

**ADSORPTION ISOTHERM CORRELATION FOR OCTANE  
ADSORPTION ON ACTIVATED CARBON**

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**CHEMICAL ENGINEERING  
UNIVERSITI TEKNOLOGI PETRONAS  
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**CERTIFICATION OF APPROVAL**

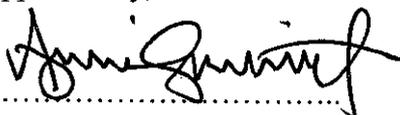
**Adsorption Isotherm Correlation for Octane Adsorption on Activated  
Carbon**

by

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A project dissertation submitted to the  
Chemical Engineering Programme  
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Approved by,



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1) Carbon, Activated  
2) Adsorption

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## 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.



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AHMAD FAHILI BIN MOHD ASRIDIN

## ABSTRACT

Adsorption is defined as the concentration of gas molecules near the surface of a solid material. The adsorbed gas is called adsorbate and the solid where adsorption takes place is known as the adsorbent. Adsorbent means having capacity or tendency to adsorb or causes to accumulate on a surface. The four most widely used adsorbents in decreasing order of commercial usage are activated carbon, molecular-sieve zeolites, silica gel and activated alumina.

Hydrocarbon refers to any of a class of organic chemical compounds composed only of the elements carbon and hydrogen such as methane, phenol and butadiene. The carbon atoms join together to form the framework of the compound; the hydrogen atoms attach to them in many different configurations.

Adsorption isotherm is the relationship between the partial pressure of an adsorbate gas and the surface coverage of the adsorbent at constant temperature. Not all the correlations can best fit all the data which covers wide range of the temperature and pressure found in most process situations

The objectives of this project are to search for possible software to be used to regress or correlate adsorption isotherms for data at a wide range of temperature and pressure.. Based on the analysis, comparison study on different types of adsorption isotherms is conducted. The comparison is also done for different type of regression method from Statistical Analysing System (SAS) and MATLAB programming.

The scope covers the study of a few selected adsorption isotherms, which are Modified Antoine's Equation, Langmuir, Sips (Langmuir-Freundlich), Toth, Dubinin-Radushkevich and Dubinin-Atakhov isotherms. The data used to determine the best adsorption isotherm is Octane Adsorption on Activated Carbon (M. Shariff, A., 1995). From the data on Octane, the pressure (kPa) and  $q$  (mol/kg) is given, thus deriving from this, the unknown variable properties can be achieved. Microsoft Excel has been identified as the software that will be used to correlate the adsorption Isotherm for Octane Adsorption on Activated Carbon.

From the results obtained, the best fit of adsorption isotherm data is determined by calculating the variance, where the lowest value of residual obtained shows the best fit.. Verification of the method used is done by comparing the result with published literature .The comparison study will be done between the result obtained from SAS and MATLAB programming using the same adsorption data, to identify the best software for regression of Adsorption Isotherms.

It can be concluded that, for nonlinear regression, the best approach is Microsoft Excel, since it can provide better fit for the adsorption isotherm of hydrocarbon adsorption. This method is capable for fitting adsorption data which covers wide range of temperature and pressure. Sips equation is the best correlation for the representation of octane adsorption on activated carbon as it gives the smallest value of variance.

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## NOMENCLATURE

A, B, C	Antoine constant for the particular component	
a, b, c, d, e, f, g, h	HBT constant	
A	Sticking coefficient	
b	Affinity constant	kPa <sup>-1</sup>
b <sub>0</sub>	Affinity constant at some reference temperature, T <sub>0</sub>	kPa <sup>-1</sup>
E <sub>0</sub>	Characteristic energy of the adsorption for reference adsorbate	J/mol
M <sub>w</sub>	Molecular weight	kg/mol
n	Parameter characterizing system heterogeneity	
n <sub>0</sub>	Parameter n at reference temperature, T <sub>0</sub>	
P	Pressure	kPa
P <sub>s</sub>	Saturated vapour pressure	MPa
q	Adsorbed amount	mol/kg
q <sub>m</sub>	Monolayer capacity	mol/kg
q <sub>s</sub>	Saturation adsorbed concentration	mol/kg
q <sub>s,0</sub>	Saturation capacity at reference temperature, T <sub>0</sub>	mol/kg

