ASPEN SIMULATION OF METHYLENE BLUE ADSORPTION USING COCONUT SHELL BASED ACTIVATED CARBON

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by

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LIST OF SYMBOLS

Symbol	Description	Unit
C_o	Initial concentration of adsorbate	mg/L
C_t	The effluent of adsorbate at time, t	mg/L
q_o	Prediction adsorption capacity	mg/g
N_o	Prediction adsorption capacity	mg/L
k_{TH}	Thomas model constant	mL/min.mg
k_{YN}	Yoon-Nelson model constant	min^{-1}
k_{AB}	Bohart-Adams model constant	L/min.mg
Q	Inlet flow rate	mL/min
$m_{adsorbent}$	Mass of adsorbent	g
τ	50% adsorbate breakthrough	min
Z	Bed height	cm
U_0	Superficial Velocity	cm/min
t	time	min
P	Pressure	Pa
μ	Dynamic viscosity	kg/m.s
v_z	Superficial velocity of fluid through bed	m/s
D_z	Axial dispersion coefficient	m^2/s
q	Concentration of adsorbate in solid phase	mg/g
C	Concentration of adsorbate in liquid phase	mg/L
ε_b	Bed void fraction	kg/m^3
ρ_s	Solid density	kg/m^3

K_i	Global mass transfer	s^{-1}
D_p	Effective pore diffusivity coefficient	cm^2/s
H_b	Height of adsorbent layer	cm
D_b	Internal diameter of adsorbent layer	mm
E_i	Inter particle voidage	m3 void/ m3 bed
R_p	Adsorbent particle radius	mm
ψ	Factor of the adsorbent particle	-
ε_p	Particle porosity	-

LIST OF ABBREVIATION

CH	Coconut Husk
CS	Coconut Shell
MB	Methylene Blue

ABSTRAK

Metilena Biru (MB) adalah pewarna kationik yang terdapat di dalam air sisa. Dalam projek ini, penjerapan MB dilakukan melalui simulasi dinamik dan data simulasi disahkan dengan hasil eksperimen. Ianya dianalisis berdasarkan pengaruh kepekatan awal, kadar aliran, dan tinggi lapisan pada suhu tetap 303.15 K. Menurut lengkung bulus yang diramalkan, MB dijerapkan dalam jumlah yang lebih besar pada karbon aktif tempurung kelapa dan mempunyai masa tepu yang tinggi pada kepekatan awal yang lebih rendah, kadar aliran yang lebih rendah dan tinggi lapisan yang lebih tinggi dalam semua eksperimen dan simulasi. Lengkung bulus dianalisi menggunakan model Thomas, Bohart-Adams, dan Yoon-Nelson dalam keadaan yang berbeza. Bentuk lelurus model digunakan untuk menyesuaikan data ujikaji dan simulasi. Analisis lelurus regresi untuk kedua-dua data menunjukkan bahawa setiap model mempunyai ciri-ciri yang bererti seperti kapasiti penjerapan (model Thomas), pemalar kadar (model Bohart-Adams) dan 50% bulus (model Yoon-Nelson). Hasil kajian menunjukkan bahawa kedua-dua data eksperimen dan simulasi disesuaikan dengan baik oleh model Thomas, sementara model Bohart-Adams dan Yoon-Nelson juga didapati memadai untuk menjelaskan ciri-ciri dinamik lajur. Nilai R^2 diperoleh untuk data simulasi hampir dengan kesatuan, namun nilai R^2 untuk data eksperimen kurang memuaskan untuk model Thomas. Model yang dicadangkan oleh data simulasi lebih sesuai daripada eksperimen. Bagaimanapun, model kesuluruhanya memuaskan, menyiratkan bahawa andaian ketepatan, persamaan dan model parameter yang dianggarkan sesuai.

ABSTRACT

Methylene Blue (MB) is a cationic dye that has been found in wastewater. In this project, the adsorption of MB through dynamic simulation was carried out and the simulation data were validated with the experimental result. It was analyzed based on the effect of initial concentration, flow rate, and bed height at constant temperature 303.15 K. According to predicted breakthrough curves, MB is adsorbed in greater amounts on coconut shell activated carbon and has high saturation time at lower initial concentration, lower flow rate and higher bed height in all experimental and simulation. The breakthrough curves were analyzed using Thomas, Bohart-Adams, and Yoon-Nelson models under different conditions. The linear form of the models was used to fit the experimental and simulation data. Linear regression analysis for both data indicated that each model has its significant characteristics such as adsorption capacity (Thomas model), rate constant (Bohart-Adams model) and 50% breakthrough (Yoon-Nelson model). The results showed that both experimental and simulation data well represented by Thomas model, while both Bohart-Adams and Yoon-Nelson model were also found adequate for explaining the dynamic behaviour of the column. The R^2 value for simulation data close to unity, however the R^2 for experimental data is poor for Thomas model. The model proposed by simulation data has a better fit than the experimental results. In any case, the overall model is encouraging, implying that the accuracy assumptions, equations, and estimated model parameters are appropriate.

CHAPTER 1

INTRODUCTION

1.1 Background

In the development industry, synthetic dyes are one of the organic compounds have overwhelmed demand and widely used in the industries such as textiles, rubber, paper and cosmetic. Dye has a tendency to stick to the surfaces of materials such as fabrics to impact colour (Edokpayi et al., 2018).Therefore, the application of synthetic chemical dyes in different industries has increased markedly over the years leading to dye-containing industrial effluent discharged into marine ecosystems (Edokpayi et al., 2018). Methylene blue ($C_{16}H_{18}ClN_3S$), MB is a cationic dye mostly applied in chemical indicators and dyes (Kuang et al., 2020).

Processes of printing and dyeing in industries will lead to the producing amount of organic dye wastewater which have characteristics such as high chromaticity, high organic matter concentration and poor biodegradability that will cause water pollution and big concern to the environment (Kuang et al., 2020). It is important to remove methylene blue in wastewater because the acute disclosure to methylene blue may cause an increase in heart rate, shock, vomiting, jaundice and tissue necrosis in human (Amran et al., 2011). Hence, to treat the dye wastewater, adsorption method is chosen to treat dye wastewater as it have high efficiency, low cost, simple operation and insensitive toxic substances (Kuang et al., 2020).

