

UTILIZATION OF SHRINKING CORE MODEL AS CO₂
MODELLING SORPTION ONTO RUBBER-SEED SHELL
ACTIVATED CARBON

FAUDZIAH BINTI ISMAIL

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Utilization of Shrinking Core Model as CO₂ Modelling Sorption onto Rubber-Seed Shell Activated Carbon

by

Faudziah Binti Ismail

24403

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JANUARY 2021

Universiti Teknologi PETRONAS,
32610, Bandar Seri Iskandar,
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,



(AZRY B BORHAN)

UNIVERSITI TEKNOLOGI PETRONAS
BANDAR SERI ISKANDAR, PERAK

January 2021

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.



FAUDZIAH BINTI ISMAIL

ABSTRACT

This study aims to fill the research gap on activated carbon from Rubber Seed shell which is considered an agricultural waste and can be found it abundance in Malaysia. The focus of study is on the adsorption of Carbon Dioxide (CO₂) onto Rubber Seed Shell Activated Carbon (RSS AC) using the Shrinking Core Model (SCM) developed using MATLAB. The SCM is then be simulated under varying temperature and initial concentrations of CO₂ while determining the effective pore diffusivity of RSS AC using local optimization. Literature review has been conducted on topics of the SCM, the operating parameters and the variable required to develop the SCM. The model is described as a spherical particle that undergoes a reaction which decreases the radius of the core but the radius of the particle remains constant. Moreover, optimum operating parameters for the adsorption process for CO₂ onto RSS AC occurs at low temperatures and high pressure. In addition to that, there are three types of variable data involved in developing the model which are adsorption isotherm, adsorption kinetics and activation energy. The activation energy was found to be at 23.74 kJ/mol at 298 K which explains the adsorption process is physisorption due to weak Van Der Waals. Execution of project was shown in the flowchart, where the sequence of actions to complete the objective stated in the beginning of the Final Year Project II. The results show that the developed SCM using MATLAB has successfully been modeled according to a generalized SCM. It was developed using a fundamental equation and boundary conditions that of a SCM coded into MATLAB using the partial differential method. In addition to that, the effect of the temperature on the adsorption rate for a SCM has shown to increase with an increase in temperature. In the case of the parameter of concentration of CO₂ in bulk phase seems to not give an effect on the adsorption rate. The optimized effective diffusivity for adsorption of CO₂ onto RSS AC was obtained at $9.877 \times 10^{-5} \text{ m}^2/\text{s}$ where the value in comparison to literature review are quite close.

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CHAPTER 1

INTRODUCTION

1.1 Background

Mathematical modelling is utilized to generalize the experimental results and formulate knowledge about the process behavior Ayas & Yilmaz (2014). It is a requirement for good engineering model that is to be close representation of the reality which can be simulated without too many mathematical complexities. It has been identified that the Shrinking Core Model (SCM) which is widely used, best and simplest model to study a non-catalytic fluid-solid system.

Application of the SCM or also known as Unreacted-Core-Shrinking Model is described as a non-catalytic heterogenous reaction model. Early research was focused on the use of shrinking core model on the solid-gas system by Levenspiel in 1979 (Wen, 1968). The understanding of the model is that the size of the solid particle is unchanged when the solid particle comes in contact with a gas or liquid. (Fluid-Particle Reactions, n.d). It is widely used in various industries such as chemical and metallurgical industries (Wen, 1968). The SCM is used to obtain a comprehensive understanding on the adsorption of fluid on the adsorbent particle.

The adsorbent particle in this study is an Activated Carbon made from Rubber Seed Shell which was created by the previous researcher. Rubber Seed Shell Activated Carbon (RSS AC) will be used to adsorb the Carbon Dioxide, CO₂. Activated Carbon is used as an adsorbent due to its highly porous material with good selectivity which enables it to be an effective adsorbent to remove contaminants (Djedouani et al., 2016). Thus, the SCM will be utilized to study the adsorption of CO₂ onto RSS AC.

1.2 Problem Statement

Rubber is one of the important commodities in Malaysia. Rubber can be used to manufacture various product ranging from gloves to tyres. According to the Malaysia Rubber Board (2019), an estimated of 1.2 million hectare of rubber plantation land in Malaysia. This leads to an abundant waste of Rubber Seed Shell as the fruit of the rubber tree will burst open when ripe and scattering its many seed in order to reproduce (Rainforest Alliance, 2012). Consequently, the shell of the rubber seed will have no use afterwards which opens up opportunity to convert it into useful products such as Rubber Seed-Shell Activated Carbon.

Various research has been made on activated carbon produced from numerous biomass sources but there is limited study being conducted on Rubber Seed Shell Activated Carbon. In an effort to address the research gap, the yet to be tested Shrinking Core Model is utilized to study on the adsorption of Carbon Dioxide onto Rubber Seed-Shell Activated Carbon.

1.3 Objectives

The objective of the project:

1. To develop a Shrinking Core Model (SCM) for simulation and analysis of CO₂ adsorption onto Rubber Seed Shell Activated Carbon.
2. To simulate the developed SCM under varying operating parameters.
3. To determine effective pore diffusivity in Rubber Seed-Shell Activated Carbon by local optimization.

1.4 Scope of Study

The scope of study for this project:

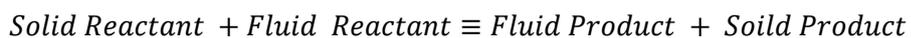
1. Using MATLAB with a fundamental equation and boundary equations to simulate Shrinking Core Model through a partial differential method.
2. Using experimental data from previous researcher to analyze the SCM developed under varying temperature and initial concentrations of CO₂ to observe the concentration profile of CO₂ adsorption onto RSS AC.
3. Using optimization function in MATLAB to obtain the optimized effective diffusivity by inserting the estimates of parameters into the MATLAB coding.

CHAPTER 2

LITERATURE REVIEW

2.1 Mechanism of Kinetic Model

The kinetic model researched on is the Shrinking Core Model which depicts a reaction that occurs at the outer skin of the particle and progressively moves into the solid and may leave behind the converted material and inert solid referred to as “ash” (*Unreacted Shrinking Core Model Definition*, n.d.). This reaction is known as a solid-fluid reaction and is classified into five types, whereby the more general form of a heterogenous non-catalytic reaction is that the reactant and product components exist in both fluid and solid phases (Wen, 1968).



Łupiński et al. (2006) used a more realistic approach by assuming the solid particle remains unchanged throughout the reaction while reacting with the fluid reactant in an isothermal condition. Several assumptions were made by Ayas & Yilmaz, (2014) to facilitate the mathematical modelling of the physical properties of the reaction which is similar to Lupinski et al (2006) whereby the assumption of the Shrinking Core Model is assumed isothermal and isobaric.

The Figure 2.1 is a representation of the Shrinking Core Model with its boundary layers which is obtained from Shrinking Core Model, n.d., (November 11, 2020).

