MODELLING AND SIMULATION OF CATIONIC DYE ADSORPTION USING MODIFIED METAL-ORGANIC FRAMEWORK-5 (MOF-5)

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by

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LIST OF SYMBOLS

Bi	Biot Number	-
C	Liquid phase concentration at time t	mg/L
C_e	Equilibrium liquid phase concentration at time t	mg/L
C_o	Initial liquid phase concentration	mg/L
D_p	Pore diffusion coefficient	m^2/s
k_f	External mass transfer coefficient	m/s
K_L	Langmuir isotherm constant	L/mg
N	Adsorption rate at time t	mg/s
q	Adsorption capacity	mg/g
q_e	Adsorption capacity at equilibrium	mg/g
q_m	Maximum adsorption capacity	mg/g
R	Radius of particle adsorbent	m
r	Radius of concentration front	m
t	Time	s
V	Volume of liquid phase	L
W	Mass of adsorbent	g
ρ	Adsorbent density	kg/m^3

LIST OF ABBREVIATIONS

BET	Brunauer, Emmett and Teller
IMT	Internal Mass Transfer
MB	Methylene Blue
MO	Methyl Orange
MOFs	Metal Organic Frameworks
MOF-5	Metal Organic Framework 5
MOF-235	Iron Terephthalate
RMSE	Root Mean Squared Errors

PEMODELAN DAN SIMULASI PENJERAPAN PEWARNA KATIONIK MENGGUNAKAN KERANGKA LOGAM-ORGANIK-5 (MOF-5) YANG DIUBAHSUAI

ABSTRAK

Pemodelan dan simulasi penjerapan pewarna kationik dengan menggunakan Kerangka Logam Organik-5 (MOF-5) yang diubah suai telah dikaji. Model matematik dikembangkan berdasarkan model model dwi-rintangan yang termasuk koefisien pemindahan jisim luaran dan koefisien resapan liang yang mengawal proses pemindahan jisim dalam penjerapan kelompok. Perisian MATLAB R2020b digunakan untuk menganggar parameter pemindahan jisim yang merupakan pekali pemindahan massa (k_f) dan pekali penyebaran liang (D_p) dengan memadankan data simulasi dengan data eksperimen dari kajian yang lain. Nilai k_f dan D_p dianggarkan masing-masing 66.8 m/s dan 2.1514×10^{-7} m^2/s. Dengan menggunakan parameter yang diperkirakan, hasil simulasi menunjukkan bahawa model memberikan korelasi yang baik dengan data eksperimen berdasarkan kepekatan awal yang berbeza. Parameter yang dianggarkan digunakan untuk mengkaji penjerapan pewarna dengan menggunakan MOF-5 yang diubah di bawah faktor yang berbeza seperti modifikasi MOF-5, kepekatan pewarna awal, suhu dan jisim adsorben. Disimpulkan bahawa kecekapan penyingkiran pewarna lebih tinggi untuk MOF-5 yang telah diubahsuai ($H_6P_2W_{18}O_{62}$/MOF-5). Bukan itu sahaja kepekatan pewarna awal yang lebih rendah, suhu yang lebih tinggi dan jisim adsorben yang lebih tinggi juga menyebabkan kecekapan penyingkiran pewarna menjadi lebih tinggi.

MODELLING AND SIMULATION OF CATIONIC DYE ADSORPTION USING MODIFIED METAL-ORGANIC FRAMEWORK-5 (MOF-5)

ABSTRACT

Modelling and simulation of cationic dye adsorption by using modified Metal-Organic Framework-5 was studied. Mathematical model was developed based on a two-resistance model which included external mass transfer coefficient and pore diffusion coefficient that controls the mass transfer process in batch adsorption. MATLAB R2020b software was used to estimate the mass transfer parameters which are mass transfer coefficient (k_f) and pore diffusion coefficient (D_p) by matching the simulation data with the experimental data from literature. The value of k_f and D_p were estimated to be 66.8 m/s and 2.1514×10^{-7} m^2/s respectively. By using the estimated parameters, simulation results showed that the model provided good correlation with the experimental data based on different initial concentrations. The estimated parameters were used to study the adsorption of Methylene Blue (MB) by using modified MOF-5 under different factors such as modification of MOF-5, initial dye concentration, temperature and the mass of adsorbent. It was concluded that the dye removal efficiency was higher for modified MOF-5 ($H_6P_2W_{18}O_{62}$/MOF-5). Not only that, the lower initial dye concentration, higher temperature and higher adsorbent mass also result in higher dye removal efficiency.

CHAPTER 1

INTRODUCTION

1.1 Background

Nowadays, dye wastewater is currently produced in many industries since dyes are used in a wide range of industrial applications such as, textile, cosmetic, leather, printing, paper, food and other industries. In all the industries, so far 700,000 tons and 10,000 different types of dyes are produced worldwide annually (Gupta et al., 2011). There are several groups of dyes that can be determine on the basis of their compound structure but the most commonly groups are azo dyes. Dyes are considered hazardous and harmful toward environment because dyes absorb and reflect sunlight in the water, then this will reduce the photosynthetic activity of algae and seriously influences the food chain causing interferes with the growth of aquatic organisms (Fernández et al., 2010).

There are many techniques have been developed for dyes removal from waters or wastewaters to reduce their impact on the environment such as adsorption on inorganic or organic matrices, enzymatic decomposition, decolourization by oxidation processes and photochemicals process. The methods of dye removal from industrial may be divided into 3 main categories which are biological, physical and chemical processes. Each method has the advantages and disadvantages but the adsorption technique is widely used for remove dye from wastewater (Adeyemo et al., 2012).

In adsorption, the selection of suitable adsorbents is very important, since adsorbents have different properties that will affect the adsorption capacity. Recently, the adsorbent with high selectivity towards targeted harmful dyes such as cationic dyes methylene blue (MB) and anionic dyes methyl Orange (MO) have attracted the interest of many researchers due to their great potential in the separation of controlled dyes

and controlled chemicals while treating industrial wastewater. One of the adsorbent that have high selectivity is metal organic framework (MOFs). MOFs have some unique characteristics such as ultrahigh porosity, incredibly large BET surface area, multiple coordination sites, big pore volume that can bring into various applications such as gas separation and storage, sensors, energy storage and so on (Liu et al., 2016).