Furthermore, this adsorption method is using activated carbon as an adsorbent as it has large surface area, high adsorption capacity, porous structure and high purity standards and this will causes it a highly valued adsorbent material (Taufik et al., 2007).

Then, lignite, coal and peat and wood and coconut shell are the most common natural substances used as a base material for making activated carbon (Dev Bharadwaj et al., 2016). Coconut shell is used due to its hardness and abrasion resistance when it is converted into activated carbon. In addition, coconut shell has a chemical composition similar to hardwood which mainly composed of lignin and cellulose (Taufik et al., 2007).

1.2 Problem Statement

In reaching the inspiration to be one of the most developed countries, the fourth industrial evolution became a key role in growing the economy. Thus, the increasing of industries such as textile, leather and rubber which used synthetic chemical dyes for various applications resulting in dye-containing industrial effluent discharged into wastewater. Consequently, wastewater becomes one of the major contributors to environmental pollution and is one of the issues concerned nowadays. The presence of dyes in water bodies will cause unpleasant staining of the water surface that will inhibit penetrations of sunlight needed for photochemical and biological activities by aquatic life (Edokpayi et al., 2018). Additionally, the presence of dyes in wastewater will have a variety of organic compounds and toxic substances which are harmful to aquatic organisms and decrease the quality of the water (Hameed et al., 2007).

Methylene blue (MB), widely used in the textile industry needs to be treated in wastewater effluent because it can give eye burns, vomiting and methemoglobinemia (Hameed et al., 2007). In this context, the treatment of wastewater effluent is important because it can have negative impacts on water consumption. One of the effective techniques for dye removal from wastewater is by adsorption using activated carbon. Adsorption has been described as an effective separation process for treating industrial

and domestic effluents (Okeola & Odebunmi, 2010). Activated carbon is selected as adsorbent due to its effectiveness for the removal of a wide variety of organic and inorganic pollutants from aqueous or gaseous media (Rivera-Utrilla et al., 2011). Coconut shell activated carbon has been chosen as adsorbent while the adsorbate selected was methylene blue solution for the process. The adsorption of methylene blue is determined via the dynamic simulation of the adsorption column using Aspen Adsorption V10. For the simulation purpose, the adsorbent and adsorbate are chosen, and some parameters are manipulated for breakthrough curve analysis.

1.3 Objectives

The aim of this final year project is:

1. To perform the simulation using Aspen Adsorption V10 on different parameters.
2. To analyse the fixed bed adsorption data with the dynamic model.

CHAPTER 2

LITERATURE REVIEW

2.1 Literature Review

2.1.1 Adsorption

Adsorption is characterized as a surface accumulation of adsorbate on the adsorbent. The adsorbate is the solute retained on the solid surface in adsorption processes and the solid on which it is retained is called an adsorbent. Then, a solution containing absorbable solute encounters a solid with a highly porous surface structure, liquid-solid intermolecular forces of attraction cause some of the solute molecules from the solution to be concentrated on the solid surface. This phenomenon of an adsorbed phase having a different composition from the bulk fluid phase becomes the basis of separation by adsorption technology (Nageeb, 2013).

2.1.2 Type of adsorption method

In adsorption, there are two types of adsorption methods which are chemisorption and physisorption and this depends on the strength of the interaction between substrate and adsorbate (Sims et al., 2019). Firstly, when adsorbate becomes covalently bound to the substrate by sharing or transferring electrons with interactions that are usually two orders of magnitude stronger than that of physisorbed species, chemisorption occurs. On the other hand, physisorption is a general term describing all weak electrostatic interactions including Van Der Waals interactions, dipole-dipole, and London forces. All these bonds are considered the weakest of interactions and can be broken easily (Sims et al., 2019).

2.1.3 Activated Carbon

Activated carbon is widely used as an adsorbent for adsorption process. However, the commercially available activated carbon is expensive, therefore activated carbon acquired from industrial and agricultural waste rich in carbonaceous materials such as coconut shell is chosen as adsorbent (Edokpayi et al., 2018). Moreover, this biomass can be obtained in low cost, renewable and abundantly available (Bello & Ahmad, 2012). In Malaysia, coconut (*Cocos nucifera*) is one of the main industrial crops with 142,000 ha of planted land. Besides, the conversion coconut shell (CS) into activated carbon also provide advantages that can help in reducing the cost of waste disposal and give a potentially cheap alternative to existing commercial activated carbon (Bello & Ahmad, 2012).

Activated carbon from the CS is efficiently adsorbed MB dye from an aqueous solution. Then, it is found the monolayer adsorption capacity to be 222.0 mg/g and fitted with Langmuir isotherm. The feasibility of adsorption of MB dye on agricultural solid waste have good adsorption capacities (Taufik et al., 2007). A study from Amran et al., (2011) proved that the mixture of agricultural waste (MAW) consisted of empty coconut bunch, banana stalk, coconut frond, oil palm frond and bamboo leaf as adsorbent is prepared without using the chemical or physical treatments gives the increasing amount of MB with increasing in the initial MB concentration from 21.49 mg/g to 87.55 mg/g with an increase dye concentration 50 mg/l to 300 mg/l. This is also due to the initial concentration MB that provides a driving force to overcome all mass transfer resistance also enhance the adsorption process.

AL-Aoh et al., (2014) provided a comparative analysis on the performance of activated carbon from coconut husk and commercial activated carbon for MB

adsorption in a batch system. It was observed the efficiency of MB removal from coconut husk (CH) adsorbent is higher compared to commercial activated carbon. This is because the CH has a higher surface area which is 5435 m^2/g compared to commercial activated 1061 m^2/g , larger pore diameter 29.76 compared to commercial activated carbon 21.06 A, higher mesopore percentage 63.418 % compared to commercial activated carbon, 41.32 % which able it more effective in adsorbing dye.

Referring to Taufik et al., (2007), in preparing the CS activated carbon, produced char is impregnated with an equivalent weight of potassium hydroxide at an impregnation ratio of 1:1. Then, to unclog the pores from tar and other chemical residues, activated char is cooled to room temperature under nitrogen influence and washed a few times with hot deionized water and hydrochloric acid (0.01M). Besides, the adsorption capacity at equilibrium is increased from 99.38 mg/g to 227.0 mg/g by increasing the initial MB concentration from 100-500 mg/l.

