RIBOFLAVIN ADSORPTION ON MESOPOROUS CARBON BY USING ASPEN ADSORPTION SIMULATION

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by

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LIST OF SYMBOLS

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_Z	Axial dispersion 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 ($m\ s^{-1}$)
K_i	Global mass transfer coefficient (s^{-1})
R_p	Adsorbent particle radius (m)
r_p	Pore radius (m)
T	Solution temperature (K)
v_i	Interstitial velocity of the solution ($m\ s^{-1}$)
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	Particle porosity
ε_b	Bed void fraction
τ_p	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	The association factor of solvent

LIST OF ABBREVIATIONS

EGRAC	Erythrocyte Glutathione Reductase Activity Coefficient
FAD	Flavin Adenine Dinucleotide
FMN	Flavin Mononucleotide
GAC	Granular Activated Carbon
IP	Isotherm Parameter
PEG	Polyetheluen Glycol
PMMA	Poly (Methyl Methacrylate
RF	Riboflavin
SBA	Santa Barbara Amorphous
UAE	Ultrasonic Ssisted Extraction

ABSTRAK

Riboflavin merupakan salah satu vitamin B dan merupakan komponen penting dalam flavin mononucleotide dan flavin adenine dinucleotide (FAD). Riboflavin merupakan warna kuning dan warnanya memantulkan cahaya apabila terdedah kepada cahaya ultraungu. Dalam project ini, penyerapan riboflavin dianalisis dengan mengunakan perisian Aspen Adsorption. Ada 3 pemboleh ubah yang perlu dipertimbangkan untuk menjalani simulasi iaitu kada aliran suapan (10, 20, and 30 mL/min dengan ketinggian lapisan dan kepekatan RF awal, 2 cm dan 50 ppm masing-masing), ketinggian lapisan (2, 4, dan 6 cm dengan kadar aliran suapan dan kepekatan awal sebagai pemalar, 10 mL/min dan 50 ppm masing-masing), dan kepekatan awal (50, 100, dan 200 ppm dengan kadar aliran suapan dan ketinggian lapisan sebagai pemalar, 10 mL/min dan 2 cm masing-masing) Mengambil 303.15 K suhu tetap untuk semua simulasi. Graf penembusan penjerapan riboflavin menunjukkan masa yang lebih singkat diambil untuk mencapai titik penembusan dengan meningkatkan kadar aliran awal dan kepekatan awal riboflavin untuk simulasi dan eksperimen. Jika tidak, meningkatkan ketinggian lapisan akan memberikan hasil negatif pada penjerapan riboflavin. Kajian penjerapan riboflavin juga dianalisis dengan menggunakan tiga model yang berbeza (Thomas, Yoon-Nelson, dan Adam-Bohart). Model Thomas dan Model Yoon-Nelson menunjukkan prestasi yang lebih baik daripada Adam-Bohart dengan menganalisis nilai R^2

.

ABSTRACT

Riboflavin is one of the B vitamins and essential component of flavin mononucleotide and flavin adenine dinucleotide. Riboflavin is yellow and naturally fluorescent when exposed to ultraviolet light. In this project, adsorption of riboflavin was analysed using Aspen Adsorption software. There are 3 condition that consider performing this simulation which is initial flow rate (10, 20, and 30 mL/min at constant bed height and initial concentration of RF, 2 cm and 50 ppm respectively), bed height (changing the bed height 2 , 4, and 6 cm at constant initial flowrate and initial concentration of RF, 10 mL/min and 50 ppm respectively), and initial concentration varied the initial concentration at 50, 100, and 200 ppm at constant initial flow rate 10 mL/min and 2 cm bed height). Taking 303.15 K for the fixed temperature for all the simulation. Breakthrough curve of riboflavin adsorption show shorter time taken to reach the breakthrough point by increasing the initial flow rate and initial concentration of riboflavin for both simulation and experimental. Otherwise, increasing the bed height will give negative result on adsorption of riboflavin. The study of riboflavin adsorption also being analysed by using three different model development (Thomas, Yoon-Nelson, and Adam-Bohart). The result show Thomas Model and Yoon-Nelson Model exhibit better performance than Adam-Bohart by analysing the R^2 value.

CHAPTER 1

INTRODUCTION

Chapter 1 introduces the overview of this research and significance of simulation of riboflavin adsorption. In general, this chapter summarizes the research background of riboflavin and simulation using Aspen Plus V10, the problem statement and the objectives of this final year project.

1.1 Research Background

Riboflavin is one of the B vitamins. This vitamin is an essential component of flavin mononucleotide and flavin adenine dinucleotide. Riboflavin is yellow and naturally fluorescent when exposed to ultraviolet light. In addition, ultraviolet and visible light will inactivate riboflavin and its derivatives easily. The risk of riboflavin loss from exposure to light is the reason why milk is not typically stored in glass containers. Riboflavin is a vitamin that is required for normal growth and wellbeing. It aids the body's energy production by allowing carbs, proteins, and lipids to be broken down, as well as allowing oxygen to be utilised by the body.

Vitamin B2 is a water-soluble vitamin that must be replenished on a regular basis because it gets flushed out of the body. The easiest way to receive this vitamin is to consume riboflavin-rich meals. According to the University of Maryland Medical Center, riboflavin can be found in eggs, almonds, dairy products, meats, broccoli, brewer's yeast, Brussel sprouts, wheat germ, wild rice, mushrooms, soybeans, green leafy vegetables, whole grain and enriched cereals and bread.

Treatment process for adsorption of riboflavin include liquid-liquid extraction, ultrasonic assisted extraction, and adsorption of activated carbon. Cost effective technique are most recommended for the treatment of riboflavin. Generally, riboflavin

have been used by pharmaceutical industry are extremely high. So needed of technologies are demanded to get the desired product at it best yield.