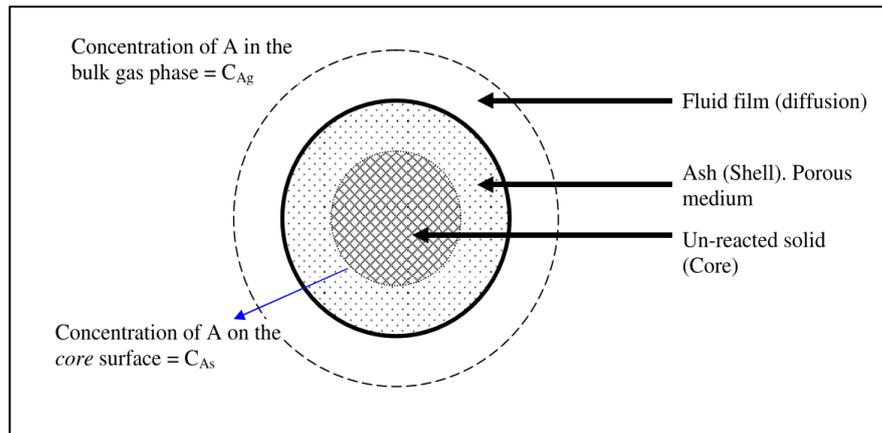


Figure 2.1: Spherical particle over which gas is flowing.

The steps in which the reaction would occur is stated by Wen (1968), “(1) diffusion of the fluid reactants across the fluid film surrounding the solid, (2) diffusion of the fluid reactants through porous solid media, (3) adsorption of the fluid reactants at the solid reactant surface, (4) chemical reaction with the solid, (5) desorption of the fluid products from solid reaction surface, (6) diffusion of the product away from the reaction surface through the porous solid media and through the fluid film surrounding the solid”.

As stated by Djedouani et al., (2016), the Shrinking Core Model has been widely used and established to be the best and simplest representation for majority of non-catalytic fluid-solid system. Thus, it is justifiable to use this model to study the adsorption rate in a heterogenous non-catalytic system.

2.1.2 Assumption on Shrinking Core Model

In addition to that the assumptions that are required for developing the Shrinking Core Model (SCM) is also important to be determined. It makes it more possible to develop a model that represents the reality better with the said assumptions in place without too much mathematical complexities.

After reviewing several literature reviews and also understanding how the model is to better suit the study of the adsorption process of CO₂ on to Rubber Seed Shell Activated Carbon, the following assumption in Table 2.1 are used to modelled the SCM.

Table 2.1: Comparison of Assumptions for SCM in Literature Review

Assumption	Reference
<ul style="list-style-type: none"> • Spherical shape over which fluid flowing • Overall particle size and physical; structure unchanging • Reaction elementary 	<i>(Unreacted Shrinking Core Model Definition, n.d.)</i>
<ul style="list-style-type: none"> • Isothermal reaction • Pseudo steady state approximation • SCM is spherical in size • As reaction progresses the radius of particle is unchanged while the radius of unreacted core decreases. 	Wen, C. Y. (1968)
<ul style="list-style-type: none"> • Adsorbed phase volume is negligible compare to bulk gas phase volume 	Saha, B. B., Jribi, S., Koyama, S., & El-Sharkawy, I. I. (2011)
<ul style="list-style-type: none"> • Unreacted core of particle size is reduced • Most models use pseudo steady state 	Szubert, A., Łupiński, M., & Sadowski, Z. (2006).
<ul style="list-style-type: none"> • Finite and infinite volume • Cylindrical, particle size unchanged • Reacts isothermally with fluid • Constant and uniform bulk concentration in fluid phase 	Djedouani, D., Chabani, M., Amrane, A., & Bensmaili, A. (2016).
<ul style="list-style-type: none"> • Rigid hydrate shell • Constant particle Radius R_p • Constant partial pressure 	Dashti, H., Thomas, D., Amiri, A., & Lou, X. (2019).

<ul style="list-style-type: none"> • Sorbent particle is spherically symmetric with uniform diameter • Assumption amine layer is thin enough and coated on the wall of the pores uniformly • Radial CO₂ diffusion is negligible 	<p>Ge, K., Yu, Q., Chen, S., Shi, X., & Wang, J. (2019).</p>
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The assumptions being made by each literature is seen to be based on the focus of the research. Thus, it is required for us to define the assumptions for the SCM being developed so that it would reflect in the derivations done for it.

2.2 The Effect of Temperature and Pressure

Partial pressure of CO₂ and the temperature whereby the modelling is conducted is an integral part of the process. It is to be identified the optimum temperature and pressure to run the modelling. An article written by Singh and Kumar (2016), that conducted an experiment to study the capability of CO₂ to be adsorbed onto the Activated Carbon (AC) based on the different pressure (1 bar ,5 bar, 10bar and 20 bar) and temperature (298K, 308K, 318 K and 338K).

The results from the experiment shows that the adsorption capacity increases with an increase in CO₂ supply pressure. The trend showed that in the beginning the amount of CO₂ adsorbed was fast and gradually decreases as it reaches equilibrium state. This is explained that as the CO₂ come into direct contact with AC it will form a stronger binding force and once all the pores get occupied by the adsorbate, no more CO₂ are adsorbed.

When temperature is increased, the adsorption capacity is seen to decrease. This is due to the decrease in adsorbent density during adsorbate-adsorbent interactions. The amount of CO₂ adsorbed at 298K and 20 bar was at 405.20 mg/g which is at its highest. Thus, the adsorption capacity is seen to be at its highest at high pressure and low temperature. Figure 2.5 below shows a comparison to the experiment and other literature where comparison is done by (Singh, V. K., & Kumar, E. A., 2016).

Adsorbents	Pressure P (bar)	Amount of CO ₂ adsorbed (mg/g)				Activation Energy (E _a) (kJ/mol)	Ref.
		Temperature T (K)					
		298	308	318	338		
Activated carbon	1	102.95	91.44	89.85	74.93	23.74	This study
	5	226.61	215.92	203.39	181.06	22.92	
	10	310.85	287.16	258.04	225.26	20.73	
Zeolite 5A	20	405.20	366.32	341.34	291.26	18.97	This study
	1	117.95	106.17	103.11	95.23	12.25	
	5	145.65	139.43	135.37	125.23	11.42	
AC-h	10	158.32	146.46	142.85	132.65	9.27	[9]
	20	160.69	152.62	148.12	142.03	7.23	
	0.5	71.12	59.32	46.43	23.67	-	
AC-h	3.0	269.45	224.65	190.32	173.47	-	[9]
AC-h	20.0	807.34	656.76	643.34	605.34	-	[9]
Zeolite 13X	0.5	91.23	85.45	78.33	73.34	-	[9]
Zeolite 13X	3.0	122.23	110.23	105.45	101.78	-	[9]
Zeolite 13X	20.0	202.34	189.34	167.34	155.34	-	[9]
Corncob-derived AC-h	0.01 (301 K)		116.74			25.50	[15]
Coconut shell	-					17.00	[16]

Figure 2.2: Amount of CO₂ adsorbed and activation energy for different types of activated carbon and zeolites from various literature reviews.