2.1.4 Breakthrough Curves

Breakthrough curve is defined as the movement of the mass transfer zone (MTZ). The mass transfer zone travels forward across the adsorbent bed as the activated adsorbents becomes exhausted over time. When the mass transfer zone moves forward, it leaves the contaminants-saturated area of the adsorbent behind. Therefore, the mass transfer zone's edge reaches the column's end and breakthrough occurs(Chowdhury et al., 2015). In order to study the breakthrough curve in fixed-bed column, the effects of initial concentration, feed flow rate and bed height were investigated in this work.

A finding from Man et al., (2015) found that the MB adsorption per unit adsorbent decreased with increases in the flow rate at constant bed height. Then, it observed that as column bed height increased from 10 to 25 cm, the breakthrough time, saturation time and adsorption capacity of MB onto CH increased slightly. This is owing

to the adsorbent's increased surface area, which resulted in a longer contact time with the MB solution. Besides, Edokpayi et al., (2018) studied the removal of MB in aqueous solution using activated carbon from CS in their article. According to their findings, the percentage removal of MB decreases from 38% to 6% as the initial concentration of MB increases from 50 to 300 mg/L. Furthermore, the observed trend could be explained by the fact that when concentration increases, the number of MB molecules that can attach to the adsorbent particle is limited.

2.1.5 Breakthrough Curve Modelling

Mathematical correlations for adsorption in a fixed-bed column are based on the assumptions of axial dispersion, external mass transfer, intraparticle diffusion and nonlinear isotherms.

2.1.5(a) Thomas Model

The hypothesis of the Thomas model postulated on the assumption of Langmuir kinetics of adsorption-desorption that rate driving forces follow second-order reversible reaction kinetics. Next, for sorbate-sorbent interactions, this model assumes that there is no axial dispersion. Furthermore, according to this model, the adsorption rate is maintained by the surface reaction between adsorbate and the unused capacity of the adsorbent (Patel, 2019).

The linearized expression developed by Thomas model is given by:

$$\ln\left(\frac{C_o}{C_t} - 1\right) = \frac{k_{TH} q_o m_{adsorbent}}{Q} - k_{TH} C_o t \qquad (2.1)$$

Where, C_o is the initial concentration of MB (mg/L), C_t is the effluent MB concentration at time t (min), k_{TH} is Thomas model constant (mL/min.mg), q_o is prediction adsorption capacity (mg/g), $m_{adsorbent}$ is the mass of adsorbent (g) and Q is the inlet flow rate (mL/min)

2.1.5(b) Yoon-Nelson Model

Yoon-Nelson presented a simple theoretical assumption that ignores properties of adsorbate, type of adsorbent and any physical characteristics of the adsorption bed. Furthermore, according to this model, the decreasing rate of adsorption is directly proportional to adsorbate adsorption and breakthrough on the adsorbent (Patel, 2019). The linearized expression developed by the Yoon-Nelson model is given by:

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = k_{YN}t - \tau k_{YN} \qquad (2.2)$$

Where C_o is the initial concentration of MB (mg/L), C_t is the effluent MB concentration at time t (min), k_{YN} is Yoon-Nelson model constant (min^{-1}), τ is the time required for 50% adsorbate breakthrough (min).

2.1.5(c) Bohart-Adams Model

Bohart and Adams proposed a basic equation for the relationship between C_t/C_0 and time in a continuous system. According to this model, it proposed that rate of adsorption depends upon the concentration of the sorbing species as well as the residual capacity of adsorption (Patel, 2019).

The linearized expression developed by the Yoon-Nelson model is given by:

$$\ln\left(\frac{C_o}{C_t} - 1\right) = \frac{k_{AB}N_oZ}{U_0} - k_{AB}C_ot \qquad (2.3)$$

Where C_o is the initial concentration of MB (mg/L), C_t is the effluent MB concentration at time t (min), k_{AB} is Bohart- Adams model constant (L/min.mg), N_o is prediction adsorption capacity (mg/L), Z is the bed height (cm) and U_0 is the superficial velocity (cm/min).

2.1.6 Aspen Adsorption Simulation

Aspen Adsorption V10 is used to perform simulation of the MB adsorption in fixed bed column by using CS as activated carbon. In this simulation, liquid phase adsorption is chosen as the process for MB removal.

2.1.7 Model assumption

Based on Juela (2020), there are few assumptions made during simulating the MB adsorption model. Below are the assumptions listed

- Bed orientation assumed vertical with downward.
- The model was defined as a set of equations for the adsorbent bed layer.
- The equations used are based on the momentum balance, kinetic model, and adsorption isotherm.
- According to literature (Taufik et al., 2007), the adsorption equilibrium is defined by the Langmuir non-linear isotherm.
- The particle bed has a constant cross-section.
- The adsorption system operates under isothermal conditions.

2.1.8 Mathematical model

2.1.8(a) Momentum balance

The adsorption bed is expressed via Carman-Konzeny equation which valid for laminar flows in porous media (Juela, 2020).

$$\frac{\partial P}{\partial z}\frac{2R_p\psi\varepsilon^3{}_p}{v_z(1-\varepsilon_p)} = \frac{-1.5 \text{ x } 10^{-3}\mu\,(1-\varepsilon_p)}{2R_P\psi} \qquad (2.4)$$

Where

P = pressure across the bed (Pa)

ψ = factor of the adsorbent particle

μ = dynamic viscosity

ε_p = particle porosity

v_z = superficial velocity of fluid through bed (m/s)

2.1.8(b) Mass balance

$$-\varepsilon_b D_z \frac{\partial^2 C}{\partial_z{}^2} + \frac{\partial(v_z C)}{\partial_z} + \varepsilon_b \frac{\partial C}{\partial t} + \rho_a \frac{\partial q}{\partial t} = 0 \qquad (2.5)$$

Where

D_z = axial dispersion coefficient (m^2/s)

q = concentration of adsorbate in solid phase (mg/g)

C = Adsorbate concentration in liquid phase(mg/L)

z = distance along the bed (m)