1.2 Problem statement

In order to produce a lot of riboflavin to sell in into industry. We must find the most effective with very high yield and low cost will take into consideration. There are many adsorbents to be used to adsorb the riboflavin, but what is the most suitable adsorbent to be used. In (Mohd Din, Ahmad and Hameed, 2015) multi-modal mesoporous carbon synthesized from polyethylene glycol 400 (PEG-400) by hard-templating method to adsorb riboflavin. Besides, selection of adsorption parameter also plays important to give best performance. Finding the best riboflavin adsorption condition is very demand during these recent studies. This is because riboflavin uses are widely in the pharmaceutical industry. But the pandemic situation are the obstacle to carried out the experiment hands on, so, simulation is the best solution to achieve my objective. On the other hand, all the experiment needs to run in Aspen Simulation (Juela, 2020).

1.3 Objective

I. To develop and perform simulation of riboflavin adsorption in pharmaceutical by ASPEN Adsorption V10.

II. To analyze the aspen simulated with dynamic adsorption models.

CHAPTER 2

LITERATURE REVIEW

2.1 Adsorption

2.1.1 Adsorption theory

Adsorption is the assimilation of a gas, liquid, or dissolved substance by the surface of a solid and is physicochemical wastewater treatments process that gaining prominence as a means of producing high quality effluent that is low in dissolved organic compounds. Such waste streams require treatment, conventional methods for the removal of heavy metals from wastewater. Adsorption has become a well-established separation technique to remove dilute pollutants as well as offering the potential of regeneration, recovery, and recycling of the adsorbed materials. The adsorption process is different with absorption process. Adsorption is the process by which molecules of a substance, such as a gas or a liquid, collect on the surface of another substance, such as solid. Meanwhile, absorption is the processes by which the molecules are attracted to the surface but do not enter the solid's minute spaces.

2.1.2 Adsorption fundamental

Adsorption on solids is a molecular attraction-driven process in which molecules in a fluid phase are concentrated at the point of contact with a solid. Van der Waals forces, which are physical interactions between a molecule's electrical fields and can result in condensation, generate the attraction. The attraction to the surface is enhanced because foreign molecules prefer to satisfy an imbalance of forces on atoms on the solid's surface compared to atoms within the solid where they are surrounded by atoms of the same kind. The adsorbent is the adsorbate or adsorptive material that

adsorbs onto the solid phase, and the solid is the adsorbent. Adsorbents have a porous structure that allows them to absorb large amounts of water.

2.2 Adsorbent

2.2.1 Definition

Adsorbent is a substance that absorb an adsorbate that has relatively high selectivity towards the adsorbent. Adsorbate will contact adsorbent and bind together in adsorption process. Adsorbent is very important based on its properties and performance for them to be chosen as an adsorbent in reactor column. Mesoporous carbon and Fe3O4 magnetic nanoparticles are commonly used for riboflavin adsorption (Kamran et al., 2014; Konggidinata et al., 2017; Liu et al., 2010; M. Kisler et al., 2001; A. T. Mohd Din et al., 2013)

2.2.2 Mesoporous carbon

Multi-modal carbon mesoporous were used to adsorbed riboflavin synthesized by polyethylene glycol 400(PEG-400). In the research of Mohd Din et al., (2015), adsorption performance was investigated on water-soluble riboflavin at 298, 313 and 323 K. The equilibrium data were fitted to selected non-linear two-parameter adsorption isotherm models (Langmuir, Freundlich and Temkin) and three-parameter adsorption isotherm models (Koble-Corrigan, Redlich-Peterson, Sips and Toth)(A. T. Mohd Din et al., 2015).

Mesoporous (MCM-48) also used to adsorb vitamin b due to its structural stability. (Liu et al., 2010) studied Structurally stable MCM-48 mesoporous silica has been facilely synthesized in basic medium by a new method using mixtures of cationic surfactant CTAB and nonionic surfactant P123 as co-template at an extremely low molar ratio of CTAB to SiO2 (0.125:1) (Liu et al., 2010).

Other article that are using mesoporous are by (Guo et al., 2005) which ordered mesoporous carbon coated with poly (methyl methacrylate) (PMMA) to adsorb the vitamin B12. In this studied, mesoporous carbons CMK-3 and CMK-1 with different pore size distributions were prepared for the adsorption of VB12 from SBA-15 and MCM-48. CMK-3 had larger adsorption capacity than CMK-1. After coating with PMMA, they all exhibited higher adsorption than their initial mesoporous carbons. This is because the adsorption was influenced by surface properties and the pore structure (Guo et al., 2005).

2.2.3 Activated carbon

Activated carbon is a type of carbon that has been processed to make it exceedingly porous, allowing for a high amount of surface area for adsorption or chemical reactions. The pyrolysis of a range of organic materials (e.g. coconut shells, bones, coal, lignite, peat, and wood) in tightly controlled atmospheres produces activated carbon. The porosity of activated carbon and, as a result, its internal surface area, varies according on the kind of material and the pyrolysis circumstances. The presence of oxygen changes the surface of carbon within the porous structure, altering its adsorptive characteristics. (Vadi & Hadipour, 2011)

Various amounts and types of residual metallic impurities, including aluminium, may have been left in the activated carbon depending on the material from which it was made. As water passes through the carbon, these toxins may leak into the water. Adsorbents use a combination of chemical and physical methods to remove organic impurities as well as the compounds that give water its colour, taste, and odour. The most used adsorbent is activated carbon, which is identical to regular charcoal. Activated carbon, on the other hand, is heated and oxidised to make it porous and capable of adsorbing or capturing pollutants in water.

Activated carbon, on the other hand, is heated and oxidised to make it porous and capable of adsorbing or capturing pollutants in water. Not only does activated carbon attract recognised pollutants, but it also attracts naturally dissolved organic materials (much of which is harmless). As a result, continuous monitoring is required to guarantee that the carbon doses are sufficient to adsorb all pollutants. Granular activated carbon (GAC) and powdered activated carbon are the two types of activated carbon that are commonly used (PAC). The particle size and diameter of the two differ physically. In general, activated carbon outperforms ion exchange when it comes to eliminating organic compounds.