R	Universal gas constant	Joule/mol.K
T	Temperature	K
T <sub>0</sub>	Reference temperature	K
T <sub>R</sub>	Relative temperature	K
t	Parameter in Toth isotherm	
t <sub>0</sub>	Parameter t at reference temperature, T <sub>0</sub>	
ρ <sub>A</sub>	Density of adsorbed phase	kg/cm <sup>3</sup>
V <sub>m</sub>	Liquid molar volume	cm <sup>3</sup> /mol
V*	Characteristic volume	cm <sup>3</sup> /mol
V <sub>R</sub> <sup>(0)</sup>	Corresponding state function for normal fluids	
V <sub>R</sub> <sup>(δ)</sup>	Deviation function	
W	Volume of adsorbate	cm <sup>3</sup> /kg
W <sub>0</sub>	Maximum volume of adsorbate to occupy	cm <sup>3</sup> /kg
y <sub>i</sub>	response value	
ŷ <sub>i</sub>	predicted value	
θ	Fraction of monolayer coverage	
gamma	Activity coefficient	
ω <sub>SRK</sub>	Acentric factor from the Soave-Redlich-Kwong equation of state	
delta T <sub>0</sub>	Ratio of surface to pore volume diffusion	

# CHAPTER 1

## INTRODUCTION

### 1.1 Background of Study

Adsorption is defined as the concentration of gas molecules near the surface of a solid material. The adsorbed gas is called adsorbate and the solid where adsorption takes place is known as the adsorbent. Adsorption is a physical phenomenon (usually called physisorption) that occurs at any environmental condition (pressure and temperature) but only at very low temperature it becomes measurable. Thus physisorption experiments are performed at very low temperature, usually at liquid nitrogen or liquid argon boiling temperature at atmospheric pressure. Adsorption takes place because of the presence of an intrinsic surface energy. When a porous material is exposed to a gas, an attractive force acts between the exposed surface of the solid and the gas molecules. The result of these forces is characterized as physical (or Van der Waals) adsorption, in contrast to the stronger chemical attractions associated with chemisorptions. The surface area of a solid includes both the external surface and the internal surface of the pores.

Due to the weak bonds involved between gas molecules and the surface (less than 10 Kcal/mole), adsorption is a reversible phenomenon. Gas physisorption is considered non-selective, thus filling the surface step by step (or layer by layer) depending on the available solid surface and the relative pressure. Filling the first layer enables the measurement of the surface area of the material because the amount of gas adsorbed when the mono-layer is saturated is proportional to the entire surface that includes the internal and external surface. The complete adsorption/desorption analysis is called adsorption isotherm.

Adsorbent means having capacity or tendency to adsorb or cause to accumulate on a surface. The four most widely used adsorbents in decreasing order of commercial usage are activated carbon, molecular-sieve zeolites, silica gel, and activated alumina (Seader and Henley, 1998). Activated Carbon is produced from the carbonaceous matters such as wood, coals, and rice husks. It is been used for a wide range of applications which one of it is in adsorption processes. It serves as important adsorbents due to its large surface area and non-polar or slightly polar surfaces, which promotes higher adsorption rate compared to other adsorbents.

Adsorption isotherm is the relationship between the partial pressure of an adsorbate gas and the surface coverage of the adsorbent at constant temperature. In other words, adsorption isotherm is the relationship of adsorbed material with operating pressure or concentration at constant temperature. Adsorption isotherm is used for modeling and scale up purposes. There are many classes of adsorption isotherms that have been developed all these years. Brunauer et al., (1940), has divided isotherms of physical adsorption into five types as shown in Figure 1.1.