ε_b = bed void fraction

ρ_a = bed bulk density (kg/m^3)

2.1.8(c) Kinetic model

Kinetic model is assumed linear lumped resistance proposed by Gluekauf and Coates. It is based on the LDF model in solid phase which mass transfer phenomena are grouped as a single global factor (Juela, 2020).

$$\frac{\partial q}{\partial t} = K_i\,(q_e - q) \tag{2.6}$$

Where

$q_e = \text{instantaneous equilibriumconcentration}(mg/g)$

K_i = global mass tranfer coefficient

K_i can be estimated using equation:

$$\frac{1}{K_i} = \frac{R_p}{3k_{fi}} + \frac{{R_p}^2}{15\varepsilon_p D_p} \tag{2.7}$$

D_p = effective pore diffusivity coefficient

CHAPTER 3

METHODOLOGY

The simulation of MB adsorption in fixed bed columns using CS activated carbon be conducted through Aspen Adsorption V10. The simulated results will be compared and validated with experimental data obtained from the study by Taufik et al., (2007).

3.1 Research Flowchart

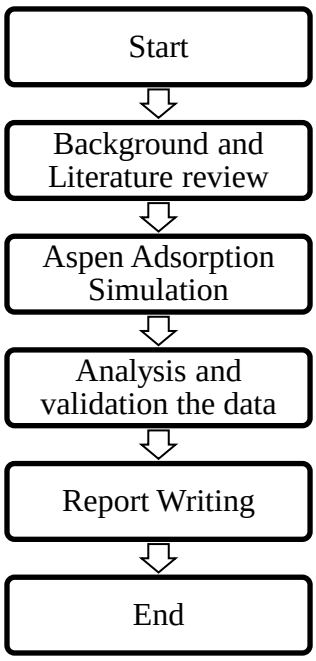


Figure 3.1 Flow diagram for a research project on MB adsorption

3.2 Simulating Environment

Aspen Adsorption simulator is used for modelling and simulation process. The simulation is based on the experimental data published by (Taufik et al., 2007). In this simulation, results obtained represented in the form of concentration breakthrough curves and the effect of parameters on the adsorption breakthrough curves such as flow rate, initial concentration, and bed height.

Table 3.1 Surface area and pore volume properties of CS850A provided by (Taufik et al., 2007)

Properties	Adsorbent (CS850A)
Total surface area (m^2/g)	1026.0
Micropore area (m^2/g)	943.2
Mesopore area (m^2/g)	82.5
Total pore volume (cm^3/g)	0.5768
Average pore diameter (nm)	2.249

Table 3.1 illustrates the physical properties of the prepared activated carbon from CS (CS850A) acquired from the experiment that was carried out by (Taufik et al., 2007) that will be used in the simulation.

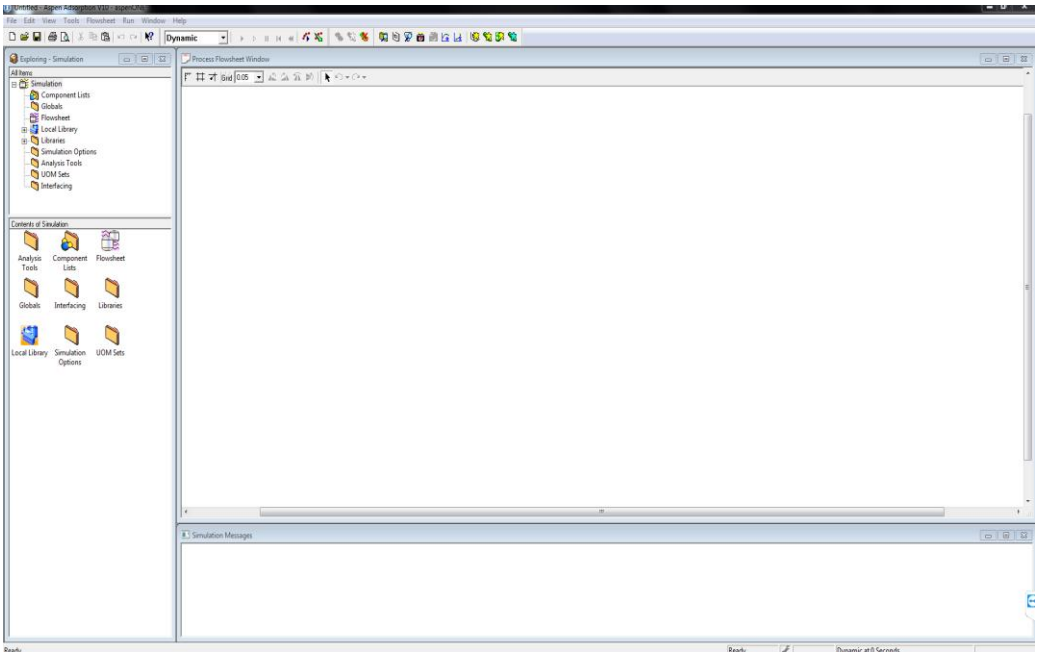


Figure 3.2 The simulation environment of Aspen Adsorption V10

Figure 3.2 illustrates the simulation environment of Aspen Adsorption. In this environment, it consists of the platform where the flowsheet and most of the work such as to define chemistry, create property sets and installing streams, unit operations, columns and sub flow sheets is done.