2.3 Adsorbate

2.3.1 Definition

Any substance that has adsorbed on a surface is referred to as an adsorbate. Charge transfer happens between the adsorbate and the metal during the adsorption process, resulting in a dipole moment.

Ions, atoms, and molecules from liquids, gases, and dissolved solids adhere to a specific surface in this process. On the adsorbent surface, this forms an adsorbate layer. It is the inverse of absorption, in which a solid or liquid absorbent dissolves the fluid or absorbate. Adsorption can occur in a variety of physical, natural, chemical, and biological systems and is commonly used in industrial applications such as the production of synthetic resins, activated charcoal, and confining, as well as the use of waste heat to generate cold water for air conditioning and other similar processes.

The pharmaceutical business benefits from adsorbate and the adsorption process since it helps extend the neurological exposure of many medications. Aside

from these, adsorption is important in corrosion prevention, polymer adsorption, and a variety of other industrial and biological applications.

2.3.2 Riboflavin

Riboflavin is one of the B vitamins, which are all water soluble. In certain foods, riboflavin is naturally present, added to some food items, and available as a dietary supplement. This vitamin is an essential component of flavin mononucleotide (FMN; also referred to as riboflavin-5'-phosphate) and flavin adenine dinucleotide, two major coenzymes (FAD). These coenzymes play major roles in the production of energy; cellular function, growth, and development; and fat, drug, and steroid metabolism. FAD is necessary for the conversion of the amino acid tryptophan to niacin (sometimes called vitamin B3). Similarly, FMN is required to convert vitamin B6 to the coenzyme pyridoxal 5'-phosphate. Furthermore, riboflavin helps to maintain normal blood levels of homocysteine, an amino acid.

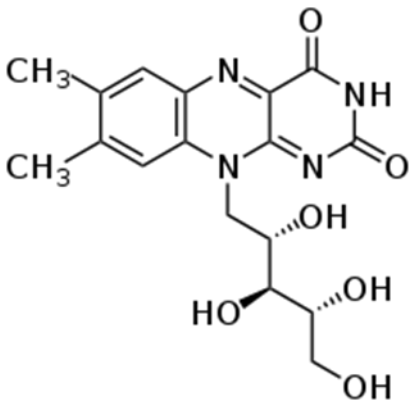

Figure 2.1: Structure of Riboflavin

More than 90 percent of dietary riboflavin is in the form of FAD or FMN; free-form and glycosides or esters compose the remaining 10 percent. In the proximal small intestine, much of the riboflavin is absorbed. The body consumes small amounts of single-dose riboflavin above 27 mg and stores only small amounts of riboflavin in the

liver, heart, and kidneys. They are either not absorbed as excess quantities are ingested or the minimal amount that is absorbed is excreted in urine.

Bacteria in the large intestine produce free riboflavin that can be absorbed by the large intestine in amounts that depend on the diet. More riboflavin is produced after ingestion of vegetable-based than meat-based foods.

Riboflavin is yellow and naturally fluorescent when exposed to ultraviolet light. In addition, ultraviolet and visible light will inactivate riboflavin and its derivatives easily. Long-term light therapy to treat jaundice in newborns or skin disorders may lead to riboflavin deficiency because of this sensitivity. The risk of riboflavin loss from exposure to light is the reason why milk is not typically stored in glass containers.

Riboflavin status is not routinely measured in healthy people. A stable and sensitive measure of riboflavin deficiency is the erythrocyte glutathione reductase activity coefficient (EGRAC), which is based on the ratio between this enzyme's in vitro activity in the presence of FAD to that without added FAD. The most appropriate EGRAC thresholds for indicating normal or abnormal riboflavin status are uncertain. An EGRAC of 1.2 or less is usually used to indicate adequate riboflavin status, 1.2–1.4 to indicate marginal deficiency, and greater than 1.4 to indicate riboflavin deficiency.

Another widely used measure of riboflavin status is fluorometric measurement of urinary excretion over 24 hours (expressed as total amount of riboflavin excreted or in relation to the amount of creatinine excreted). Because the body can store only small amounts of riboflavin, urinary excretion reflects dietary intake until tissues are saturated. Total riboflavin excretion in healthy, riboflavin-replete adults is at least 120 mcg/day; a rate of less than 40 mcg/day indicates deficiency. This technique is less

accurate for reflecting long-term riboflavin status than EGRAC. Also, urinary excretion levels can decrease with age and increase with exposure to stress and certain drugs, and the amount excreted strongly reflects recent intake.

2.3.3 Application of riboflavin

As mentioned earlier, riboflavin is vitamin B2 and it is widely uses in pharmaceutical industry for medication purposes. Riboflavin can be taken by mouth to prevent low levels of riboflavin (riboflavin deficiency) in the body, for various types of cancer, and for migraine headaches. It is also taken by mouth for acne, muscle cramps, burning feet syndrome, carpal tunnel syndrome, and blood disorders such as congenital methemoglobinemia and red blood cell aplasia. Some people use riboflavin for eye conditions including eye fatigue, cataracts, and glaucoma.

Some people also take riboflavin by mouth to maintain healthy hair, skin, and nails, to slow aging, for canker sores, multiple sclerosis, memory loss including Alzheimer's disease, high blood pressure, burns, liver disease, and sickle cell anemia.

2.4 Application of Model

2.4.1 Thomas Model

Thomas Model is based on the assumption that the process follows Langmuir kinetics of adsorption-desorption with no axial dispersion. It describes that the rate driving force obeys the 2nd order reversible reaction kinetics.(Chowdhury et al., 2013) The linearized form of the model is given as:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left(\frac{k_{TH} q_0 m_{adsorbent}}{Q} - k_{TH} C_0 t\right)} \qquad (2.1)$$

where k (mL/mg min) is the Thomas rate constant $q0$ (mg/g) is the equilibrium adsorbate uptake and mm is the amount of adsorbent in the column.

