulation.

Where,

q_e is amount of solute removed per unit mass of adsorbent (mg g^{-1}),

w_i is amount of solute removed per unit mass of adsorbent (kmol kg^{-1}),

q_{max} is maximum adsorption of the solid phase in monolayer (mg g^{-1}),

IP_1 is maximum adsorption of the solid phase in monolayer (kmol kg^{-1}),

k_L is energy constant related to the heat of adsorption (Lmg^{-1}),

IP_2 is energy constant related to the heat of adsorption ($m^3\ kmol^{-1}$).

Therefore using right expression (7) the value of IP_1 and IP_2 must be obtained by using equation (8) below.

$$IP_1 = \frac{q_{max}}{1000M}; \qquad IP_2 = 1000k_L M \tag{8}$$

Where,

M is the molecular weight of chloramphenicol (g mol^{-1})

k_L and q_{max} is obtained from Mohd Din, Ahmad and Hameed,(2015) article which are 0.01 L/mg and 209.68 mg/g respectively. While the M_{CAP} and M_{Water} are 323.032 g/mol and 18.02 g/mol respectively.

3.1.2 Determination of Adsorbent and Bed Properties

Adsorbent and bed properties were determine using equation (*Pushnov, A.S. Calculation of average bed porosity. Chem Petrol Eng 42, 14–17 (2006). https://doi.org/10.1007/s10556-006-0045-x,* no date; Lal, 2017) from these articles. The formula (9) were shown below and the constant for bed porosity were shown in the Table 3.1.

$$Adsorbent\ porosity, \varepsilon_{\boldsymbol{p}} = \frac{pore\ volume, V_p\ \left[\frac{cm^3}{g}\right]}{particle\ density, \rho_s\ \left[\frac{g}{cm^3}\right]} \tag{9}$$

Table 3.1 Bed porosity constants

Shape	Coefficients		
	A	B	n
Spheres	1.0	0.375	2
Cylinders	0.9198	0.3414	2
Lumps of irregular shape	1.5	0.35	1
Rashing rings	0.349	0.5293	1

From Table 3.1, assume that the shape Φ = 1 which is circle. Hence bed porosity will calculated as expression (10) below.

$$Bed\ porosity, \varepsilon_{\boldsymbol{b}} = \frac{A}{\left(D/d_p\right)^n} + B \tag{10}$$

Where,

D is the column wall inner diameter (cm),

d_p is the diameter of particle (cm),

A, B & *n* are the constant which dependent on the shape of adsorbate.

Bed porosity also can be expressed as below equation (11).

$$Bed\ porosity, \varepsilon_b = 1 - \left(\frac{\rho_b}{\rho_s}\right) \tag{11}$$

Where,

ρ_b is the bulk density of the bed (g/ cm^3),

Next from equation above, the bulk density can be calculated by using algebraic method. Finally, tortuosity is been calculated by using adsorbent porosity with below equation (12).

$$Tortuosity, \tau = \varepsilon_p + 1.5(1 - \varepsilon_p) \quad (12)$$

Tortuosity is define as effective diffusivities in the bulk material per within the pore space.

3.1.3 Determination of Global Mass Transfer Coefficient

The parameter of MTC is shown in Table 3.2.

Table 3.2 MTC parameter

Property	Value	Unit
α_A	2.258	-
M_s	18.02	g mol^{-1}
η_s	0.001	kg m^{-1} s^{-1}
T	303.25	K
V_m	121.94185	cm^3 mol^{-1}
ρ_{sol}	998.6	kg m^{-3}
η_{sol}	1.05×10^{-3}	kg m^{-1} s^{-1}

The global mass transfer coefficient (K_i) can be expressed as equation (13) and were inserted into parameter in simulation bed as MTC.

$$\frac{1}{K_i} = \frac{R_P}{3k_{fi}} + \frac{R_p^2}{15\varepsilon_p D_p} \quad (13)$$

In calculating MTC, the effective pore diffusivity coefficient (D_p) has been estimated using equation (14).

$$\frac{1}{D_p} = \tau_p \left(\frac{1}{D_m} + \frac{1}{D_k}\right) \quad (14)$$