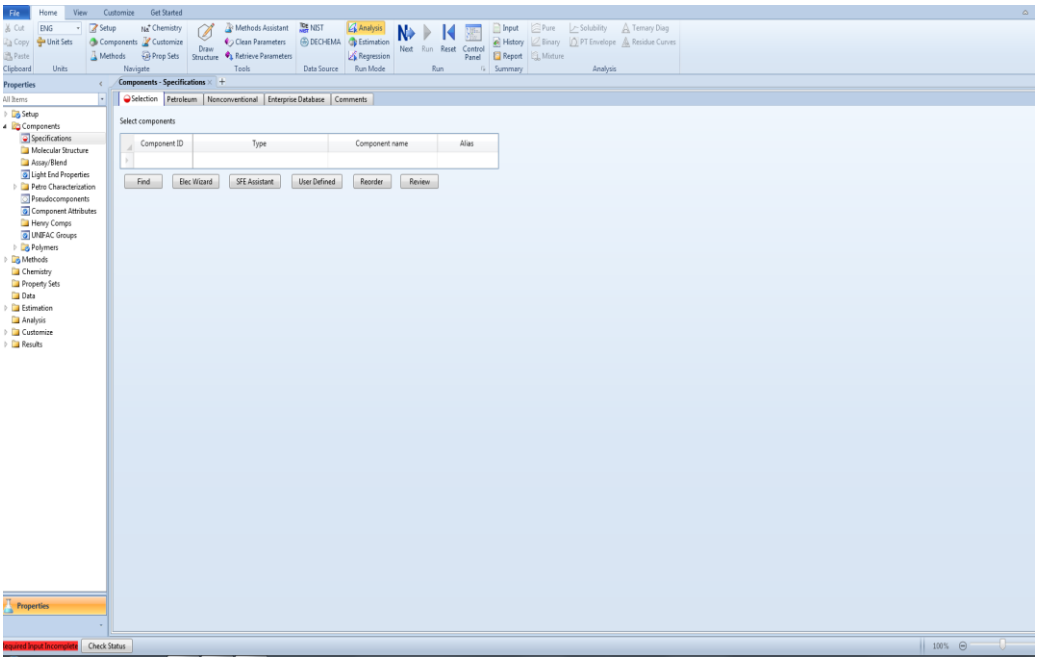


Figure 3.3 The properties plus window to specify components

Within the Properties environment window **Figure 3.3,** this is where the input selection of nomenclature of components is added. Aspen Adsorption will recognize the added components and will fill in the remaining component information.

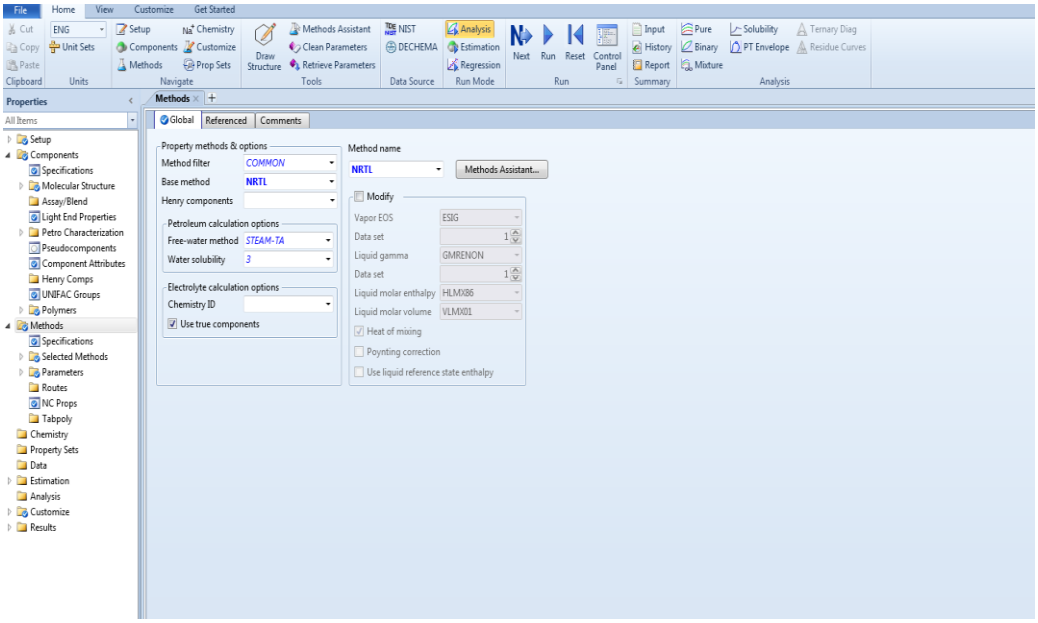


Figure 3.4 Specification of base method (NRTL)

Figure 3.4 shows the Method environment window, the base method NTRL is chosen for the simulations.

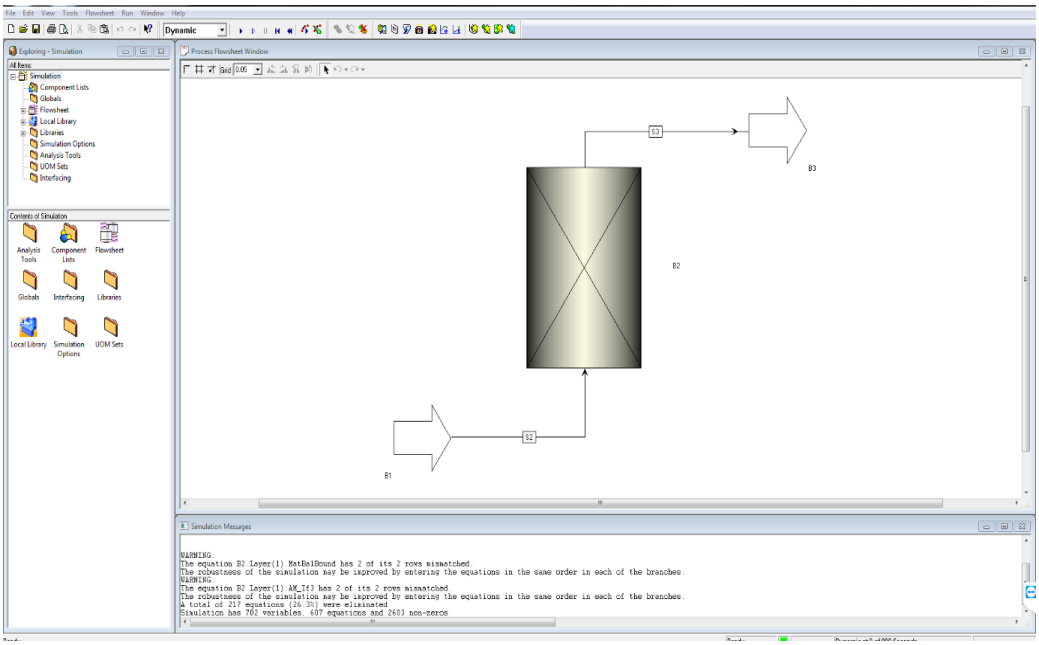
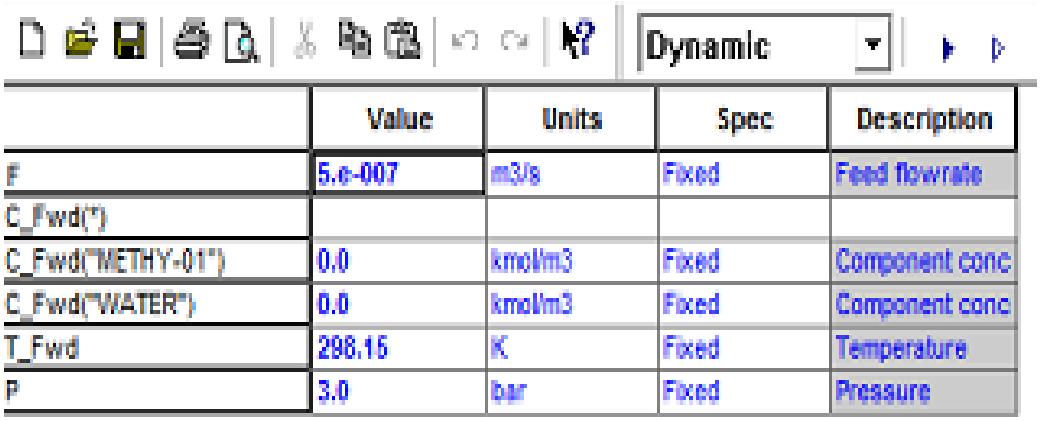