2.4.2 Yoon-Nelson Model

Yoon and Nelson have devised a straightforward model. This model is not only simpler than others, but it also does not require any comprehensive information on the adsorbate, the type of adsorbent, or the physical features of the adsorption bed. The Yoon and Nelson equation for a single component system is represented in equation (2.2), where K_{YN} is the rate constant (1/min), t is the breakthrough (sampling) time, and K_{YN} is the rate constant (1/min) (min). The parameters K_{YN} and for the adsorbate of interest must be determined before theoretical breakthrough curves can be calculated for a single-component system.(Chowdhury et al., 2013)

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left(\frac{k_{AB} N_0 z}{U_0} - k_{BA} C_0 t\right)} \tag{2.2}$$

2.4.3 Adam-Bohart Model

This model was established based on the surface reaction theory, and it assumed that equilibrium is not instantaneous. Therefore, the rate of adsorption was proportional to both the residual capacity of the activated carbon and the concentration of the sorbing species.(Chu, 2020) The mathematical equation of the model can be written as:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left(\frac{k_{AB} N_0 z}{U_0} - k_{BA} C_0 t\right)} \tag{2.3}$$

where C_0 and C_t are the inlet and outlet adsorbate concentrations, respectively, z (cm) is the bed height, U_0 (cm/min) is the superficial velocity. NN_0 (mg/L) is the situation concentration and K_{AB} (L/mg min) is the mass transfer coefficient.

2.5 Riboflavin removal processes

There are few techniques to remove riboflavin that are commonly used in the recent practice.

2.5.1 Liquid-liquid Extraction

Another complementary method for the extraction and purification of vitamins is LLE. This technique is suitable for fat-soluble vitamin. The use of very hazardous volatile chemicals renders this approach experimental and not suited for clinical or routine usage for high throughput analysis, despite its current resurgence. (Hewavitharana, 1996)

2.5.2 Ultrasonic Assisted Extraction

This method is very high efficiency which can save more time and get the higher yield of extraction for vitamin. This technique is enhanced by ultrasonic energy to produce higher efficiency of extraction. UAE are commonly used in recent practice. The easy part as mentioned earlier is where to collect the solvent after ultrasonic process. We just need to filter or centrifugation to get the final product. (Hewavitharana, 1996)

2.5.3 Adsorption using Activated Carbon

The adsorption of pollutants onto the surface of a filter is the basis of activated carbon filtration, which is a widely utilised technology. This approach is effective for eliminating some organics (unwanted taste and odours, micropollutants), chlorine, fluoride, and radon from drinking water or wastewater. Microbial pollutants, metals, nitrates, and other inorganic contaminants, on the other hand, are not affected. The type of activated carbon employed, the water composition, and the operating settings all influence adsorption efficiency. Activated carbon filters come in a variety of shapes

and sizes to meet the needs of households, communities, and businesses. Activated carbon filters are generally simple to instal, but they require energy and professional labour, and they can be expensive owing to the need to replace the filter material on a regular basis. (Kamran et al., 2014)(Zhang et al., 2018)

CHAPTER 3
METHODOLOGY

3.1 Overview of research methodology

This final year project is focus on simulation of riboflavin in aqueous solution using ordered mesoporous carbon. The simulation tool is using Aspen Adsorption V10 to be carried out the simulation. Before running the simulation, all the requirement data must be collected from literature. After getting the data from the simulation. Further calculation needs to plot breakthrough curve and analyse the curve for different variables.

Below is research flowchart of my final year project.

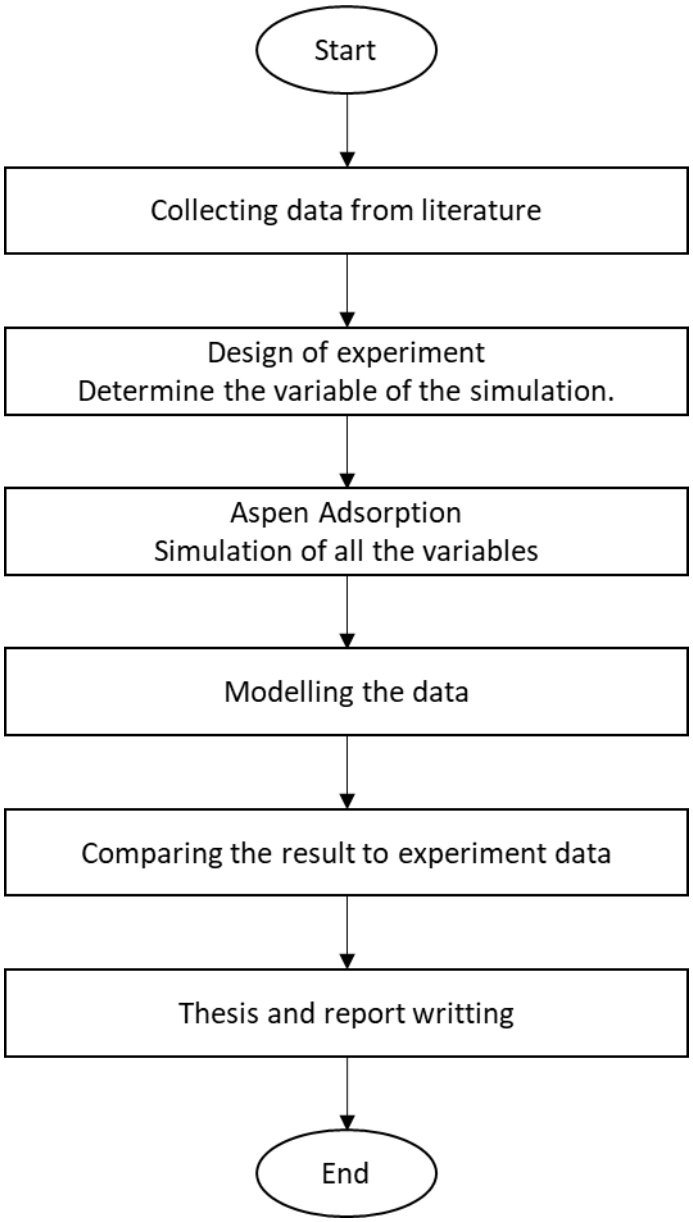

Figure 3.1: Research Flowchart

3.2 Research Methodology Steps

3.2.1 Parameter collection

Before proceeding to run the simulation, all the require parameter and data need to collect from the literature. There are many data need to be extract from the literature to run the simulation. For the adsorption of riboflavin on ordered mesoporous carbon, the equilibrium model used in this study is described by the Langmuir isotherm(Azam T Mohd Din et al., 2009). Langmuir's model is expressed in equation:

$$q_e = \frac{q_{max}.k_L.C}{1 + k_L C} \quad (3.1)$$

$$w_i = \frac{IP_1.IP_2.C}{1 + IP_2.C} \quad (3.2)$$

The equation on the left side is the general form of Langmuir isotherm, while on the right side is the form that Aspen Adsorption® presents this isotherm. Where, qe and wi are the amount of solute removed per unit mass of adsorbent, in unit of mg/g and kmol/kg respectively. qmax and IP1 are the maximum adsorption of the solid phase in monolayer, in unit of mg/g and kmol/kg respectively. k_L and IP2 are the energy constant related to the heat of adsorption, in unit of L/mg and m^3/kmol respectively.

Table 3-1: Properties taken from the literature.

Properties	Value	Units
Total surface area	940	m^2/g
Micropore area	433	m^2/g
Total pore volume	1.54	cm^3/g
Micropore volume	0.214	cm^3/g
Average pore width	6.5	Nm
qmax	61.34	mg/g
K_L	2.15	L/mg
Molecular weight RF, M	376.36	g/mol

By using all the data extract from literature, isotherm parameter IP1 and IP2 can be calculated using equation. Which are M is stand for molecular weight for riboflavin.

$$IP_1 = \frac{q_{max}}{1000M} \quad (3.3)$$

$$IP_2 = 1000 k_L M \quad (3.4)$$

Then, we need to determine the adsorbent properties and bed properties. All the properties we need are to input the properties before running the simulation. These data are to calculate the input parameter for adsorbent and bed. Below is all the equation needed to calculate the adsorbent properties and bed properties.

$$Adsorbent\ porosity, \varepsilon_p = \frac{pore\ volume\ \left[\frac{cm^3}{g}\right]}{particle\ density\ \left[\frac{g}{cm^3}\right]} \tag{3.5}$$

$$Tortuosity, \tau = \varepsilon_p + 1.5\left(1 - \varepsilon_p\right) \tag{3.6}$$

All these equations were used to calculate the properties for adsorbent and bed. All the sample calculation are attached in appendix excel file attached. all the properties calculated are show in the table below:

Table 3-2: Calculated parameter for simulation

Properties	Value	Unit
Isotherm parameter 1	0.000163	kmol/kg
Isotherm parameter 2	809.174	m^3/kmol
Adsorbent porosity, Ɛp	0.7722665	-
Bed porosity, Ɛb	0.381944	-
Bulk density, ρb	1.3171	g/cm3
Tortuosity, τ	4.882684	-
Solid density	0.779221	g/cm3

3.2.2 Mass transfer coefficient calculation

The global mass transfer coefficient (K_i) and its corresponding resistance are presented in Eq. (3.7) (Tavan et al., 2019).

$$\frac{1}{K_i} = \frac{R_P}{3k_{fi}} + \frac{R_p^2}{15\varepsilon_p D_p} \tag{3.7}$$

Where, the effective pore diffusivity coefficient (D_p) was estimated using the following correlation (Tavan et al., 2019).

$$\frac{1}{D_p} = \tau_p \left(\frac{1}{D_m} + \frac{1}{D_k}\right) \tag{3.8}$$

The molecular diffusion coefficient (D_m) was estimated using the following correlation for nonelectrolytes in an infinitely dilute solution (Wilke & Chang, 1955).

$$D_m = 7.4 * 10^{-8} \frac{(\alpha_A M_s)^{0.5} T}{\eta_s V_m^{0.6}} \tag{3.9}$$

In Eq. (3.9), D_m is in $cm^2\ s^{-1}$, M_s is molecular weight of solvent ($g\ mol^{-1}$), T is temperature (K), η_s is the dynamic viscosity of solvent ($kg\ m^{-1}\ s^{-1}$), α_A is the association factor of solvent, and V_m is solute molar volume at its normal boiling point ($cm^3\ mol^{-1}$). For acetaminophen, V_m might be estimated from the linear regression obtained by Fuerst et al. (Fuerst et al., 2015) at 693.2 K.

$$\ln (V_m) = 6.844x10^{-4}T + 4.596 \tag{3.10}$$

As the ACT solution has two solvents (water and methanol), the average values of M_s, η_s, and α_A were calculate using the Eq. (3.11).

$$A = \sum x_i A_i \tag{3.11}$$

Where A is the average property (M_s, η_s, or α_A), and x_i is the molar fraction of solvent i (water, methanol). α_A for water is 2.26, and for methanol is 1.9 (Wilke & Chang, 1955). M_s for water is 18.01 $g\ mol^{-1}$, and for methanol is 32.04 $g\ mol^{-1}$. Finally, η_s at 18 °C for water is 0.001 $kg\ m^{-1}\ s^{-1}$, and for methanol is 0.0006 $kg\ m^{-1}\ s^{-1}$. Both M_s, η_s, T, V_m and α_A are shown in Table S2.

The Knudsen diffusion coefficient (D_k), and the tortuosity factor (τ_p) were estimated by Eqs. (312), and (3.13), respectively (Tavan et al., 2019).

$$D_k = 97 r_p \left(\frac{T}{M_s}\right)^{0.5} \quad (3.12)$$

$$\tau_p = \varepsilon_p + 1.5(1 - \varepsilon_p) \quad (3.13)$$

The external film mass transfer coefficient (k_{fi}) was calculated using Eq. (3.14) (Ohashi et al., 1981).

$$\ln (V_m) = 6.844x10^{-4}T + 4.596 \quad (3.14)$$

$$Sh = \frac{k_f d_p}{D_m} = 2 + 1.58 Re^{0.4} Sc^{1/3}$$

Where Reynolds number and Schmidt number are estimated by Eq. (3.15).

$$Re = \frac{d_p v_s \rho_{sol}}{\eta_{sol}}; \quad Sc = \frac{\eta_{sol}}{\rho_{sol} D_m}; \quad (3.15)$$

Where ρ_{sol} and η_{sol} were calculated using Eq. (3.11) and are shown on the Table 3.3.