To predict the performance of adsorbent in industrial scale, the batch adsorption studies in a stirred batch absorber can provide useful information regarding equilibrium and kinetic. In adsorption, there are two resistances occur which is the external liquid film resistance and the resistance in the adsorbent particle. The mass transport within the adsorbent particles is assumed to be a pore diffusion and there is adsorption of the adsorbate into the pores with a co-current solute distributed all along the pore wall (Jena et al., 2003).

1.2 Problem Statement

Most of industries in Malaysia such as food, textile, cosmetics, paper and dye production industries are producing dye wastewater. One of the treatment strategies for efficient removal of dyes from waste-water is by using adsorption. Modified metal organic framework 5 (MOF-5) can be one of the adsorbent to remove the dyes from wastewater. The prediction of the dye adsorption rate by the adsorbent particle is important for evaluating the adsorbent performance in the dye removal process. Thus, modelling and simulation can be carried out to predict the rate of adsorption for dye removal from wastewater by using modified MOF-5. This model also can help to predict the performance of modified MOF-5 to remove dye from wastewater in industrial scale. There are many factors that will influence the rate of adsorption such as adsorbent particle size, mass of adsorbent, initial adsorbate concentration and

volume of adsorbate solution. Therefore, the factors of rate of adsorption can be studied based on the mathematical model prediction of the adsorption rate.

1.3 Research Objective

The objectives of the research are:

- To develop a mathematical model for batch adsorption of cationic dye by using modified Metal Organic Framework 5.
- To solve mathematical model and unknown parameters which provide best fit of the model with experimental data by run the simulation in MATLAB program.
- To study various factors that influence adsorption process such as modification of MOF-5, temperature, initial dye concentration, and mass of adsorbent by run the simulation in MATLAB program

1.4 Scope of Study

There are a few models that can be used to simulate the adsorption of cationic dye by using modified MOF-5. After selecting the model, the mathematical model need to solve and estimate the unknown parameter which provide best fit of the model with experimental data. Then, the simulation-based work was done to simulate the adsorption of cationic dye by using modified MOF-5. The simulation has done by using MATLAB R2020b. Unlike previous experimental works done by other researchers, this work focused solely on a simulation-based approach rather than experimental in order to study the effects of adsorption such as modification of MOF-5, temperature, initial dye concentration, and mass of adsorbent. The simulation results obtained was compared with the experiment data from literature.

1.5 Thesis Organization

Chapter 1 outlines discuss about the general information about the dyes removal by using modified MOF-5, problem statement, objective and study scope of this research. Chapter 2 discusses the literature review regarding the adsorption, metal organic frameworks, adsorption of cationic dyes by using modified MOF-5 and several model that will be selected to do the simulation. Chapter 3 covers the methodology of the research include the overall study structure, theory of the model and the mathematical model development. Chapter 4 present the result and discussion of the simulation including the estimation of parameter. The estimated parameters will be used to study the various factor of adsorption. Then, the results obtained from simulation data will be compared with the experimental data from the literature. The last part of this thesis is Chapter 5 that concludes all finding obtained in this study and recommendation of the research to improve the research.

CHAPTER 2

LITERATURE REVIEW

2.1 Adsorption

There are many techniques to eliminate hazardous substance from aqueous solution such as oxidation, photochemical, electrocoagulation and so on but among this techniques adsorption is widely used in industries because it is highly efficient, inexpensive and simple in operation (Liu et al., 2016). Adsorption is a mass transfer process that involves the accumulation of substances at the interface of two phases, such as, liquid–solid, gas–liquid, gas–solid or liquid-liquid. The material that adsorbing the substance is known as adsorbent, while the substance that being adsorbed is defined as adsorbate (Gisi et al., 2016)

2.2 Adsorption Isotherm

Further studies for analysis of adsorption equilibrium is begin with classification of adsorption isotherm. The most commonly adsorption isotherm equation used is Langmuir and Freundlich isotherm (Kinniburgh, 1986). Even this article published in 1986, this adsorption isotherm are widely used by current researches on the adsorption of dyes from water or waste water by using various sorbent such as MOF-5 (Liu et al., 2016), activated carbon (Malik et al., 2007), bone char (Maria & Mansur, 2016) and sugarcane dust (Ho et al., 2005).

The original Freundlish equation describes adsorption in terms of adsorbate concentration as shown in equation (2.1) (Freundlich, 1906). From the equation, C_e is the concentration of the solution at equilibrium (mg/L), k_f is Freundlich constant (L/g), q_e is the amount of adsorption at equilibrium state and 1/n is an empirical parameter related to adsorption intensity (Liu et al., 2012).

$$\ln(q_e) = \ln(k_f) + \frac{1}{n}\ln(C_e) \quad (2.1)$$

Langmuir isotherm equation was developed by Langmuir (Langmuir, 1916) in equation (2.1) is often used to describe sorption of a solute from a liquid solution as shown in equation (2.2) (Ho et al., 2005). Until now, many publications have been reported to study the equilibrium adsorption using the Langmuir model, especially for liquid phase systems. For liquid system, this equation is derived based on four assumptions which are all adsorption sites are equivalent, monolayer adsorption occur, interaction between adjacent adsorbed molecules are negligible, and all adsorption sites are occupied by solute or solvent molecules. Equation (2.2) shows the Langmuir isotherm equation:

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

where C_e is the equilibrium concentration of adsorbate (mg/L). q_m is the maximum adsorption capacity (mg/g) and K_L is the Langmuir constant (L/g).

2.3 Metal-Organic Frameworks

Metal-organic frameworks (MOFs) is the one of the highly porous materials classes and it's also are unparalleled in their degree of tenability and structural diversity as well as their range of chemical and physical properties. The unique feature of MOFs is their porosity that allows the diffusion of molecules into the bulk structure. Figure 2.1 shows that the MOFs are actually the porous structures constructed from the coordinative bonding between metal ions and organic linkers or bridging ligands (Sharmin & Zafar, 2016).