Figure 3.5 Flow of the adsorption process

Flow diagram of the adsorption process is drawn after completed the input parameters. It is drawn using the dynamic tab in the Aspen Adsorption library. The process flowsheet **Figure 3.5** consists of 3 blocks which are feed block, adsorption column block and product block. The specification of feed, bed and product is done afterwards.



Dynamic

	Value	Units	Spec	Description
F	5.e-007	m3/s	Fixed	Feed flowrate
C_Fwd(")				
C_Fwd("METHY-01")	0.0	kmol/m3	Fixed	Component conc
C_Fwd("WATER")	0.0	kmol/m3	Fixed	Component conc
T_Fwd	298.15	K	Fixed	Temperature
P	3.0	bar	Fixed	Pressure

Figure 3.6 Input parameters for feed stream

The input parameters, **Figure 3.6** that need to be specified in the simulation such as flow rate, the concentration of adsorbate, concentration of solvent, temperature, and pressure of the adsorption process.

	Value	Units	Spec	Derivative	Description
C(1,")					
C(1,"METHY-01")	0.0	kmol/m3	Intial	0.0	Bulk concentration
C(1,"WATER")	0.0	kmol/m3	Initial	0.0	Bulk concentration
W(1,")					
W(1,"METHY-01")	1.e-010	kmol/kg	RateInitial	0.0	Solid I_Loading
W(1,"WATER")	1.e-010	kmol/kg	RateInitial	0.0	Solid I_Loading

Figure 3.7 Input parameters for product stream

The input parameters as shown in **Figure 3.7** that need to be specified in the simulation such as bulk concentration of adsorbate and solvent.

	Value	Units	Description
Hb	1.0	m	Height of adsorbent layer
Db	1.0	m	Internal diameter of adsorbent layer
Ei	0.4	m3 void/m3 bed	Inter-particle voidage
RHOs	1000.0	kg/m3	Solid density
MTC(*)			
MTC("METHY-01")	1.0	1/s	Constant mass transfer coefficients
MTC("WATER")	1.0	1/s	Constant mass transfer coefficients
IP(*)			
IP(1,"METHY-01")	1.0	n/a	Isotherm parameter
IP(1,"WATER")	1.0	n/a	Isotherm parameter
IP(2,"METHY-01")	1.0	n/a	Isotherm parameter
IP(2,"WATER")	1.0	n/a	Isotherm parameter
IP(3,"METHY-01")	1.0	n/a	Isotherm parameter
IP(3,"WATER")	1.0	n/a	Isotherm parameter
Direction	0.0	n/a	Specified flow direction

Figure 3.8 Input parameters for product stream

The input parameters **Figure 3.8** that need to be specified for product stream to run the aspen adsorption simulation such as mass transfer coefficients, isotherm parameter, height of adsorbent layer, internal diameter of adsorbent layer, inter-particle voidage and solid density.

3.3 Determination of Adsorption Model

The Thomas model in linear form is shown as below:

$$\ln\left(\frac{C_o}{C_t}-1\right)=\frac{k_{TH}q_o m_{adsorbent}}{Q}-k_{TH}C_o t \tag{3.1}$$

The Bohart-Adams model in linear form is shown as below:

$$\ln\left(\frac{C_o}{C_t}-1\right)=\frac{k_{AB}N_o Z}{U_0}-k_{AB}C_o t \tag{3.2}$$

The Yoon-Nelson model in linear form is shown as below:

$$\ln\left(\frac{C_t}{C_0-C_t}\right)=k_{YN}t-\tau k_{YN} \tag{3.3}$$

Microsoft Excel Solver function is used to determine the value of constant model that consisting of $k_{TH,}$ k_{AB} , k_{YN}, q_o , N_o and τ. After obtaining constant values for each model, the simulated and experimental results will be fitted to the Thomas, Bohart-Adams, and Yoon-Nelson models. Next, the above equations have not been linearized to get the model's coefficient to reduce the error caused by linearization of the equation.

First and foremost, for the Thomas and Bohart-Adams models the graph of $\ln\left(\frac{C_o}{C_t}-1\right)$ versus t is plotted and the constant value of k_{TH} , k_{AB} , q_o and N_o are used as the initial guess for the Solver iteration. While, for the Yoon-Nelson model, the trial and error for k_{YN} and τ is applied for the initial guess for the Solver iteration. Then, using the Thomas, Bohart-Adams, and Yoon-Nelson mathematical equation with the earlier estimation values for the parameters substituted. The square of normalized error is then calculated using the following equation:

$$\varepsilon^2=\left(\frac{(C/C_0)_{estimated}-(C/C_0)_{data}}{(C/C_0)_{data}}\right)^2 \tag{3.4}$$

The objective cell for the Solver in predicting the value of the constant parameters will be the sum of the squares of normalized error, where the solver minimizing the value of the sum of the squares of normalized error by doing iterations and modifying the parameter values. The Objective Cell in the Solver is the sum of the square of normalized error and set it to "Min". Then, the cell for the tab "By Changing Variable." is set as the cell for the constant parameters and then it will be estimated by the Solver. Afterwards, the “Make Unconstrained Variables Non-Negative” box is then unchecked to make sure that the iterations run and solve. Following the steps outlined before, the coefficient for Thomas, Bohart-Adams and Yoon-Nelson will be calculated.