Table 3.3: Property table for mass transfer coefficient

Property	Value	Unit
α_A	2.258	-
M_s	18.07	g mol^{-1}
η_s	0.001	kg m^{-1} s^{-1}
T	291.15	K
V_m	159.24	cm^3 mol^{-1}
ρ_{sol}	998.6	kg m^{-3}
η_{sol}	1.05×10^{-3}	kg m^{-1} s^{-1}

3.2.3 Run Simulation

After collecting the data, Aspen Adsorption needed to run the simulation. The simulating environment in ASPEN ADSIM consist of the area where the flow sheet and most of the work such as defining and installing streams, unit operations, columns and sub flow sheets is done. First, we need to input the component list, by selecting the configure properties, it will edit it using aspen Plus for the component input. There are only two components for this simulation, which are riboflavin and water. Then the software will run the property analysis by clicking the run button and it will come back

at original software. At the Aspen Adsorption software, we need to create the diagram by connecting the liquid feed to liquid bed and ending at liquid product. The model simulation is shows in figure below:

. *B1 for liquid feed, B2 for liquid bed and B3 for liquid product

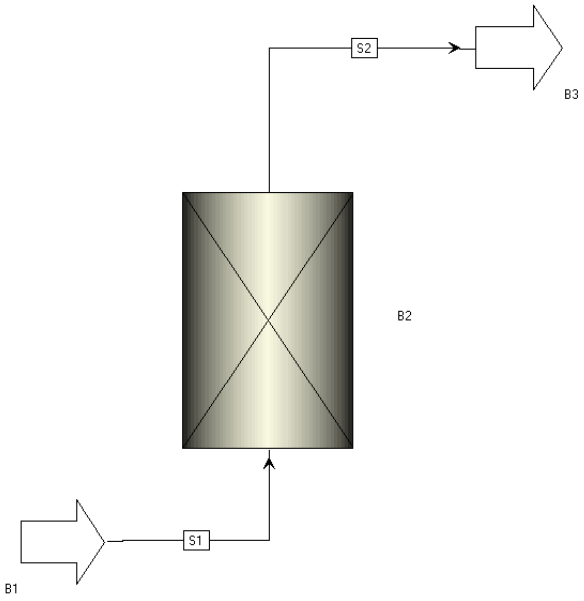

Figure 3.2: Adsorption flowsheet on Aspen Adsorption

Before running the simulation, the software needs us to input all the parameter needed. As the parameter already calculated in Table 3.4, 3.5 and 3.6. We just plug in all the parameter into the software, and all the constants. Then, we run the simulation based on variable of the given experimental data. The variable that needs to run are show in the table below.

3.2.3(a) Changes in Flow rate.

Table 3.4: Variable for Flowrate change

Set	Bed height (cm)	Initial concentration (ppm)	Flow rate (mL/min)
1	2	50	10
2	2	50	20
3	2	50	30

3.2.3(b) Change in bed height

Table 3.5: Variable for Bed Height

Set	Bed height (cm)	Initial concentration (ppm)	Flow rate (mL/min)
1	2	50	10
2	4	50	10
3	6	50	10

3.2.3(c) Change in initial concentration

Table 3.6: Variable for initial concentration

Set	Bed height (cm)	Initial concentration (ppm)	Flow rate (mL/min)
1	2	50	10
2	2	100	10
3	2	200	10

After the software run the simulation. The result data need to be collected at the product icon in result tab. The result shows in table and we transfer the data into excel file.

3.2.4 Result calculation

The raw data for the simulation was collected and sort to get the desired data at time of breakthrough. To make discussion based on the data. We are modelling the data into 3 different model which are Thomas Model, Yoon-Nelson Model and Bohart-Adams Model. All the data were calculate using specific equation based on the model. This is to study the analysis of the breakthrough curve based on different dynamic model.

Sorting data was done by selecting the time taken for the adsorption of the Riboflavin until the data reach the breakthrough time. Then the data were divided by initial concentration to be in concentration ratio, C/C_o. To linearise the data, we

need to further calculate the data into $\ln(C/C_o - 1)$. Graph were plotted $\ln(C/C_o - 1)$ against time. The gradient and the intercept for the graph are taken to calculate the parameter for Thomas Model (k_{Th} and q_e).

3.2.5 Comparison of simulation result and experimental results

The results of the experimental and simulation breakthrough curves were compared using two different error functions (Hokkanen et al., 2018; Lucas et al., 2004).

Sum of squared errors (SSE)

$$SSE = \sum_{i=1}^{n} (x_{i,cal} - x_{i,meas})^2 * 100 \quad (3.16)$$

Absolute average deviation (AAD)

$$AAD = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{x_{i,meas} - x_{i,cal}}{x_{i,meas}} \right| \quad (3.17)$$

Where $x_{i,meas}$ are the experimental C/C_i values, $x_{i,cal}$ corresponds to the C/C_i values obtained from the simulator, and n represents the total amount of data. Finally, the two breakthrough curves (experimental and simulator), were compared using the coefficient of determination R^2 . (Hokkanen et al., 2018).

$$R^2 = 1 - \frac{\sum_{i=1}^{n} (x_{i,cal} - x_{i,meas})^2}{\sum_{i=1}^{n} (x_{i,meas} - \bar{x})^2} \quad (3.18)$$

Where, $\bar{x}$ is the average of the experimental C/C_i values.