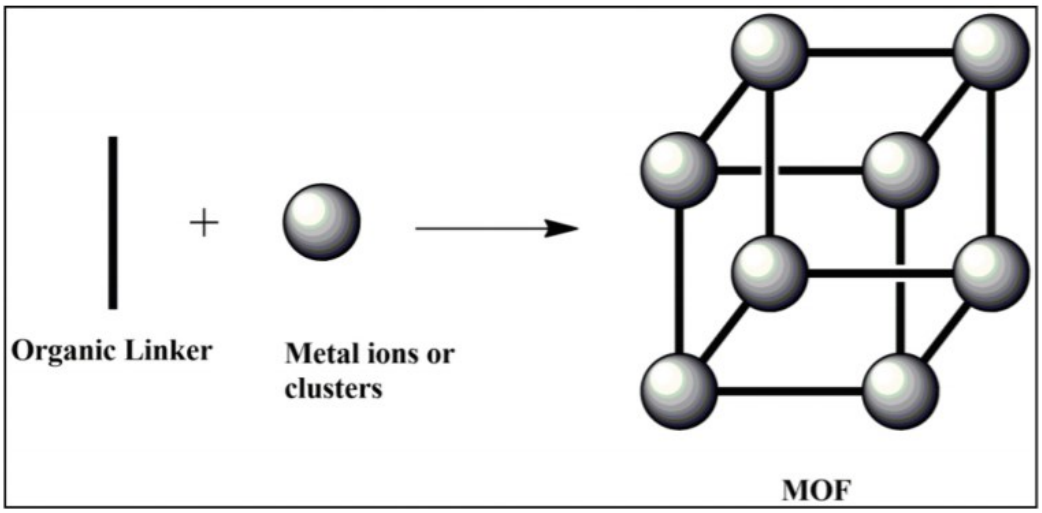


Figure 2.1: Structure of MOFs (Sharmin and Zafar, 2016).

There are several applications of different MOFs such as molecular adsorption and separation, catalysis, sensing, contaminant absorption, drug delivery, and renewable energy. Table 2.1 shows some examples of MOFs and their applications.

Table 2.1: Example of MOFs and their application

MOF	Metal	Organic Linker	Application	References
MIL-101 and MIL-100	Cr	1,4-benzenedicarboxylate moieties or H_3btc	Drug delivery	(Horcajada et al., 2006)
MOF-5 Zn_4	Zn	1,4-benzenedicarboxylate moieties	Methane Storage	(Eddaoudi et al., 2002; Li et al., 1999)
MOF-74, Zn_2 ($C_8H_2O_6$)	Zn	2,5-dihydroxybenzene-1,4-dicarboxylic acid	Adsorption and storage	(Rowsell & Yaghi, 2006)
Cu-BTC(MOF-199)	Cu	Benzene-1,3,5-tricarboxylate	Antibacterial	(Rodríguez et al., 2014)
$H_6P_2W_{18}O_{62}$/MOF-5	Zn	1,4-dicarboxybenzene	Dye adsorption	(Liu et al., 2016)

2.4 Dye Adsorption

There are many techniques have been developed for removal dyes from waters or wastewaters as shown in Table 2.2. Each method has the advantage and disadvantage but the adsorption technique is widely used for remove dye from wastewater. Besides being widely used for dye removal, adsorption also has wide applicability in wastewater treatment industry (Gupta & Suhas, 2009).

Table 2.2:Various method to remove dye from water or wastewater (Santos et al., 2007; Liu et al., 2016; Robinson et al., 2001)

Physical/Chemical Method	Description	Advantage	Disadvantage
Fenton reagents	Oxidation reaction using mainly H_2O_2-Fe(II)	Effective decolourization	Sludge generation
Ozonation	Oxidation reaction using ozone Gas.	No alteration of volume	Short half-life (20min)
NaOCl	Oxidation reaction using Cl+ to attack the amino group	Initial and acceleration of azo bond cleavage	Release of aromatic amines
Activated carbon	Dye removal by adsorption	Can remove variety of dyes	Regeneration difficulties
Photochemical	Oxidation reaction using mainly H_2O-UV	No sludge generation	Formation of by-products
Ion exchange	Ion exchange resin	Regeneration: no adsorbent loss	Not effective for all dyes
MOF-5	Dye removal by adsorption with modification Wells–Dawson acids	fast adsorption rate and selective adsorption ability towards the cationic dyes.	Not effective for all dyes

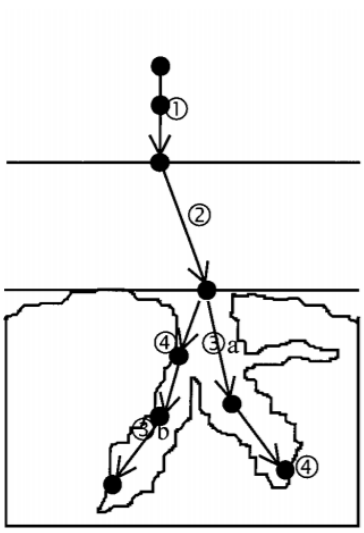
In adsorption, the selection of suitable adsorbents is very important, since adsorbents have different properties that will affect the adsorption capacity. Recently, Metal organic frameworks (MOFs) have attracted much attention due to their potential applications in industries such as gas storage, molecular separations, heterogeneous catalysis, and drug delivery (Sumida et al., 2012). MOFs also have high selectivity towards targeted harmful dyes such as cationic dyes methylene blue (MB) and anionic dyes methyl Orange (MO) (Liu et al., 2016). Not all MOFs is suitable to be made as adsorbent, as reported by Haque et al., 2011. They also reported that iron terephthalate (MOF-235) has been used for dye removal in wastewater and the result shows that adsorption capacities of MOF-235 are much higher than those of an activated carbon. Not only that, Liu et al., (2016) reported that modified MOF-5 also can be use as adsorbent.