CHAPTER 4
RESULT AND DISCUSSION

4.1 Model validation

The simulation of MB adsorption model is validated by using the published experimental result for MB removal using CS as the adsorbent. In their experiment, an initial concentration range from 100-500 mg/L was used (Taufik et al., 2007). In the simulation, the effects of flow rate, bed height and initial concentration on the breakthrough curves were investigated. In this work, the breakthrough time is considered at the ratio $C_t/C_0 = 0.1$. **Table 4.1** lists the variable parameters and their ranges. Only one parameter was varied at a time, while the other two remained constant.

Table 4.1 Model parameters values used for simulation

Parameter	Values
Height of adsorbent layer, Hb (cm)	2
Internal diameter of adsorbent layer, Db (mm)	24
Inter –particle voidage, Ei (m^3 void / m^3 bed)	0.375
Adsorbent particle radius, Rp (mm)	0.31875
Solid density, ρ_s (kg/ m^3)	2131
Constant mass transfer coefficients MB, K_i (s^{-1})	0.001607758
Isotherm parameter, IP_1 MB	0.00069395
Isotherm parameter, IP_1 water	0.055
Isotherm parameter, IP_2 MB	15834.2
Isotherm parameter, IP_2 water	0.055

In this work, using the parametric values published by Taufik et al., (2007), the proposed mathematical model for the fixed-bed adsorption column is simulated and

validated. The results obtained using the simulation are compared with the experimental data published by Taufik et al., (2007).

4.2 Effects of initial concentrations on breakthrough curves

The effect of breakthrough curves at initial concentrations of 50, 100 and 200 mg/L at a flow rate of 0.01 L/min, bed height 2 cm at temperature 303.15 K is shown in **Figure 4.1** and **Figure 4.2** For both experimental and simulation data show the breakthrough time is seen to decrease as MB initial concentration increased. Breakthrough curves were scattered, and a breakthrough occurred slowly at lower influent MB concentration.

Next, the breakthrough curves became steeper as the initial concentration increased to 100 and 200 mg/L. These results show that the saturation rate and breakthrough time are affected by changes in concentration gradient. This can be explained by the fact that when the MB concentration increases, more adsorption sites are covered (Han et al., 2009). According to this observation, steeper breakthrough curves indicated the mass transfer zone in the column system is short, and the adsorption process in the fixed bed column is mostly influenced by the intra-particle diffusion kinetic model (Fagbayigbo et al., 2020).

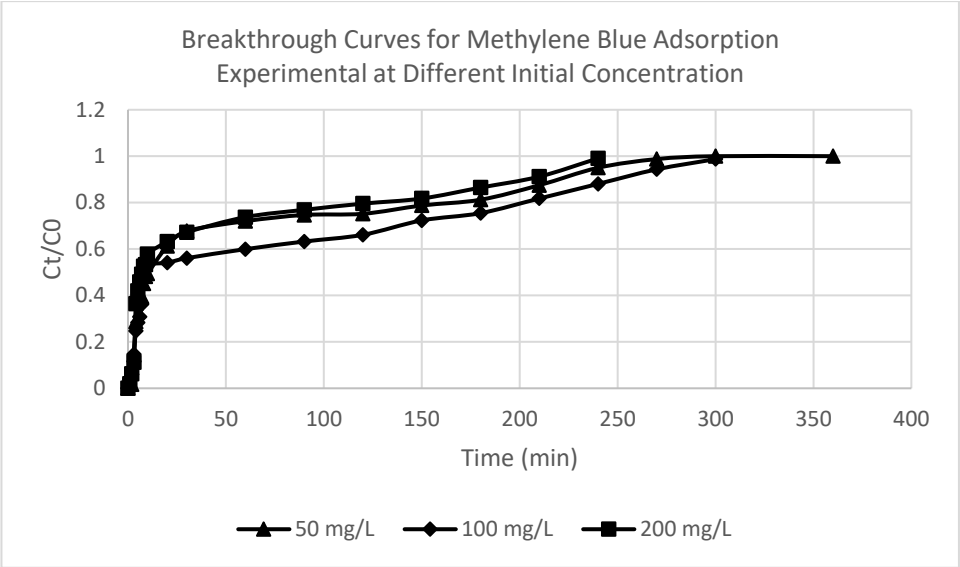


Figure 4.1 Breakthrough curves at different initial concentration on MB adsorption for experimental data