A similar study conducted by Ge, K., Yu, Q., Chen, S., Shi, X., & Wang, J. (2019), which shows that the temperature (288 K, 298K, 308K and 318K) has a significant influence on the dynamic adsorption process. In the initial stage of adsorption, the total average adsorption rate at high temperature was higher than at lower pressure. As the reaction proceeds, the total average adsorption rate of the higher temperature decreases faster than that of the lower temperature. This study supports the findings of Dashti et al., (2019), that at lower temperature, the CO₂ hydrate formation is faster which is related to the adsorption rate.

The effect of higher CO₂ partial pressure (5%, 10% and 15%) is seen to increase the adsorption rate due to it giving a greater driving force of CO₂ adsorption (Ge, K., Yu, Q., Chen, S., Shi, X., & Wang, J. 2019). However, the rise in pressure causes an increase in the total mass transfer resistance. Thus, the effect of increasing the CO₂ pressure does not significantly affect the adsorption time taken to approximate equilibrium (Ge, K., Yu, Q., Chen, S., Shi, X., & Wang, J. 2019).

2.3 Determining Variable Data for Kinetic Modelling

2.3.1 Adsorption Kinetics

In an effort to determine the suitable order of a kinetic model, the adsorption kinetics data of CO₂ adsorption were fitted into the pseudo first order and pseudo second order as shown in Figure 2.3 (Singh & Kumar, 2016).

Kinetics model	Nonlinear equation	Linear equation	Plot	Slope and Intercept	Ref.
Pseudo-first order	$\frac{dq_t}{dt} = \kappa_1 (q_e - q_t)$	$\log(q_e - q_t) = \log(q_e) - \left(\frac{\kappa_1}{2.303}\right)t$	$\log(q_e - q_t)$ vs t	Slope = $\frac{\kappa_1}{2.303}$ Intercept = $\log(q_e)$	[10]
Pseudo-second order	$\frac{dq_t}{dt} = \kappa_2 (q_e - q_t)^2$	$\frac{t}{q_t} = \frac{1}{\kappa_2 q_e^2} + \frac{t}{q_e}$	$\frac{t}{q_t}$ vs t	Slope = $\frac{1}{q_e}$ Intercept = $\frac{1}{\kappa_2 q_e^2}$	[13]

Figure 2.3: The equation of kinetics models used.

The experiment was conducted by manipulating the temperature at (298K, 308K and 338K) and also its pressure (5,10 and 20 bar) to test out the adsorption kinetics of CO₂ on to activated carbon (Singh & Kumar, 2016). The adsorption capacity of CO₂ on the activated carbon was estimated at 2.81 mg of CO₂/g respectively (Singh & Kumar, 2016). The pseudo second order exhibited a better fit compared to pseudo first order as it had a larger coefficient of correlation (R²).

A study was done on the sorption system to examine whether a pseudo first order or pseudo second order is suited would be a best fit to the data. Various types of material were tested to obtain the kinetics of the adsorption including Activated carbon. It was found out that for all the system studied the chemical reaction seems significant in the rate controlling step and the pseudo second order chemical reaction kinetics provides the best correlation of the experimental data (Ho, Y. S., & McKay, G., 1999). The pseudo first order model proposed fits the experimental data for an initial period if the first reaction step.

In an experiment where comparison was done on three kinetic models which are pseudo first order, pseudo second order and Elovich. It is focused on CO₂ adsorption on specifically Rubber Seed Shell Activated Carbon, it is also found the pseudo second order fits the experimental data well (Borhan, A., Yusup, S., Lim, J. W., & Show, P. L., 2019). Thus, further supports that pseudo second order is better suited for the adsorption process.

It can be concluded that the literature reviews on the adsorption kinetics of adsorption process clearly states that the pseudo second order model suits the experimental data better than that of the pseudo first order.

2.3.2 Activation Energy

In an attempt to model the shrinking core model for an adsorption of CO₂ onto Rubber Seed Shell Activated Carbon (RSS AC), it is required to obtain the activation energy of the solid reactant in this case is the activated carbon. Activation energy is required to understand the amount of free energy required for the adsorbate-adsorbent interaction to occur (Singh & Kumar, 2016).

The Arrhenius equation which is known to correlate with the reactivity index was stated in an experiment of CO₂ gasification of coconut shell chars (Tangsathikulchai et al., 2013). A linearized form of the Arrhenius equation was used to obtain the activation energy, Eq. 14.

$$\ln k_m = -\left(\frac{E}{R_g}\right)\left(\frac{1}{T}\right) + \ln k_0 \quad (1)$$

Whereby k_m is the char reactivity index, E is the activation energy, R_g is the universal gas constant and T is the absolute temperature. The values of k_0 and E were obtained through linear regression method (Tangsathikulchai et al., 2013).

The activation energy obtained from the use of the Arrhenius equation will indicate the type of adsorption process of the CO₂ and the Activated Carbon. This is supported in a study of CO₂ adsorption kinetics onto solid adsorbent by Singh and Kumar (2016) where the activation energies were obtained from the slope of $(-E/R)$ from a plotted graph of $(\ln k_m)$ and the inverse of temperature $(1/T)$. The activation energy found from the activated carbon subjected to different temperature (298K, 308K, 318K and 338K) and pressure (1, 5, 10 and 20 bar) is at 23.74, 22.92, 20.73 and 18.97 kJ/mol respectively.

The range of activation energy obtain for the activated carbon is within the range of physisorption as a low activation energy is cause by weak Vander Waals forces between the adsorbate-adsorbent interaction (Singh & Kumar, 2016).

2.4 Diffusion of Carbon Dioxide onto Activated Carbon

In using the SCM, the mass transfer coefficients are influenced by variables such as diffusivity, viscosity, density, solvent flow rate, and porosity of the adsorbate (Ayas & Yilmaz, 2014). Referring to the article written by Kamiuto et al. (2006), that the determined diffusion coefficient for both the micropore and macropore were stated as shown in Table 2.2.

Table 2.2: Values of Diffusion Coefficient at different temperatures

Parameters	Temperature (K)	
	303.2	343.2
Micropore (m²/s)	6.49 x 10 ⁻¹⁵	1.14x10 ⁻¹⁴
Macropore (m²/s)	21.82 x 10 ⁻⁶	3.04 x 10 ⁻⁶

The diffusion coefficients in this literature are the mean values for the micropore and macropore. It is stated by Kamiuto et al. (2006) that the diffusion

coefficients are found to increase with temperature. Although this is the case, the temperature dependencies vary from each other where for the micropore diffusion coefficient increases with \sqrt{T} while the macropore increase with an $e^{\frac{-1404}{T}}$.