Metal organic framework-5 (MOF-5), has come up with the good sorption capacity for gaseous and MOF-5 normally is used as adsorbent for hydrogen adsorption (Saha et al., 2009). Current research show that MOF-5 also can be one of the adsorbent to remove dye from wastewater but need some modification with Wells–Dawson acids $H_6P_2W_{18}O_{62}$. As reported by Liu et al., (2016) the removal rate of $H_6P_2W_{18}O_{62}$/MOF-5 (modified MOF-5) was greater (85%) than MOF-5 , this shown that the MOF-5 need some modification to get high removal rate for dye removal from wastewater

2.5 Adsorption Diffusion Model

Several mathematical models have been proposed to describe adsorption data, which can generally be classified as adsorption reaction models and adsorption diffusion models. This models are used to describe the kinetic process of adsorption. There are four steps representing for the process of adsorption by porous sorbent

particles, which are transport of solutes in the bulk of the solution, external mass transfer of the solute across the liquid film surrounding the adsorbent particles (external or film diffusion), intraparticle transport within the particle, and adsorption of the solutes onto internal surface sites. Figure 2.2 shows the four steps of adsorption (Baup et al., 2000; Lazaridis & Asouhidou, 2003).



Position	Phenomenon	Coefficient
Bulk of solution	① Diffusion/Convection	Fast
Outer layer	② External Mass Transfer	k_f
GAC particle	③a Porous Diffusion	D_p
	③b Surface Diffusion	D_s
	④ Adsorption	Instantaneous

Figure 2.2: The four steps of adsorption (Baup et al., 2000)

Film diffusion, intraparticle diffusion and mass action are involved in typical liquid/solid adsorption. In physical adsorption, mass action for kinetic study can be negligible because mass action is very rapid process. Therefore, the kinetic process of adsorption is always controlled by liquid film diffusion or intrapartical diffusion (Qiu et al., 2009).

2.5.1 Liquid Film Diffusion Model

The meaning of liquid film diffusion is the effect of the presence of the concentration gradient in the regions of bulk phase close to the solid surface. Based on this model, it is assumed that there exists a subsurface region, located near to the surface of the adsorbing particles. The concentration of sorbate in the subsurface region (c_s) is

differs from that in the bulk phase (c). By assuming the volume of this subsurface region (V_s) is very small in comparison to that of the remaining bulk phase and also free molecular flow between the bulk phase and the subsurface region, the equation (2.3) shows the concentration change in the subsurface region on terms of Fick's law (Plazinski, 2010). Where N is the concentration of the sorbate on the solid, m is the mass of applied sorbent and k_s is the external mass-transfer coefficient.

$$\frac{dc_s}{dt} = k_s(c - c_s) - \frac{m}{V_s}\frac{dN}{dt} \tag{2.3}$$

Another model of film diffusion model was proposed by Boyd et al. (1947) and equation 2.3 shows the film diffusion mass transfer rate equation:

$$ln\left(1 - \frac{q_t}{q_e}\right) = -Rt \tag{2.4}$$

where q_t is the amount of adsorbate in the adsorbent at various time, q_e is the amount of adsorbate in the adsorbent at equilibrium and R is the liquid film diffusion constant (min^{-1}). A linear plot of $ln(1-q_t/q_e)$ vs t with a slope –R if the film diffusion is the rate of limiting step (Qiu et al., 2009).

2.5.2 Intraparticle Diffusion Model

The assumption of internal diffusion models is that the diffusion of adsorbate within adsorbent is the slowest step and the adsorption onto the active sites are instantaneous. There are three models that mostly used which are, the Boyd's intraparticle diffusion model, the phenomenological internal mass transfer (IMT) model and the Weber and Morris (W&M) model (Wang & Guo, 2020).

Over the past few decades, Boyd's intraparticle diffusion equation has been used to represent the internal mass transfer processes. Actually, Boyd et al. (1947) developed

the theoretical models for ion exchange kinetics but the adsorption community found that these models also applied to adsorption systems. Since that, Boyd's diffusion models have been applied in many adsorption studies. Table 2.3 shows the Boyd's model equations (Viegas et al., 2014).

Table 2.3: Boyd's model equations (Boyd et al., 1947; Reichenberg, 1953)

Equation	
$F = \frac{q}{q_e}$	(2.5)
$B = \frac{\pi^2}{R^2} \times D_i$	(2.6)
$Bt = -ln\frac{\pi^2}{6}(1 - F(t))$	(2.7)

If the plot of *Bt* vs *t* is a linear line and passes through the origin, the adsorption process is controlled by the intraparticle diffusion and please note that the applications of Boyd's intraparticle diffusion model, the term *Bt* is the product of *B* and *t* (Wang & Guo, 2020).

2.5.3 Weber-Morris model

Weber and Morris (1963) deduced a model to describe the intraparticle diffusion process. The equation of W&M model is shown in equation (2.8). Weber-Morris found that in many adsorption cases, solute uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time t (Qiu et al., 2009).

$$q_t = k_{int} t^{\frac{1}{2}} \quad (2.8)$$

Here k_{int} is the intraparticle diffusion rate constant. The parameter k_{int} can be estimated by plotting qt vs. t. The intraparticle diffusion is the controlling process, if the plot of q_t vs $t^{1/2}$ is a linear line and passes through origin. Otherwise, the adsorption is controlled by multiple processes (Wang & Guo, 2020).

2.5.4 Film-Pore Diffusion Model

This film and pore diffusion model is based on the research by Spahn and Schlunder (1975) and it is develop based on the unreacted shrinking core mass transfer model. The assumption for this model is that the external and internal mass transfer resistance controls the adsorption rate. While the mathematical model started with three assumptions which are equilibrium occurs between the pore liquid and the interior surface of adsorbent particle, diffusion of solutes in the pores obeys Fick's first law and solute concentration can be neglected because solute concentration in the pore liquid is very small compared to that on the adsorbent surface (Choy et al., 2004; Ko et al., 2001).

The mass transfer and the concentration profile of adsorbent particle according to the film–pore diffusion model is shown in Figure 2.3. Because of the external liquid film surrounding the particle, The value of C_t will be reduce to $C_{e,t}$, and then drops further to zero at point r in the particle interior due to the internal resistance measured by D_p. The external mass transfer coefficient, k_f and the pore diffusion coefficient, D_p are the main parameters that describe the profile of a concentration decay curve (Choy et al., 2004; Spahn & Schlünder, 1975).