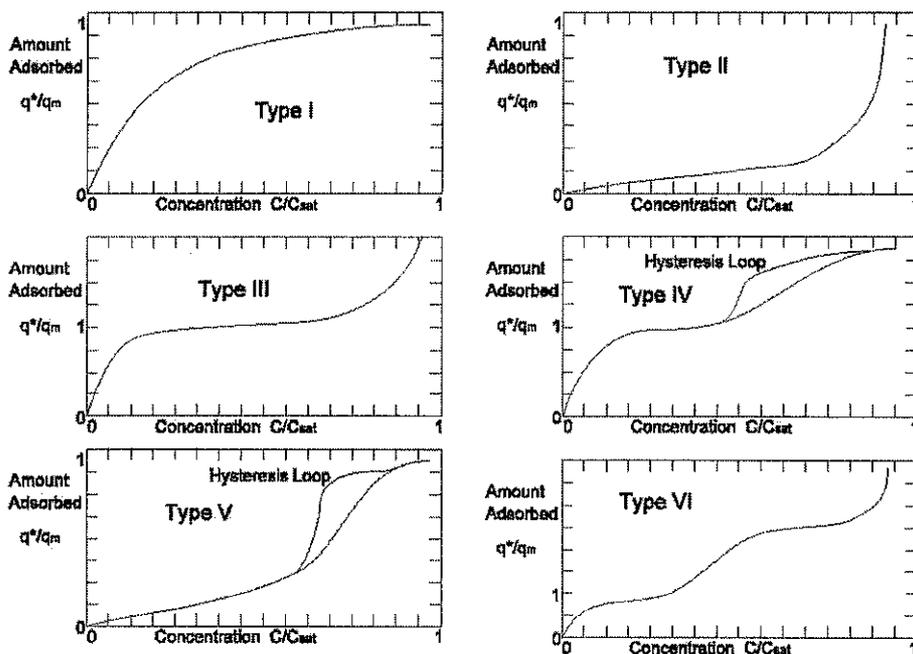


Figure 1.1 Five types of pure-component gas adsorption isotherms in the classification of Brunauer, Deming, Deming and Teller (BDDT). (Kent, 1995)

Hydrocarbon refers to any of a class of organic chemical compounds composed only of the elements carbon and hydrogen such as methane, phenol and butadiene. The carbon atoms join together to form the framework of the compound; the hydrogen atoms attach to them in many different configurations. Adsorption process has been widely used in industry for separations and fractionation of hydrocarbons. A very well known process called Parex® uses adsorption process to recover very pure *p*-xylene from mixed isomers (Kent, 1995).

This study is done to identify the best software that is available in the market, to derive, regress and correlate the adsorption isotherms, to get a curve fit that well describes the Octane adsorption of activated carbon. With this correlations or model, the design of a column or adsorption system can be done in such a way that it can optimize the adsorption process for continuous operations. The outcome of this study is very beneficial towards the community and engineers in designing.

## **1.2 Problem Statement**

There are many adsorption isotherms that are beneficial in representing the various types of adsorption equilibrium data. This is due to the wide range of application that is available nowadays. However, not all are appropriate over the wide range of temperature and pressure found in most process situations. Hence, it is almost impossible to identify one single correlation that best fits all adsorption data. Nowadays, there are many types of software that can be used to do a regression and curve fitting. Previous study that was done only specifies the type of software to be used, but does not really show how the regression is done. This study will determine the best software that will be used to regress the adsorption isotherm data and provide the best fit based on Octane Adsorption. There are many popular computer software that are capable for regression such as MATLAB, SPSS, SAS, and Microsoft Excel. Nevertheless, not all computer software is able to regress the nonlinear adsorption data which covers a wide range of temperature and pressure.

### **1.3 Objectives**

The objectives of the study are as follows:

- i) To search for possible software to be used to regress or correlate adsorption isotherms for data at a wide range of temperature and pressure.
- ii) To conduct comparison study on Adsorption Isotherms using the identified software.
- iii) To compare results obtained with other published literature on related work or similar study.

### **1.4 Scope of Study**

The data used to determine the best adsorption isotherm is Octane Adsorption on Activated Carbon (M. Shariff, A., 1995). From the data on Octane, the pressure (kPa) and  $q$  (mol/kg) is given. Deriving from this, the unknown variable properties can be achieved. Microsoft Excel has been identified as the software that will be used to correlate the adsorption Isotherm for Octane Adsorption on Activated Carbon. The comparison study will be done between the result obtained from SAS and MATLAB programming using the same adsorption data, to identify the best software for regression of Adsorption Isotherms.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Adsorption Isotherm of Pure Component Equilibria

There are many relevant published literatures of adsorption processes available nationwide. A brief and concise summary of some relevant theories on adsorption isotherms of single component is given.

Langmuir, (1916), derived an adsorption isotherm equation for the mono-molecular adsorption on energetically homogeneous surfaces. This is an important basis for the description of adsorption purposes. The equation can be written as:

$$\theta = \frac{q}{q_s} = \frac{\alpha P}{1 + \alpha P} \quad (2.1)$$

where  $\alpha$  refers to the empirical fitted constant which is dependent on temperature. The equation is useful for practical purposes as it fits Type 1 isotherms and the initial region of Type II isotherm. The equation reduces to a linear relationship at low coverage.