In another article by Wesenauer et al., (2020) on effective diffusivity which studies the suitability and restriction of a SCM, in a binary mixture of CO₂ and oxygen (O₂). The SCM is seen to be a more general approach in studying such pore structure in a solid particle where the effective diffusion coefficients are expected to be low which lease to diffusion as a limiting reaction step.

In this article, it gives the effective diffusion coefficient, D_e in a porous media which usually follows molecular and Knudsen diffusion which takes in to account temperature dependency. As it is known from article that effective diffusivity also considers factors such as porosity, tortuosity factor and shape of particle. Thus, the Arrhenius law was used to obtained the effective diffusion coefficient which gives equation 2. The D_0 is the pre-exponential factor, E_a is diffusion activation energy, R gas constant and T is temperature in kelvin.

$$D_e(T) = D_0 e^{\frac{-E_a, diff}{RT}} \quad (2)$$

From the literature review done on the effective diffusivity of activated carbon and on porous media, it can be concluded that the effective diffusion coefficient is expected to be low due to many contributing factors. The common factor seen in the articles read is the porosity of the activated carbon affects the effective diffusion coefficient

CHAPTER 3

METHODOLOGY

3.1 Developing Shrinking Core Model

From the literature review, the data to develop the SCM was collected and chosen. It begins with identifying the appropriate fundamental equation with its boundary conditions according to the assumptions made on the SCM. Further data collection on the parameters and variables needed to develop the SCM was obtained from literature review. Using the MATLAB and learning from various sources, the coding for the SCM was built around the fundamental equation with its boundary equation.

The coding uses the partial differential solver function in MATLAB to develop the SCM. After that, the coding was checked if it was able to be run, in the case it is unable to be executed, the coding is rechecked for errors. Once the coding can be executed, the result is compared to those found in literature. If the data does not represent that of a SCM, the data variable and coding are rechecked and executed again. Once the data obtained is that found in literature review which represents a SCM, it is recorded for further analysis and documented in dissertation.

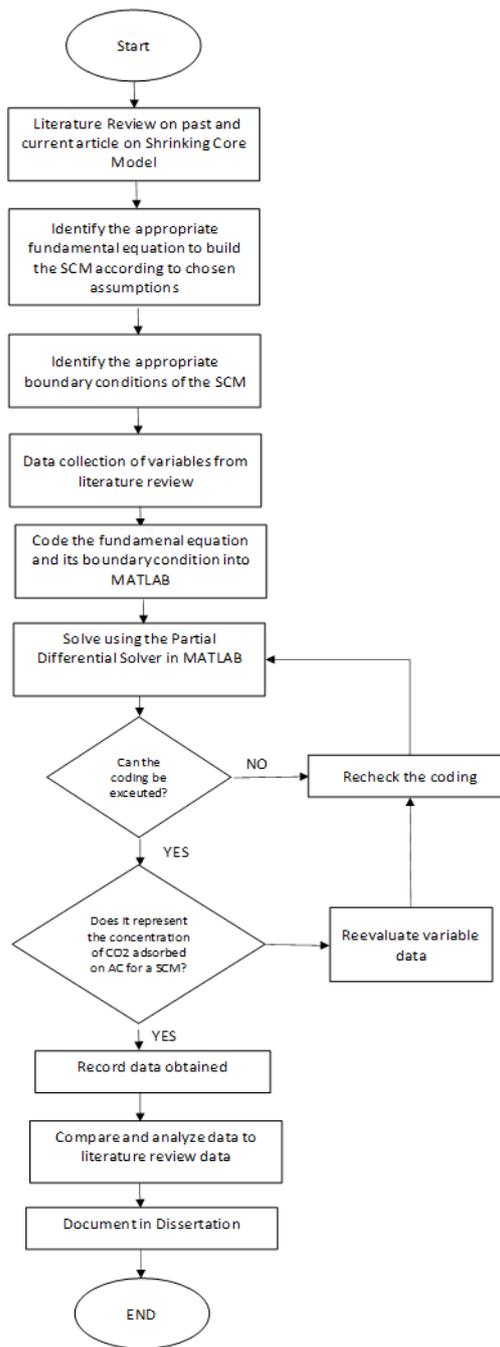


Figure 3.1: Flowchart for developing Shrinking Core Model

3.2 Effect of Temperature and Initial Concentration of CO₂

The range of viable temperature and concentration of CO₂ in the bulk phase were identified through literature review. The relevant data were obtained through literature review and calculations were inputted into MATLAB. The SCM is run for all the ranges of temperature chosen and the results are recorded. After that, the simulation is run for ranges of concentration of CO₂ in bulk phase and the result are recorded for further analysis against other literature review. It is then documented in the dissertation

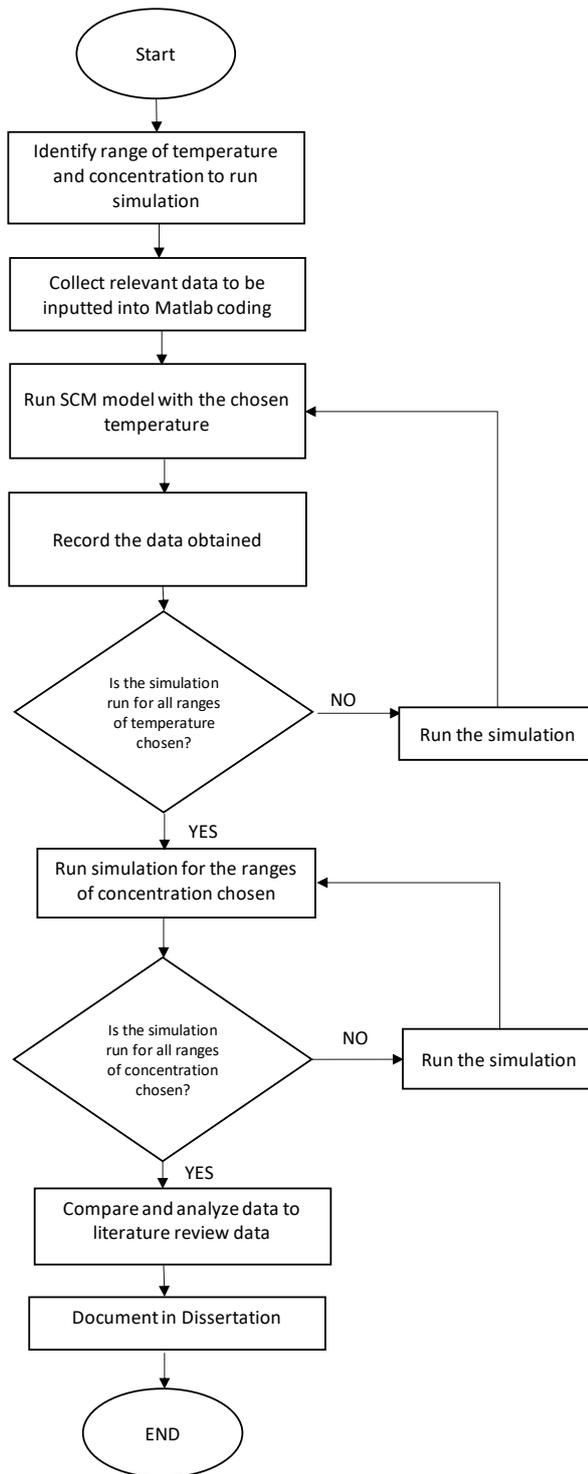


Figure 3.2: Flowchart for effect of temperature and initial concentration of CO₂

3.3 Determining the effective pore diffusivity

The third objective was executed by identifying the diffusivity equation to be used from literature review. Data collection was done for the variable required to run the MATLAB coding through literature review. The coding was done in MATLAB and solved using the optimizations function. If the coding cannot be executed, it is check for errors. After that, the value of diffusivity given is checked whether it is within the boundary and constraints set. The data is recorded and compared with other literature findings on the topic. Finally, it is documented in the dissertation.