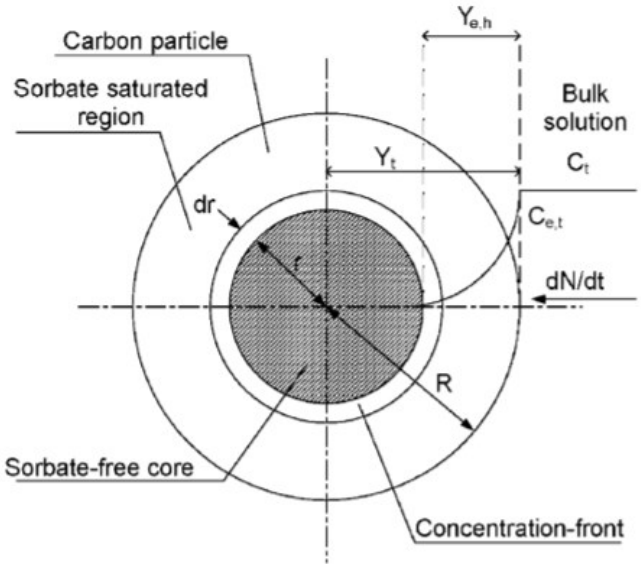


Figure 2.3: Mass transport of adsorbate and concentration profile (Choy et al., 2004)

CHAPTER 3

METHODOLOGY

3.1 Overall Study Structure

Figure 3.1 shows the flow diagram of modelling and simulation of dye adsorption by using modified MOF-5.

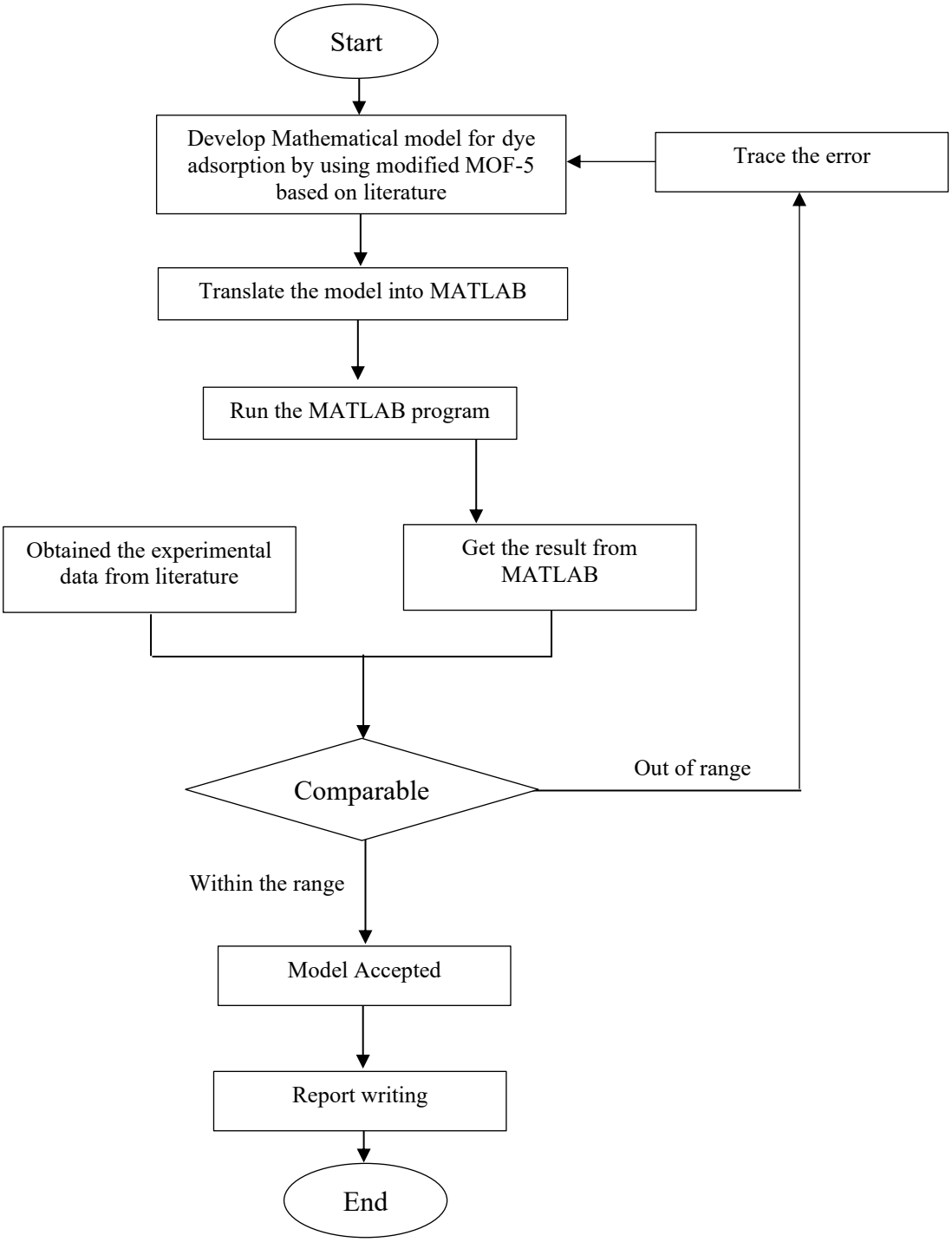


Figure 3.1**:** Flow diagram of modelling and simulation of dye adsorption by using modified MOF-5

3.2 Theory

The film-pore diffusion model by Spahn and Schlünder (1957) is used for the batch adsorption of cationic dye by using modified MOF-5 with Wells–Dawson acids (Liu et al., 2016) . Few assumptions for this model are:

1. The adsorbent particle is spherical shape
2. The mass transport of solute molecules within the pores of an adsorbent particle is only by molecular diffusion.
3. The driving force in both film and particle mass transfer is linear.
4. Pore diffusivity is independent of concentration.

The amount of dye absorbed at equilibrium, q_e was determined by using Langmuir equation as shown in equation (2.1) in Chapter 2.