Freundlich, (1926), proposed an empirical model which is popular largely due to its simplicity where it can predict experimental equilibria over a wide range of temperature and pressure. The equation is written as:

$$\theta = \alpha P^\beta \quad (2.2)$$

where both  $\alpha$  and  $\beta$  are empirical fitted constant which are a function of temperature. On the other hand, this equation does not reduce to a Henry's law limit except when  $\beta$  equals to unity.

Sips, (1948), suggested combining the Langmuir and Freundlich equations. The equation is stated as:

$$\theta = \frac{\alpha P^\beta}{1 + \alpha P^\beta} \quad (2.3)$$

where  $\alpha$  and  $\beta$  are empirical constant which are function of temperature.

Redlich and Peterson, (1959), proposed other combined of Langmuir-Freundlich isotherm. The equation can be written as:

$$\theta = \frac{\alpha P}{1 + \alpha_1 P^\beta} \quad (2.4)$$

where both  $\alpha$  and  $\alpha_1$  are empirical constant and depend on temperature while  $\beta$  is a constant which is independent of temperature. This equation converges to linear form at low pressure as does the Langmuir equation. At high pressure, this equation converges to the Freundlich form.

Polanyi, (1932), has derived a totally different theory which is the potential theory. It is based on the description of the potential field instead of the model of different adsorption sites. The models are very beneficial for adsorption on microporous materials for example activated carbon. Two of the best known equations derived from this theory are those of Dubinin-Radushkevich, (1947), and Dubinin-Astakhov, (1971).

Dubinin (1960) derived a theory of “volume filling of micropores”, which contains geometrical parameter of the micropore volume instead of the internal surface of the adsorbent. This model is widely used to predict adsorption isotherms of organic vapors on activated carbons.

Friday and LeVan (1982) had developed an empirical correlation that described the adsorption equilibrium based on the Antoine equation of water adsorbed on 4A

molecular Sieve. They used an equilibrium model to investigate solute condensation in an adiabatic adsorption bed during thermal regeneration. They found out that a liquid phase can develop in a fix-bed during thermal regeneration because of condensation of the solute. The original Antoine Equation, which was used to predict saturated vapor pressure, was modified to predict the adsorption equilibrium data over the wide range of temperature and pressure.

Hackskaylo and Levan (1985) provided the explanation on the correlation, which correlates the adsorption equilibrium data of light hydrocarbons on porous adsorbents. This modified Antoine isotherm reduces to the linear lower limit of Henry's Law at low loading and its constants are loading dependent.

## **2.2 Concluding Remarks**

There are many literatures on adsorption isotherms. There are also many overviews of the correlations or models for the prediction of adsorption equilibria. Over the years, many people have done numerous studies on adsorption isotherms. From the reviews read, it is difficult to fully understand the subject matter because the authors normally just state the method and software used, but never described on how to actually derive it. Also, from all the literature that has been read, none of the authors use Microsoft Excel to do any regression or correlation. This might be due to technological constraints and development. Hence, this study will be fully done by using Microsoft Excel, to compete with well known statistical software like SAS and MATLAB, and also to find the best possible software to do regression or correlation of adsorption isotherms.

## CHAPTER 3

### THEORY

#### 3.1 Introduction

Models or correlations of adsorption equilibria from experimental data are essential to the design of adsorption system. Adsorption isotherms can be classified into five different types, according to Brunauer et al., (1940) as shown in Figure 1.1 on page 3 of section 1.1: Background of Study. The simplest and most commonly found isotherm is Type I, which corresponds to unimolecular adsorption and applies often to gases at temperatures above their critical temperature. Meanwhile, Type II isotherm is characterized by multimolecular adsorption on non-porous solids. It is observed for gases at temperature below their critical temperature and for pressure below, but approaching the vapor pressure. Both Types I and II are desirable isotherms which exhibit strong adsorption. Type III isotherm is quite rare and undesirable because the extent of adsorption is low except at high pressures. This isotherm is characterized with non-porous solids. Type IV is characterized by multilayer adsorption on a non-porous solid with the existence of a hysteresis loop. Alternatively, Type V is associated with adsorption on porous solids with hysteresis. Hysteresis phenomenon can occur in multimolecular adsorption regions for both isotherms of types IV and V.