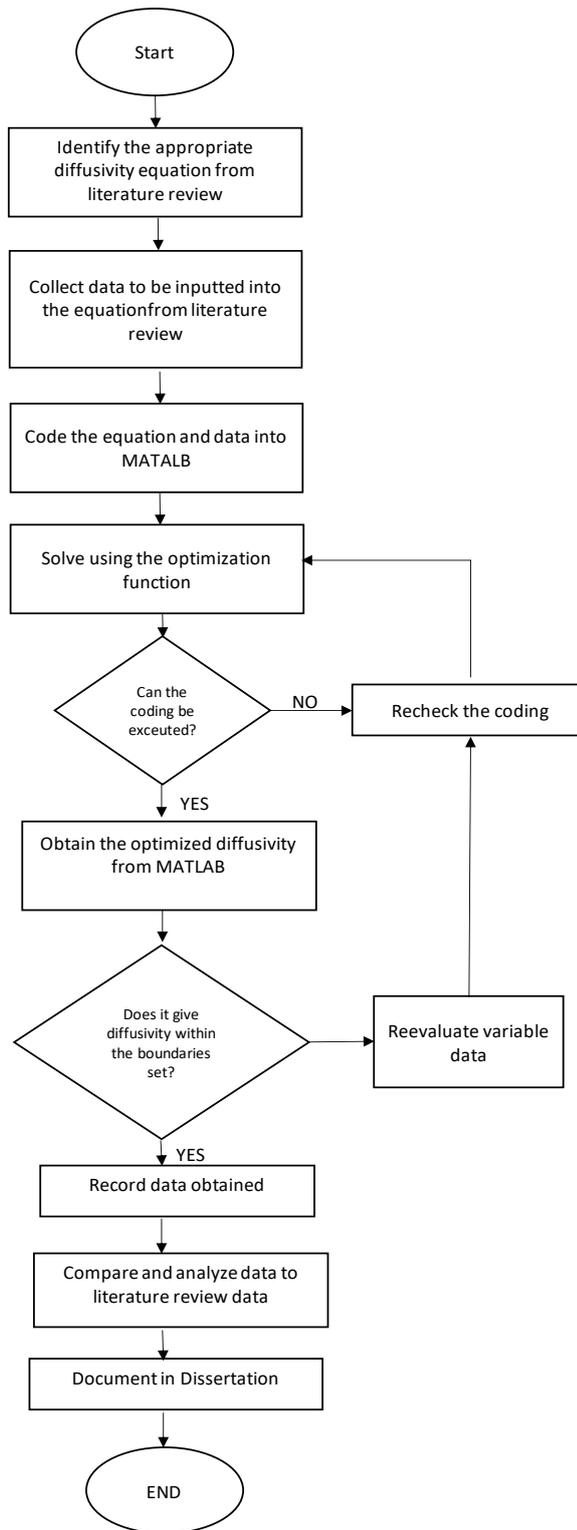


Figure 3.3.: Flowchart for determining effective pore diffusivity

CHAPTER 4

RESULTS AND DISCUSSIONS

This section comprises of three parts of the Final Year Project that has been conducted in order to meet the objective set in the beginning of this course within the stated scope of study. It is divided according to the three objectives which are developing the SCM, the effects of temperature and initial concentration of CO₂ and optimized effective diffusivity.

4.1 Developing Shrinking Core Model

The assumption made in developing the model are shown in Table 4.1:

Table 4.1: Assumptions made on Shrinking Core Model

Assumptions	Reference
1) Isothermal reaction	Wen, C. Y. (1968)
2) The adsorbent particle is spherical shape	Wen, C. Y. (1968)
3) The size of the unreacted core decreases as reaction proceeds	Szubert, A., Łupiński, M., & Sadowski, Z. (2006).
4) The overall activated carbon radius remains constant	Wen, C. Y. (1968)
5) Constant and uniform bulk concentration of the CO ₂ supplied	Djedouani, D., Chabani, M., Amrane, A., & Bensmaili, A. (2016).

Figure 4.1 shows a concentration profile across the radius of the Rubber Seed Shell Activated Carbon for a simulation time of 10000s. It is observed that there is a decrease of the concentration of CO₂ as the radius increases. At radius, r of 0.001m it is seen that the concentration of Carbon Dioxide reaches a value of zero. This shows that the center of the unreacted core is impregnable by the CO₂ as lesser amounts of CO₂ are seen to be present as it moves towards the unreacted core.

This finding is in line with Homma et al. (2005) and Wen (1968), whereby the reaction occurs on the surface of the unreacted core and produces the intermediate layer which is the product. This explains Figure 4.1 where the concentration of the CO₂ reaches zero as the reaction occurs only on the surface of the particle by adsorption.

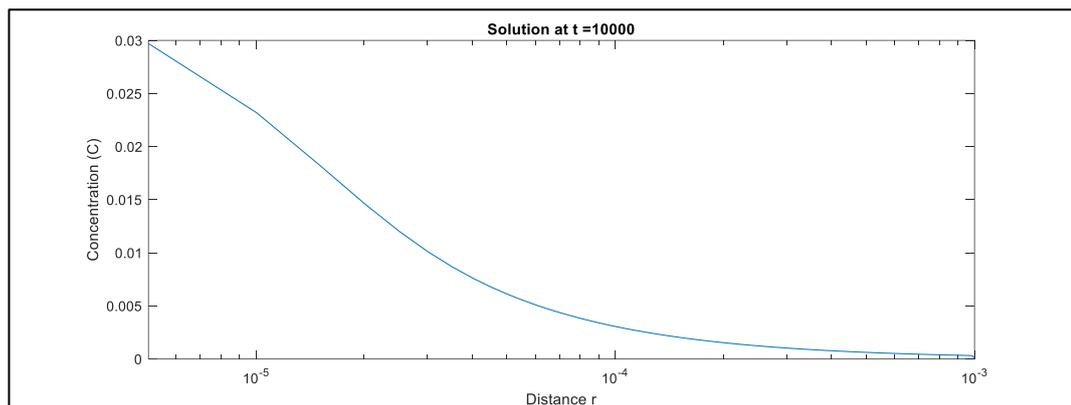


Figure 4.1 Concentration against distance in radius of the Shrinking Core Model

The data shown here is then compared to the concentration profile of gas reactant which shows an almost similar trend in an article written by (Homma et al., 2005). It is proven that the Shrinking Core Model developed using the MATLAB with the chosen equation and boundary equation is successful.