The adsorption kinetic for a spherical adsorbent for the film-pore diffusion model are derived by the following equations (Jena et al., 2003). The mass transfer at the external surface of the adsorbent particles is represented by

$$N = 4\pi R^2 k_f (C - C_e) \tag{3.1}$$

where k_f is the external mass transfer coefficient.

The mass transfer of solute through the pores is given by:

$$\mathrm{N} = 4\pi \mathrm{r}^2 \mathrm{D_p} \frac{\mathrm{dC}}{\mathrm{dr}} \tag{3.2}$$

Rearrange equation (3.2) and Integrate:

$$N \int_r^R \frac{1}{r^2} dr = 4\pi D_p \int_0^{C_e} dC$$

$$N\left(\frac{1}{r}-\frac{1}{R}\right)=4\pi D_p\ C_e \tag{3.3}$$

Rearrange equation (3.3)

$$N=\frac{4\pi D_p\ C_e}{\left(\frac{1}{r}-\frac{1}{R}\right)} \tag{3.4}$$

where D_p is the pore diffusion coefficient.

The adsorption rate N(t) is related to the differential mass balance over the system by equating the decrease in dye concentration in the solution with the accumulation of the adsorbate in MOF-5 and the mass balance on a spherical element of adsorbate particle as given by, respectively:

$$N(t)=-4\pi r^2 q_e\rho\ \frac{dr}{dt} \tag{3.5}$$

3.3 Mathematical model development

Equating equation (3.1) and (3.5) and rearrange

$$4\pi R^2 k_f(C-C_e)=-4\pi r^2 q_e\rho\ \frac{dr}{dt}$$

$$C_e=C+\frac{r^2 q_e\rho}{R^2 k_f}\ \frac{dr}{dt} \tag{3.6}$$

Equating equation (3.4) and (3.5)

$$\frac{4\pi D_p\ C_e}{\left(\frac{1}{r}-\frac{1}{R}\right)}=-4\pi r^2 q_e\rho\ \frac{dr}{dt} \tag{3.7}$$

Rearrange equation (3.7)

$$-r\frac{dr}{dt} = \frac{D_p\, C_e}{q_e \rho \left(1 - \frac{r}{R}\right)} \tag{3.8}$$

Substitute equation (3.6) into (3.8)

$$-r\frac{dr}{dt} = \frac{D_p}{q_e \rho \left(1 - \frac{r}{R}\right)}\left[C + \frac{r^2 q_e \rho}{R^2 k_f}\, \frac{dr}{dt}\right] \tag{3.9}$$

Rearrange equation (3.9)

$$-\frac{dr}{dt}\left[r + \frac{r^2 D_p}{R^2 k_f \left(1 - \frac{r}{R}\right)}\right] = \frac{D_p\, C}{q_e \rho \left(1 - \frac{r}{R}\right)} \tag{3.10}$$

The average concentration in the adsorbent particle is given by

$$q = q_e \left[1 - \left(\frac{r}{R}\right)^3\right] \tag{3.11}$$

Rearrange equation (3.11)

$$r = R\left[1 - \frac{q}{q_e}\right]^{\frac{1}{3}} \tag{3.12}$$

Differentiate equation (3.12)

$$dr = -\frac{R}{3q_e}\left[1 - \frac{q}{q_e}\right]^{-\frac{2}{3}}\, dq \tag{3.13}$$

Substitute equation (3.12) and (3.13) into (3.10)

$$\frac{R}{3}\left[1 - \frac{q}{q_e}\right]^{-\frac{2}{3}}\, \frac{dq}{dt}\left[R\left[1 - \frac{q}{q_e}\right]^{\frac{1}{3}}\, dq + \frac{\left[1 - \frac{q}{q_e}\right]^{\frac{2}{3}} D_p}{k_f\left(1 - \left[1 - \frac{q}{q_e}\right]^{\frac{1}{3}}\right)}\right] = \frac{D_p\, C}{\rho\left(1 - \left[1 - \frac{q}{q_e}\right]^{\frac{1}{3}}\right)} \tag{3.14}$$

Rearrange equation (3.14)

$$\left[1-\frac{q}{q_e}\right]^{-\frac{2}{3}}\ \frac{dq}{dt}\left[\left[1-\frac{q}{q_e}\right]^{\frac{1}{3}}\ dq+\frac{\left[1-\frac{q}{q_e}\right]^{\frac{2}{3}}D_p}{Rk_f\left(1-\left[1-\frac{q}{q_e}\right]^{\frac{1}{3}}\right)}\right]\ =\frac{3D_p\ C}{R^2\rho\left(1-\left[1-\frac{q}{q_e}\right]^{\frac{1}{3}}\right)} \tag{3.15}$$

Formula of Biot Number is given by:

$$Bi=\frac{k_f R}{D_p} \tag{3.16}$$

Substitute equation (3.16) into (3.15)

$$\frac{dq}{dt}\ =\frac{3D_p\ C\left[1-\frac{q}{q_e}\right]^{\frac{2}{3}}}{R^2\rho\left(1-\left[1-\frac{q}{q_e}\right]^{\frac{1}{3}}\right)\left[\left[1-\frac{q}{q_e}\right]^{\frac{1}{3}}\ dq+\frac{\left[1-\frac{q}{q_e}\right]^{\frac{2}{3}}}{Bi\left(1-\left[1-\frac{q}{q_e}\right]^{\frac{1}{3}}\right)}\right]} \tag{3.17}$$

Rearrange equation (3.17)

$$\frac{dq}{dt}\ =\frac{3D_p\ C\left[1-\frac{q}{q_e}\right]^{\frac{1}{3}}}{R^2\rho\left[1-\left(1-\frac{1}{Bi}\right)\left(1-\left[1-\frac{q}{q_e}\right]^{\frac{1}{3}}\right)\right]} \tag{3.18}$$

Mass balance between the liquid phase concentration and the amount of adsorbate in the adsorbent:

$$V=(C_0-C)qW \tag{3.19}$$

Rearrange equation (3.19)

$$C = C_0 - \frac{qW}{V} \tag{3.20}$$

Substitute equation (3.20) into (3.18)

$$\frac{dq}{dt} = \frac{3D_p\left[C_0 - \frac{qW}{V}\right]\left[1 - \frac{q}{q_e}\right]^{\frac{1}{3}}}{R^2\rho\left[1 - \left(1 - \frac{1}{Bi}\right)\left(1 - \left[1 - \frac{q}{q_e}\right]^{\frac{1}{3}}\right)\right]} \tag{3.21}$$