#### 3.2 Adsorption Equilibrium Models for Pure Components

There are many isotherm models that are widely used to correlate experimental adsorption isotherm data for various systems. In this study, the isotherms that will be focused on are Modified Antoine Equation Isotherms for two and three parameters, Langmuir's Isotherm, Sips Isotherm, Toth Isotherm, Dubinin-Radushkevich Isotherm and Dubinin-Astakhov Isotherm.

### 3.2.1 Modified Antoine Equation Isotherms

The Modified Antoine Equation was developed by Friday and LeVan (1982) which is an empirical adsorption equilibrium relation based on the Antoine Equation for water absorbed on 4A molecular sieve. The Original Antoine Equation was modified to correlate the experimental adsorption equilibrium data over a wide range of temperature (273K to 588K). The modified Antoine equation gave better fit in a statistical sense than that obtained with the Dubinin-Radushkevich and Dubinin-Astakov equations. The modified Antoine Equation isotherm reduces the linear lower limit of Henry's Law at Low loading and constants are loading dependent.

The original Antoine Equation:

$$\ln P_s = A - \frac{B}{C+T} \quad (3.1)$$

Where,

$P_s$ : saturated vapour pressure of pure component

T: absolute temperature

A, B, C: constants for component.

The Modified Antoine Equation:

$$\ln P = A' - \frac{B'}{C'+T} \quad (3.2)$$

Where  $A'$ ,  $B'$ ,  $C'$  are dependent on the fractional filling of the pore volume,  $\theta$ . The constants are continuous function of  $\theta$  for  $\theta \leq 1$  and become equal to the equal to the constants in the original Antoine Equation as  $\theta = 1$ .

The simplest form was when the heat of adsorption was taken to be independent of loading,

$$A' = A + \ln \theta \quad B' = B \quad C' = C \quad (3.3)$$

This is the linear isotherm that contains one fitting parameter ( $W_0$ ). For a linear variation of the heat of adsorption with loading, the constants are

$$A' = A + \ln \theta \quad B' = B + b(1 - \theta) \quad C' = C \quad (3.4)$$

Expressions which contain two fitting parameters ( $W_0, b$ ). For a more complicated dependencies of the heat of adsorption on loading,

$$A' = A + \ln \theta \quad B' = B + b(1 - \theta) \quad C' = C + c(1 - \theta) \quad (3.5)$$

Expressions which contain three fitting parameters ( $W_0, b, c$ ). Even more complex relationships of  $A'$ ,  $B'$  and  $C'$  to  $\theta$  are possible by incorporating the expansion in higher order polynomials of  $1 - \theta$  into the constants. Such an isotherm was given by Schweiger and LeVan, (1993) for the adsorption of water on BPL activated carbon.

$$A' = A + \ln \theta + a_1 (1 - \theta) + a_2 (1 - \theta)^2 + a_3 (1 - \theta)^3 + a_4 (1 - \theta)^4$$

$$B' = B + b(1 - \theta) \quad C' = C \quad (3.6)$$

Expressions which contain six fitting parameters ( $W_0, a_1, a_2, a_3, a_4, b$ ). a further modification could be expressed as

$$A' = A + \ln \theta + a_1 (1 - \theta) + a_2 (1 - \theta)^2 + a_3 (1 - \theta)^3 + a_4 (1 - \theta)^4$$

$$B' = B + b(1 - \theta) \quad C' = C + c(1 - \theta) \quad (3.7)$$

Which contains seven fitting parameter ( $W_0, a_1, a_2, a_3, a_4, b, c$ ).

### 3.2.2 Langmuir Isotherms

Langmuir isotherm was developed based on a kinetic principle, that is the rate of adsorption is equal to the rate of desorption from the surface (Do, 1998). It is the simplest isotherm for both physical and chemical adsorption. This isotherm in its usual form is based on the following implicit assumptions:

1. Adsorption of adsorbate molecules takes place at well-defined localized place.
2. Each site can accommodate one and only one molecule or atom.
3. There is no lateral interaction (interaction between neighbouring adsorbed adsorbate molecules).