The graph of the concentration profile developed from the SCM was then placed beneath a figure of the model representation of the boundary layers in a SCM such as the one did in the article by (Homma et al., 2005). It gives a similar trend to

that found in (Homma et al., 2005) but the difference is seen in the sharpness of the slope.

The comparison between the concentration profile from the one obtained from simulation against the one shown in (Homma et al., 2005) is the boundary of the SCM are not sharply define. This is explained by the Unreacted Shrinking Core Model Definition, (n.d.) where it states that in real life situation the boundary of the unreacted shrinking core may not always be clearly defined. Although this is the case, article such as Wen, (1968) and Wesenauer, (2020) supporting that the SCM approximates majority of reacting gas-solid systems better than other models.

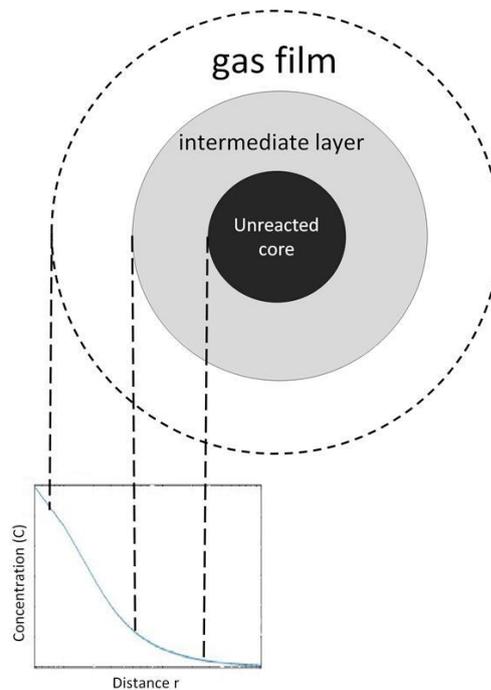


Figure 4.2: Concentration profile of the developed SCM with the model representation of the boundary layer of SCM

It is also identified that the Shrinking Core Model has a limitation whereby it can only be applied using a small value of diffusion coefficient. As Figure 4.3 shows that when using a large value of diffusion coefficient at $6.49 \text{ m}^2/\text{s}$, it is unable to give a concentration profile that of a Shrinking Core Model as it produces a linear declining graph. This graph does not follow in accordance of the concentration profile of a SCM.

The finding from the developed SCM is found to support the theory stated by Xu et al., (2012) where it states that the derived equation in a spherical geometry gives a conclusion that the reaction front velocity is directly inversely proportional to the normalized equilibrium concentration. This gives the limitation of the SCM, whereby it is not applicable using large diffusion coefficient based on the steady-state diffusion approximation of the SCM. This is true as when the developed SCM is ran using a large diffusion coefficient value, it is unable to give a similar trend to that of a generalized SCM.

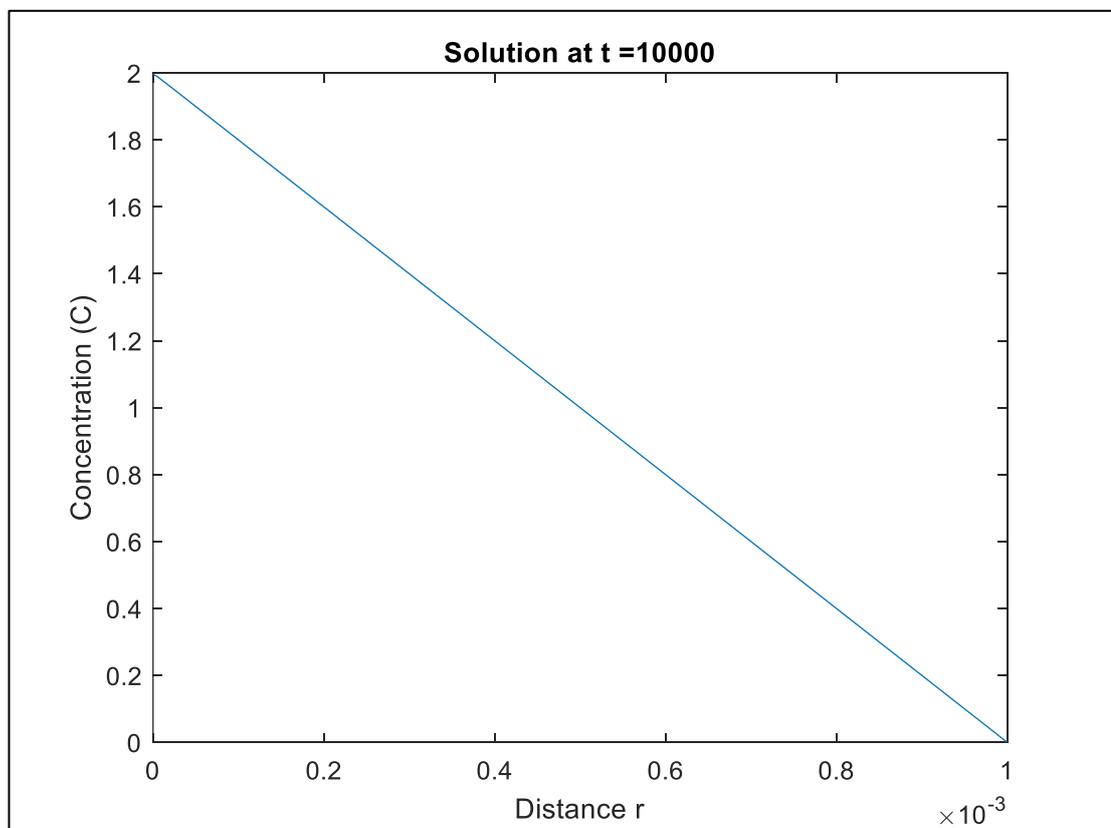


Figure 4.3 Concentration profile of CO₂ using diffusion coefficient of 6.42 m²/s

It is also found through Xu et al., (2012) that the generalized SCM is better suited in a wider range of the heterogeneous gas-solid reaction process when used with a variety or relevant parameters.

4.2 Simulation of Shrinking Core Model at different temperature and initial concentration of CO₂

4.2.1 Effect of Temperature

The developed SCM was then run at two different temperatures and the concentration profile was then recorded and analyzed. The parameters that were calculated which are relevant to the changes of temperature are stated in Table 4.2.