Equation (3.21) is solved by programming language written in MATLAB R2020b software (Appendix A). The unknown parameters which are external mass transfer coefficient (k_f) and pore diffusion coefficient (D_p) which provide best fit between experimental data and model data were estimated by minimizing the difference between experimental and simulated the data via fminsearch in MATLAB. The error of experimental and simulated data was determined by root mean squared error (RMSE) as shown in equation (3.22). Where *RMSE* is root mean squared errors, *n* is number of data per experimental data set and *x* is dimensionless liquid phase concentration.

$$RMSE = \sqrt{\frac{1}{n}\sum\left(x_{experiment} - x_{model}\right)^2} \tag{3.22}$$

The various factor of adsorption such as modification of MOF-5, initial dye concentration, temperature, and mass of adsorbent were studied based on equation (3.21). The input parameter data were taken from Liu et al. (2016) and it is shown in Table 3.1. The value of q_m and K_L in the Table 3.1 is at temperature 313 K. This data used to estimate the two unknown parameters and were used to study various adsorption parameters.

Table 3.1: Input Parameter

Parameters	**Symbols**	**Value (unit)**
Volume of liquid phase	V	0.02 (L)
Mass of adsorbent	W	0.015 (g)
Particle density of adsorbent	P	3349 (kg/m^3) *
Radius of adsorbent particle size	R	1.023×10^{-3}(m) *
Maximum adsorption capacity	q_m	51.81 (mg/g)
Langmuir constant	K_L	1.75 (L/mg)

**Calculated*

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Parameter Estimation

A MATLAB program is used to solve the diffusion model and to estimate the two unknown parameters which produce the best fit curve with the experimental data. In this model, there are two unknown parameters which are external mass transfer coefficient (k_f) and pore diffusion coefficient (D_p). The experimental data of the adsorption from Liu et al., (2016) is used to compare and to find the minimum average root mean squared error (RMSE) with the simulation data. External mass transfer coefficient is related to external liquid film resistance whereas internal pore diffusion coefficient represents the intraparticle diffusion resistance in the pores of adsorbents and these two parameter are required to be estimated by using fminsearch via MATLAB. The input parameter taken from Liu et al. (2016) as shown in Table 3.1 and this parameter was used to run the simulation.

The simulation result for estimation of unknown parameter is 66.8 m/s and 2.1514×10^{-7} m^2/s for external mass transfer (k_f) and pore diffusion coefficient (D_p) respectively. Meanwhile, the value of k_f and D_p reported by Choy et al. (2004) are 1.56 $\times10^{-6}$ m/s and 1.56 $\times10^{-11}$ m^2/s respectively. By comparing the value from simulation and experimental from Choy et al. (2004), the value of D_p and k_f for simulation were deviated from the research by Choy et al., (2004) due the different type of adsorbent and adsorbate that used in the research study. Since the k_f represent external mass transfer coefficient, therefore higher value of k_f may indicate that the effect of external film diffusion is stronger in the adsorption of methylene blue dye. The two parameters

estimated were used to study the various effect of adsorption such as initial concentration, temperature, modification of MOF-5 and mass of adsorbent.

The experimental data were than fitted with concentration profile from the film pore diffusion model simulated from MATLAB at different initial dye concentration. The film pore diffusion model fits well with the experimental results for initial concentration of 20 mg/L and 25 mg/L but for 30 mg/L the model does not fits well with experimental data. Figure 4.1 to 4.3 shows the experimental data and the simulated concentration profiles for different initial dye concentration.