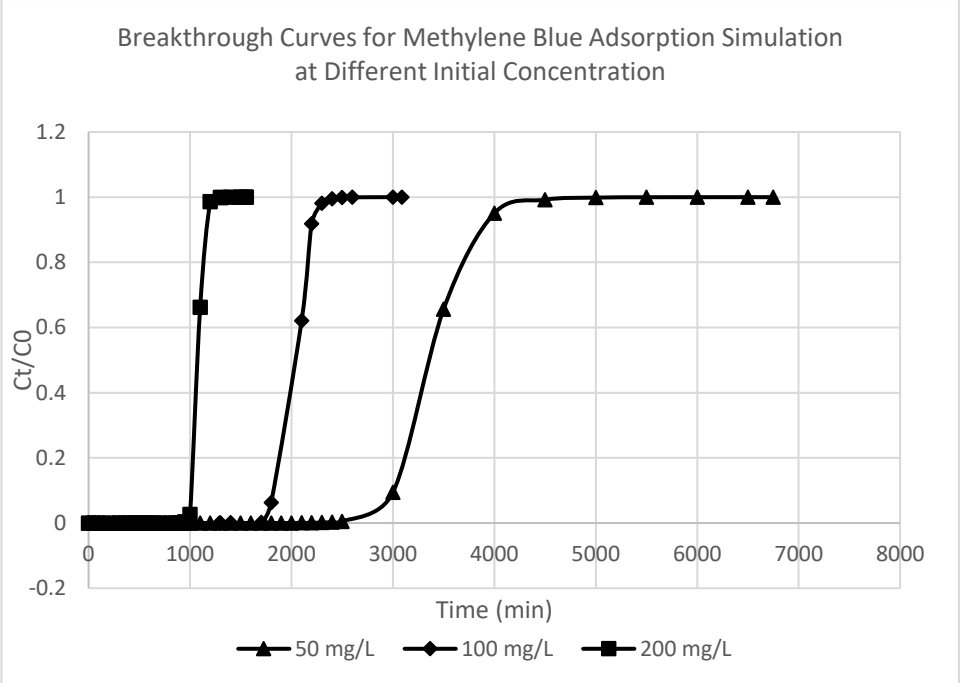


Figure 4.2 Breakthrough curves at different initial concentration on MB adsorption for simulation data

4.3 Effects of flow rate on breakthrough curves

The effect of flow rate on breakthrough curves at various flow rates which are 0.01, 0.02 and 0.03 L/min at an initial concentration of 50 mg/L, bed height of 2 cm and column temperature is maintained at 303.15 K was studied. The breakthrough curves at different flow rates for experimental and simulation data are shown in **Figure 4.3** and **Figure 4.4**.

The breakthrough occurred most rapid with a higher flow rate which is at 0.03 L/min as illustrated in **Figure 4.3** and **Figure 4.4**. This means that at a higher flow rate, the external film mass resistance on the surface of the adsorbent has the least resistance to the influent flow and it tends to shorten the contact time with the adsorbate (Fagbayigbo et al., 2020).

Next, with the decrease in flow rates from 0.03 to 0.01 L/min, the breakthrough time reaching saturation was significantly increased. This is because, at a low rate of influent, MB has more time to make contact with the adsorbent, resulting in more MB molecules being removed in the column (Han et al., 2009).

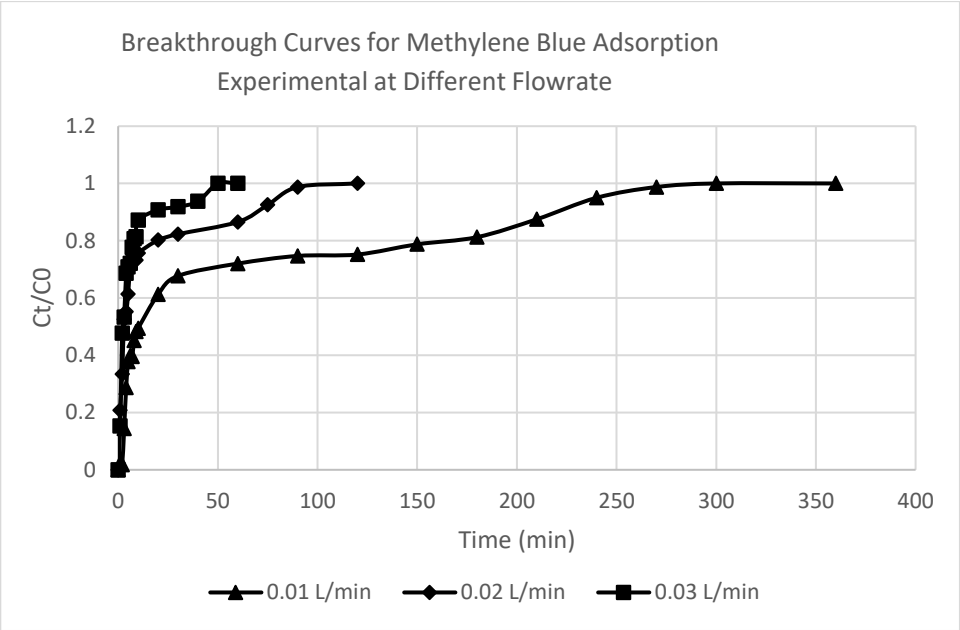


Figure 4.3 Breakthrough curves at different flowrate on MB adsorption for experimental data

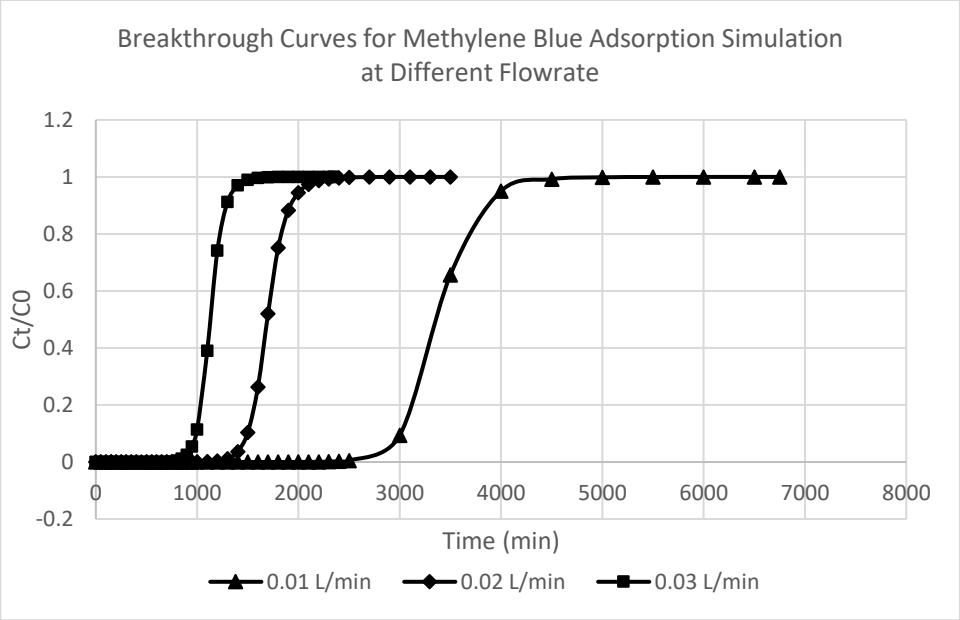


Figure 4.4 Breakthrough curves at different flowrate on MB adsorption for simulation data