CHAPTER 4
RESULT AND DISCUSSION

4.1 Comparison of the result with experiment data

4.1.1 Effect of Feed Flowrate

First study is based on different flowrate used to simulate the riboflavin adsorption. the adsorption simulation was carried out at different flow rate of 10, 20 and 30 mL/min. The effect of feed flow rate on the adsorption of RF on MC4-400 was investigate by varying the feed flow rate (10, 20 and 30 mL/min) with constant adsorbent bed height of 2 cm and inlet adsorbate concentration of 50 mg/L, as shown by the breakthrough curve in Figure. The graph revealed that when the flow rate increased, the front of the adsorption zone quickly reached the top of the column, indicating that the column was saturated early. Longer contact duration and a shallow adsorption zone have resulted from the lower flow rate. A steeper curve with a relatively early breakthrough and fatigue period resulted in reduced adsorption absorption at higher flow rates. The experimental breakthrough curve on figure 4.4, 4.5 and 4.6 is the same. The higher the feed flow rate in the adsorption experiment, the greater the RF adsorption to attain the breakthrough.

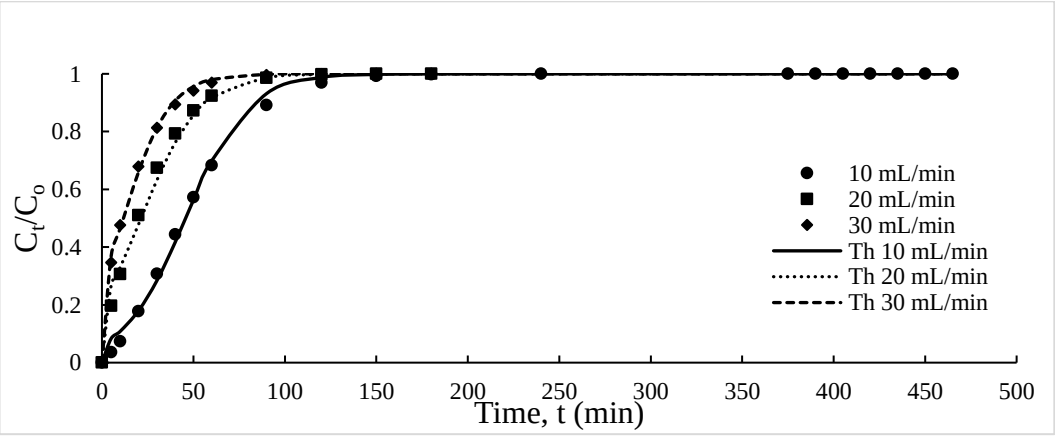

Figure 4.1: Thomas Model for Riboflavin Adsorption at Different Flow Rate (Simulation)

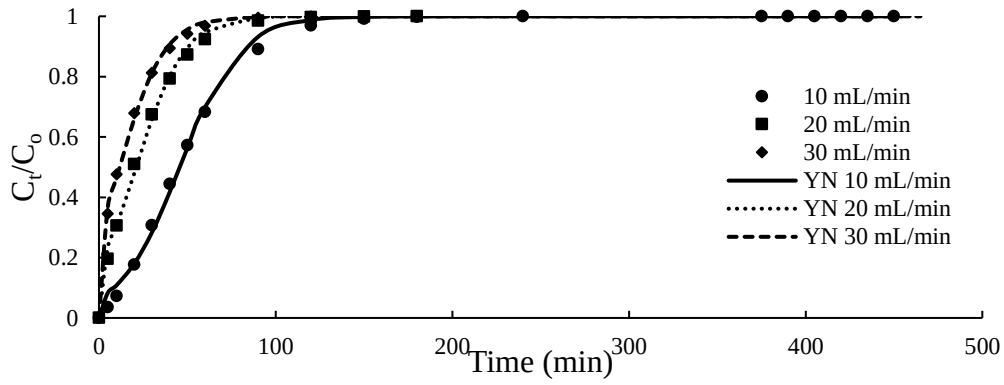

Figure 4.2: Yoon-Nelson Model for Riboflavin Adsorption Simulation at Different Flow Rate (Simulation)

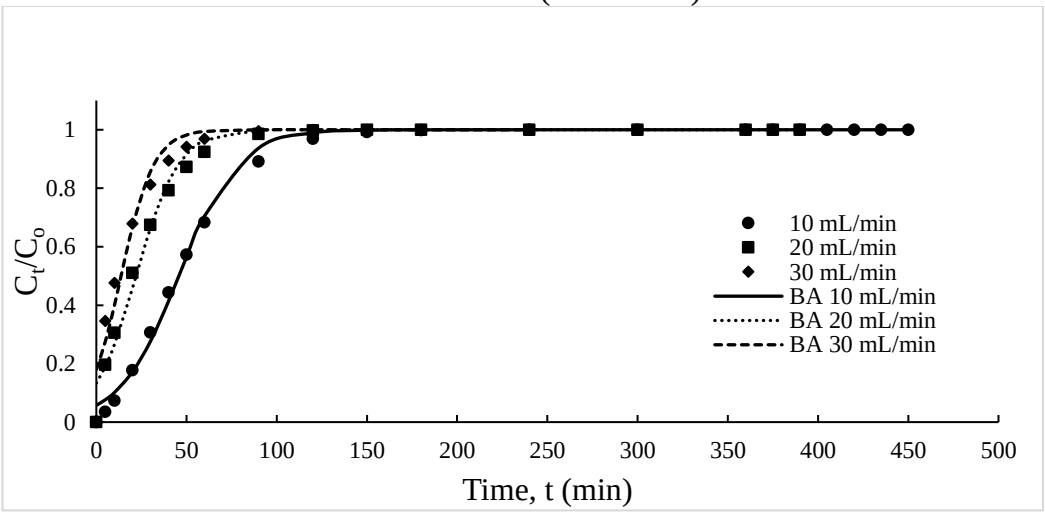

Figure 4.3: Adams-Bohart Model for Riboflavin Adsorption at Different Flow Rate (Simulation)