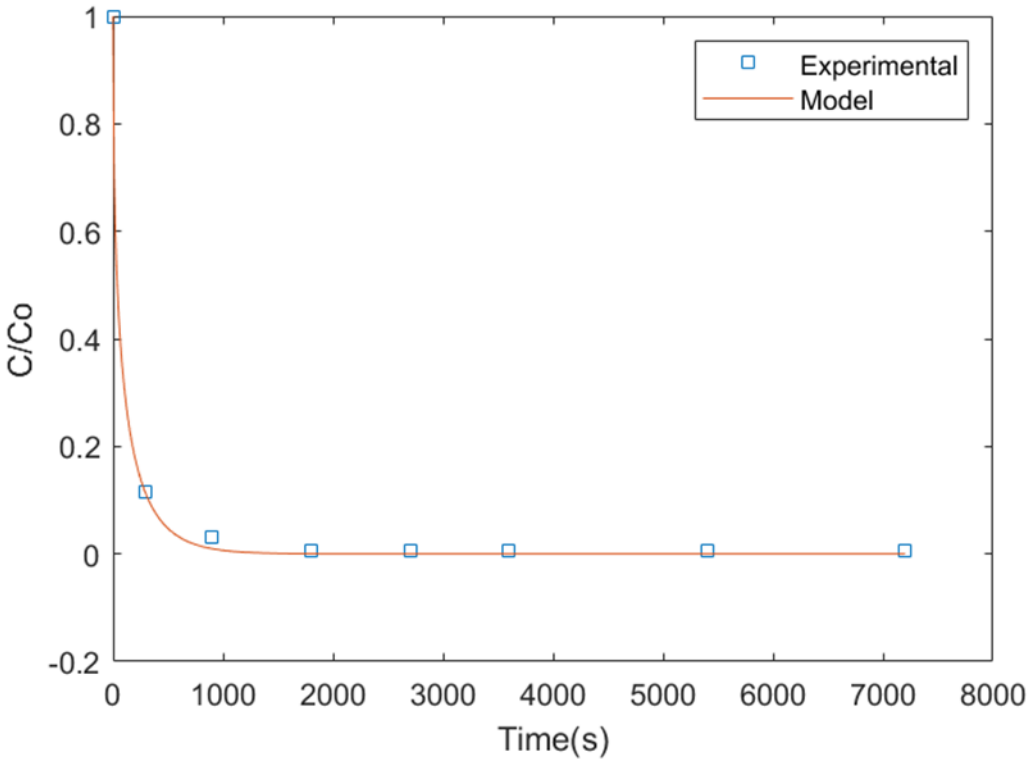


Figure 4.1: Concentration profile at initial concentration 20 mg/L

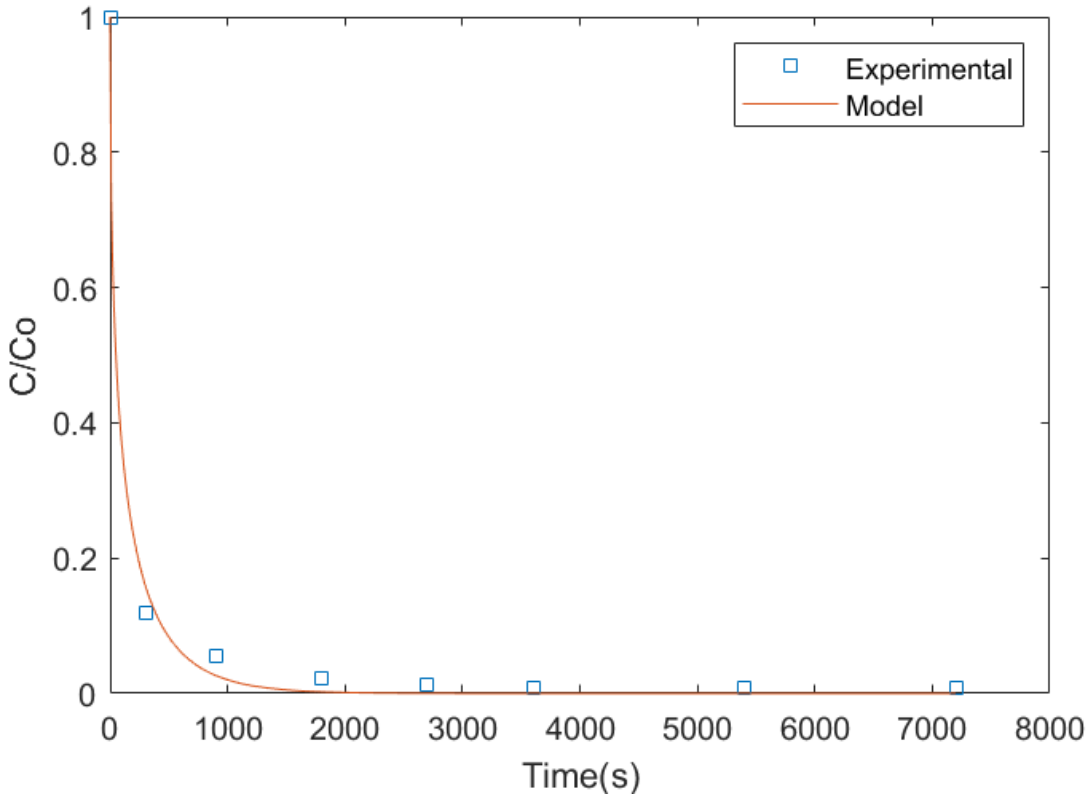


Figure 4.2: Concentration profile at initial concentration 25 mg/L

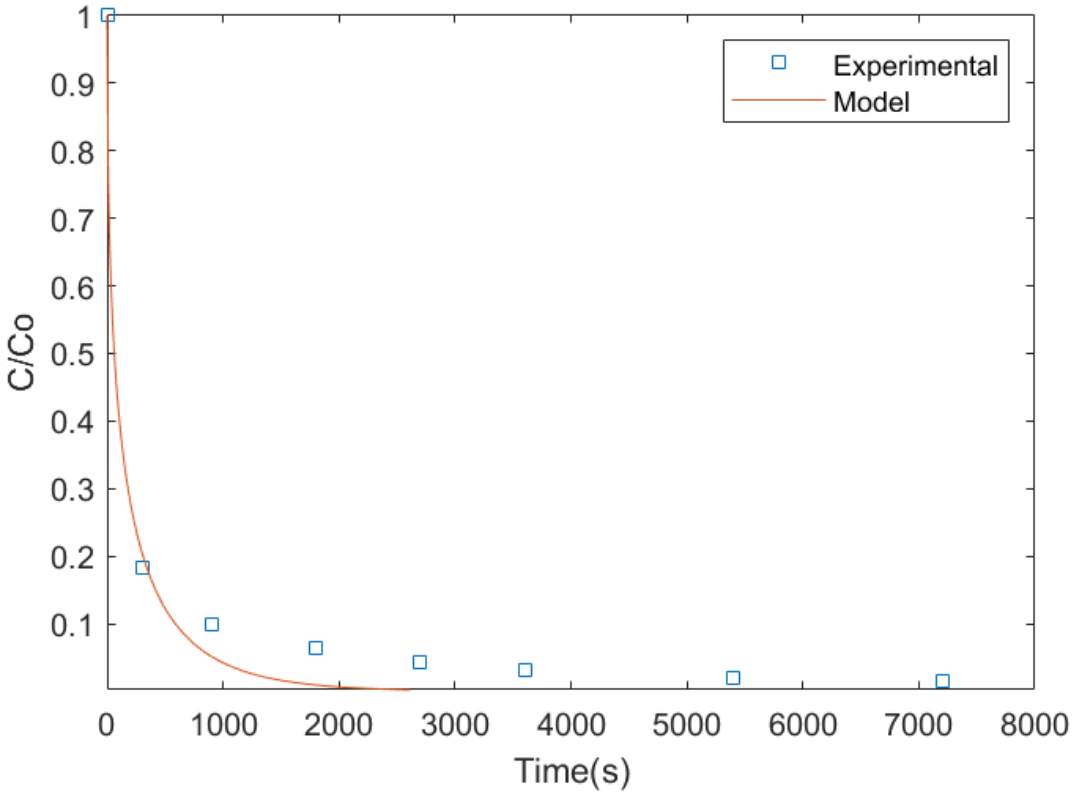


Figure 4.3: Concentration profile at initial concentration 30 mg/L