Table 4.2: Parameters for running SCM simulation for varying temperature

Parameters	Temperature (K)	
	298	343
Mass Transfer Coefficient (m/s)	1.9267×10^{-6}	2.64×10^{-6}
Concentration of bulk phase (mol/m ³)	806.840569	700.98685
Diffusion Coefficient (m ² /s)	6.49×10^{-15}	1.14×10^{-14}

Figure 4.4 shows the result of the SCM which was simulated for a temperature of 298K and 343 K with the relevant parameters as shown in Table 4.2 were included in the MATLAB. The reason for choosing these temperatures are to observe the effects between a wide range from a low temperature to a high temperature on the SCM. The data extracted from the simulation as seen in Figure 4.4 at radius of 0.2×10^{-3} m for temperatures of 298K and 343K corresponds to a concentration value of 0.00151942 mol/ m³ and 0.00266894 mol/ m³ respectively.

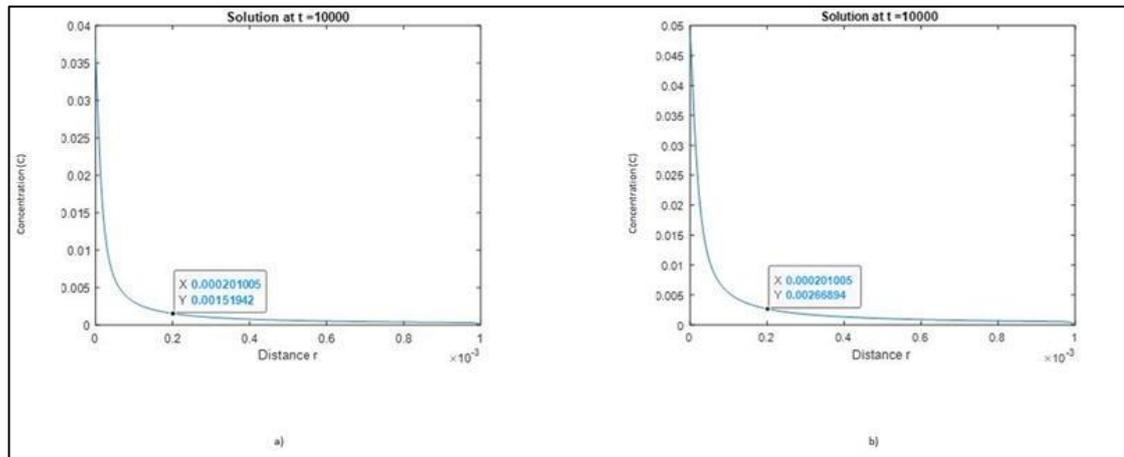


Figure 4.4: Concentration against radius of RSS AC at a) temperature of 298 K b) temperature of 343K

From the comparison in Figure 4.4, it can be observed that at the same distance of $0.2 \times 10^{-3}\text{m}$, the concentration was found to be higher when the temperature was increased which is at 343 K. However, this contradicts the findings made by the simulation in MATLAB as an increase in temperature lead to an increase concentration of CO_2 in the RSS AC. The results are inaccurate as it is expected an increase in temperature would decrease the adsorption capacity of the activated carbon. According to Jibri et al., (2017) and Hauchhum and Mahanta (2014), that an increase in temperature resulted in the lower adsorbed mass.

Singh and Kumar (2016) also supports the previous researcher, stating that the increase in temperature leads to a decrease in the adsorption rate as it relates to the decrease in adsorbent density during adsorbate-adsorbent interactions. According to Singh and Kumar (2016), at elevated temperature the adsorption capacity decreases as a result of instability of the adsorbed has on the surface of the activated carbon.

4.2.2 Effect of Initial Concentration of Carbon Dioxide

Figure 4.5 shows the simulation results ran at a temperature of 298 K with a concentration of 400 and 1300 mol/m³. Figure 4.4 (a) shows the simulation run at similar parameters but at different initial concentration of CO₂ which is at 806.84 mol/m³.

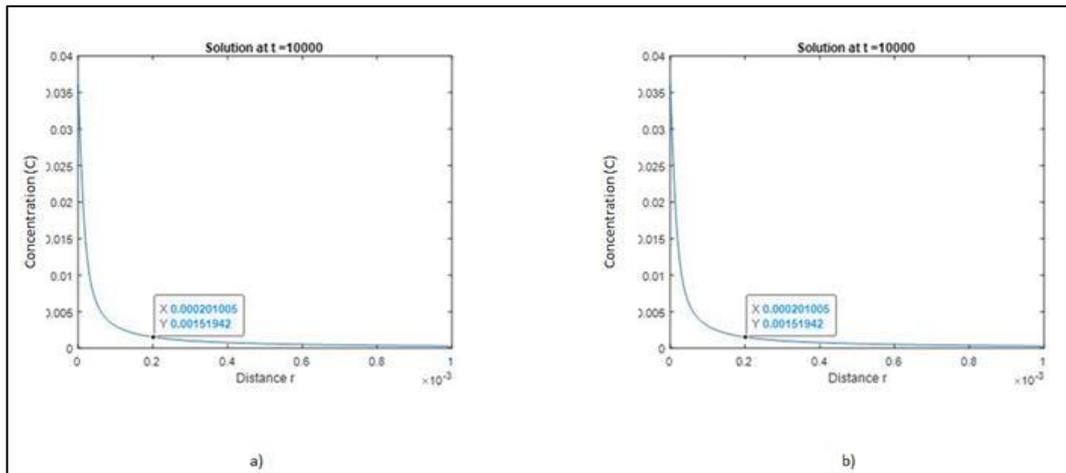


Figure 4.5: Concentration against radius of RSS AC at initial concentration of CO₂ of a) 400 mol/m³ b)1300mol/m³

The comparison using three concentration at 400mol/m³, 806.84 mol/m³ and 1300 mol/m³ shows that there is no difference in concentration at the same distance of 0.2×10^{-3} m. It can be said that the results observed is inaccurate as there should be an increase even at a small amount when the initial concentration of CO₂ is increased. The collection of data tu run the simulation from various sources may have contributed to the inaccuracy of the simulation result obtained here.

This conclusion where the developed SCM is unable to show the effect of initial concentration on the concentration profile of the RSS AC is supported by article written by Daifullah et al., (2004) on the effects of initial concentration of fluid on adsorption. The adsorption capacity of activated carbon increases with an increase in initial concentration of the fluid up to a certain limit where it will then remain constant. It is due to the limited active sites on the activated carbon surface as the molecule of

the fluid is adsorbed externally on the surface which is unfavorable to a second layer of adsorption (Daifullah et al.,2004).

In the case of this simulation, the limit of the initial concentration of CO₂ may be small which is why an increase results to no change in the concentration profile of the RSS AC. As the adsorption of CO₂ onto the RSS AC is physical adsorption, the theory suggested by Daifullah et al., (2004) may be accepted where there are limited number of active sites and the molecule has been adsorbed on most of the surfaces.