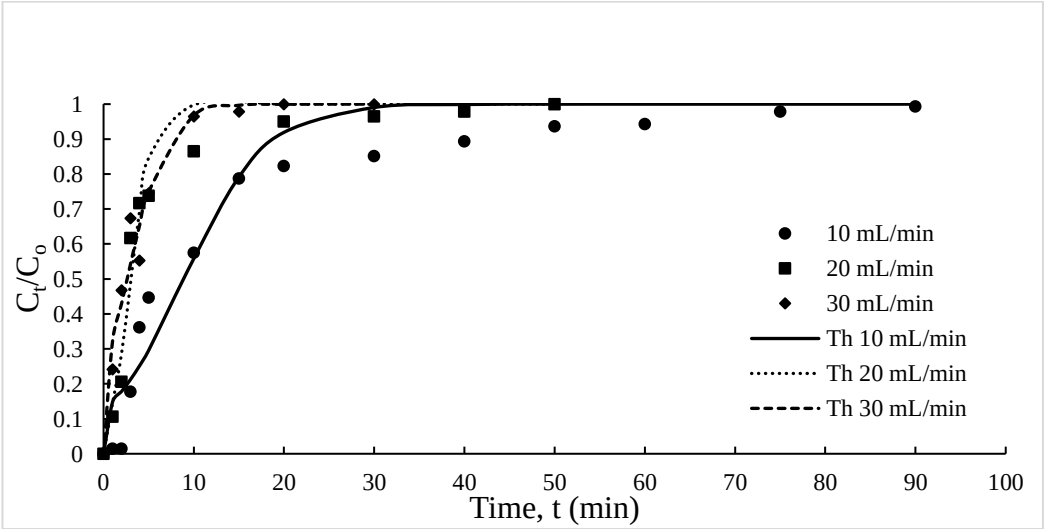

Figure 4.4: Thomas Model for Riboflavin Adsorption at Different Flow Rate (Experiment)

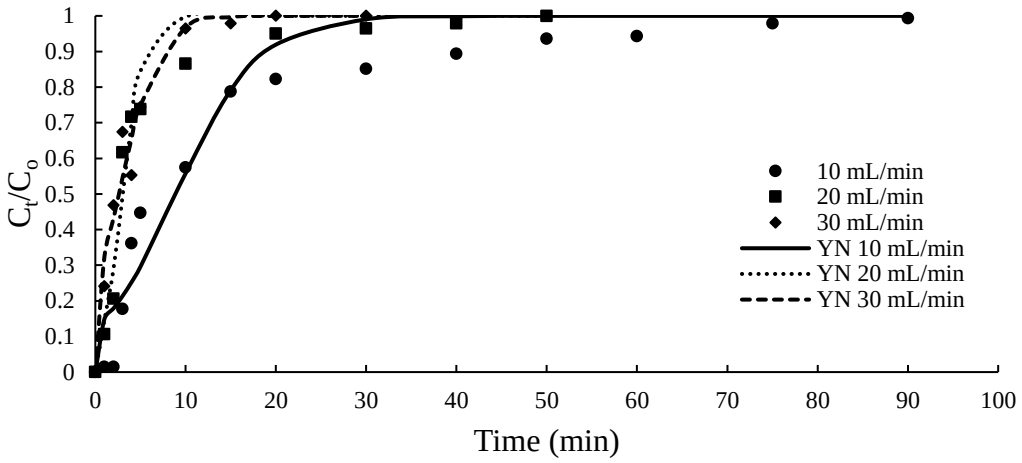

Figure 4.5: Yoon-Nelson Model for Riboflavin Adsorption Simulation at Different Flow Rate (Experiment)

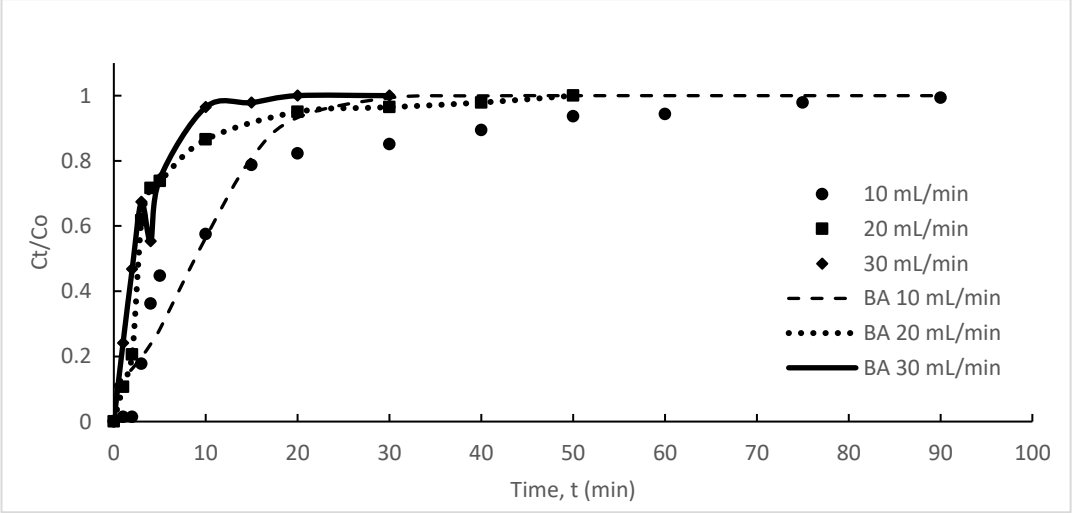

Figure 4.6: Adams-Bohart Model for Riboflavin Adsorption at Different Flow Rate (Experiment)

4.1.2 Effect on Bed Height

Figure 4.7 shows the breakthrough curve obtained for adsorption of riboflavin for three different bed height of 2,4 and 6 cm. Breakthrough curves for adsorption of Riboflavin for different Bed height (concentration 50 mg/L, flow rate 10 mL/min, , temperature (30 ± 1∘C)). and 1.2, 2.4 and 3.6 g of riboflavin mass for 2, 4 and 6 cm of