In conclusion, the initial concentration of the CO₂ does not seem to affect the adsorption capacity of the activated carbon based on the result obtained. The result of the simulation was unable to detect a difference in the adsorption capacity due to the limitation identified by Daifullah et al., (2004).

4.3 Optimization of effective diffusivity

The MATLAB coding was done to run the optimization function where the equation chosen to study the effective diffusivity of CO₂ onto Activated Carbon. The guesses of the required variable were inputted into the MATLAB and the optimization function utilized the give data to produce the optimized effective diffusivity with its given parameter at which it is to be obtained. The data obtained from the MATLAB optimization function is tabulated in Table 4.3.

Table 4.3: The estimated parameter data inputted into the optimized function for MATLAB

Parameters	Value
Estimated Diffusive pre-exponential factor, D_0 (cm ² /s)	6.3491
Estimated Temperature, T (K)	298
Estimated Activated energy, E_a (kJ/mol)	23.74

The value of the optimized effective diffusivity is 9.877×10^{-5} m²/s with a corresponding value of optimized parameters of D_0 , T and E_a of 0.004 cm²/s, 298.23 K and 20.917 kJ/mol. In comparing the result of it with Kamiuto et al., (2006) for the value of effective diffusivity it is found to be that the micropore and macropore diffusivities found in literature are a value of 6.49×10^{-15} m²/s and 21.82×10^{-6} m²/s. The simulation produced have a value quite similar to that of the effective diffusivity for a macropore of that reported for type 13X zeolite crystal.

The difference of 7.6×10^{-5} when the simulation result is compared to the value taken from literature review. As the type of activated carbon differ as well as the porous structure of the particle itself which may have contributed to the difference in value of the effective diffusivities. In addition to that, the value of effective diffusivities was directly taken from Kamiuto et al., (2006), where it is stated that the

macropore diffusion of the is controlled for the Knudsen diffusion. These factors of differences may have contributed towards the variance in the data but to a small degree.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The first simulation which was in developing the SCM was successful in representing a concentration profile to that of a SCM. The concentration profile is observed to be progressively declining as it enters the activated carbon until it reaches zero. From the developed SCM, it is also identified that it has a limitation where it is only applicable for small diffusion coefficient. When large diffusion coefficient is used in the SCM, it produces a linear declining graph which is inaccurate to that of a SCM.

The second part of the simulation where the developed SCM is run at varying temperature and initial concentration of CO₂. For the effect of temperature, it is seen in Figure 4.4 that an increase temperature, increases the concentration of the CO₂ into the RSS AC. For the effect of initial concentration, as shown in Figure 4.5 any increase or decrease of temperature does not affect the adsorption capacity of the RSS AC.

The last part of the final year project is to obtain an optimized effective diffusion coefficient. The optimized diffusion coefficient obtained is at 9.877×10^{-5} m²/s with its value of optimized parameters of D_o, T and E_a of 0.004 cm²/s, 298.23 K

and 20.917 kJ/mol. When compared with the literature review, the result is seen to be valid and accurate as the value has a difference of 7.6×10^{-5} when being compared.

5.2 Recommendations

As of the current progress of the final year project, it is the beginning of developing the SCM and identifying its limitations and characteristics. For recommendation, it is suggested that research can be done by continuing to developed the SCM that is able to simulate the outcome for the effect of temperature and initial concentration.

In addition to that, the SCM can also be experimented to be developed using other approaches such as numerical method in MATLAB. This may give different limitations and results when applied with the operating parameters. The data from the current simulation of SCM can be used as a point of reference for experimental purposes. This is to see the validity when applied outside of simulation settings.

Lastly for the optimized diffusion coefficient, it is recommended that the optimization be done for a global optimization. This will yield the best optimized version for a bigger scope rather than that specifically to the specific boundary and constraints tested here,

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APPENDICES

```

% The version where the differentiation is a longer
function longerequation
global D
global q
Rc = 0.001; %m
D= 6.49E-15; %Diffusivity coefficients of CO2 (m2/s)
%q = 0.166527893 ; % dunno wat this is for
tend= 10000; %seconds

m = 2;
r = linspace(0,Rc,200);
t = linspace(0,tend,50);

sol = pdepe(m,@pdexlpde,@pdexlic,@pdexlbc,r,t);
% Extract the first solution component as u.
Concentration = sol(:,:,1);

% A solution profile can also be illuminating.
figure, plot(r,Concentration(end,:))
title(strcat('Solution at t = ', num2str(tend)))
xlabel('Distance r')
ylabel('Concentration (C)')

%Plot surface concentration vs. time
figure, plot(t,Concentration(:,1))
title('Surface Concentration on particle')
xlabel('Time (s)')
ylabel('Concentration (C)')

function [c,f,s] = pdexlpde(r,t,u,DuDx)
global D
global Rc
Rc = 0.001;% m
c = 0.85/D;
f = (2/Rc)+DuDx;
s = 0;
% -----
--|
function u0 = pdexlic(r)
u0 = 0; %set ic for all concentration at t=0
% -----

function [pl,ql,pr,qr] = pdexlbc(xl,ul,xr,ur,t)
global q
pl = -5.78E-05; %these two set on right side
ql =6.49E-15;
pr =ur;
qr = 0; %sets right side concentration to 0

```

```

%Set initial guess values for the diffusivity
Temperatureguess = 298;
Eaguess = 23.74;
Doguess = 6.3491
%load guess value into arrays
x0=[Temperatureguess Eaguess Doguess];
%Setting Boundary
lb = [0,0,-Inf] ;
ub = [323 ,Inf ,0]   ;% Temperature

%call solver for optimization
xopt=
fmincon(@objective,x0, [], [], [], [], lb,ub,@constraint, [
]);

%Retrieve optimizid diffusion
Diffusionopt= calcDiffusivity(xopt);

%Define function to calulcate effective diffusivity
function diffusivity = calcDiffusivity(x)
    temperature= x(1);
    Ea= x(2);
    Do=x(3);
    diffusivity= exp(Do- (Ea/8.314) * (1/temperature));
end

%Define function to calculat temperature
function temp = calctemp (x)
    temperature =x(1);

    temp = temperature + 0;
end

%Define objective function for optimization
function obj=objective(x)
    obj=-calcDiffusivity(x);
end
%Define constraints for optimization
function [c ,ceq] = constraint(x)

    c(2) = x(2) - 23.74

    ceq =[];
end

```

FINAL YEAR PROJECT												
Activity	FYP I											
	1	2	3	4	5	6	7	8	9	10	11	12
1. Literature Review												
1.1 Collection of variable data for objective 1												
1.2 Collection of variable data for objective 2												
1.3 Collection of variable data for objective 3												
2. Developing the Shrinking Core Model												
3. Develop coding to obtain optimized effective diffusivity												
3. Run Shrinking Core Model under different operating parameters												
4. Progress Update 1												
5. Testing Phase												
5.1 Document data												
5.2 Analyse data												
6. Progress Update 2												
7. Draft dissertation Submission												
6. Softbound Dissertation Submission												