Langmuir isotherm in terms of fractional loading is derived by equating the rates of adsorption and desorption. The resulted equation is as below:

$$\theta = \frac{bP}{1+bP} \quad (3.8)$$

$$b(T) = b_0 \exp\left(\frac{Q}{RT} - \frac{Q}{RT_0}\right) \quad (3.9)$$

Where,

$\theta$  is the fractional coverage

$b$  is the affinity constant

$P$  is the pressure

$Q$  is heat of adsorption

$R$  is the gas constant

$T$  is temperature

$T_0$  is the reference temperature

$b$  is the affinity constant

$b_0$  is the affinity constant at the reference temperature.

The isotherm equation (3.8) reduces to Henry law isotherm when the pressure is very low, that the amount adsorbed increases linearly with pressure. When affinity constant  $b$  is larger, the surface is covered with more adsorbate molecule. This is due to the stronger affinity of adsorbate molecules towards the surface. At a given pressure, increase in the temperature will decrease the amount adsorbed.

Isotherm equation (3.8) in the form of fractional loading is not useful for data correlation. This is due to data are usually correlated in the amount adsorbed versus pressure. The Langmuir equation for data correlation is as follows:

$$q = q_s \frac{b(T)P}{1+b(T)P} \quad (3.10)$$

Where,

$q$  is amount adsorbed in mol/kg

$q_s$  is the maximum adsorbed concentration corresponding to a complete monolayer coverage.

$$q = q_s \frac{b_0 \exp\left(\frac{Q}{RT} - \frac{Q}{RT_0}\right)P}{1+b_0 \exp\left(\frac{Q}{RT} - \frac{Q}{RT_0}\right)P} \quad (3.11)$$

And,

$$q_s = q_{s,0} \exp(\text{delta}T_0 * (1 - T / T_0)) \quad (3.12)$$

Where,

$q_{s,0}$  is the saturation capacity at the reference temperature  $T_0$

$\text{delta}T_0$  is a constant parameter.

### 3.2.3 Sips Equation (Langmuir-Freundlich)

Sips equation is (also known as the Langmuir-Freundlich equation) in literature as it has the combination form of Langmuir and Freundlich equation. This equation is similar in the form to the Freundlich equation, but it has a finite limit when the pressure is sufficiently high (Do, 1998). The temperature dependence of the Sips equation is as below:

$$q = q_s \frac{(bP)^{1/n}}{1 + (bP)^{1/n}} \quad (3.13)$$

Where the affinity constant  $b$  and the exponent  $n$  are given by the following form:

$$b = b_\infty \exp\left(\frac{Q}{R_g T}\right) = b_0 \exp\left[\frac{Q}{R_g T_0} \left(\frac{T_0}{T} - 1\right)\right] \quad (3.14)$$

$$\frac{1}{n} = \frac{1}{n_0} + \alpha \left(1 - \frac{T_0}{T}\right) \quad (3.15)$$

Where,

$b_\infty$  is the affinity constant at infinite temperature

$b_0$  is the affinity constant at some reference temperature  $T_0$

$n_0$  is the parameter  $n$  at the same reference temperature

$\alpha$  is a constant parameter.

The saturation capacity  $q_s$  can be either considered as constant or it may take the following temperature dependence:

$$q_s = q_{s,0} \exp\left[\text{delta}T_0 \left(1 - \frac{T}{T_0}\right)\right] \quad (3.16)$$

Where,

$q_{s,0}$  is the saturation capacity at the reference temperature  $T_0$

$\text{delta}T_0$  is a constant parameter.

The temperature dependence of Sips equation represented by Equation (3.13) resembles the Langmuir equation. However, the difference is the additional parameter “ $n$ ” in the

Sips equation. The parameter  $n$  could be regarded as the parameter characterizing the system heterogeneity (Do, 1998). This parameter is usually greater than unity. The larger this parameter, the higher is the degree of heterogeneity. The parameter  $n$  decreases with temperature suggesting that the system is less heterogeneous as the temperature increases.

### 3.2.3 Toth Equation

Toth equation is one of the empirical equations that are valid for wide range of pressure (Do, 1998). This equation describes well many systems with sub-monolayer coverage. The Toth equation is represented as the following form:

$$q = q_s \frac{bP}{[1 + (bP)^t]^{1/t}} \quad (3.17)$$

Where,

$b$  and  $t$  are specific for adsorbate-adsorbent pairs.

These parameters are temperature dependent, with the parameter  $b$  is described as the usual form of the adsorption affinity:

$$b(T) = b_\infty \exp\left(\frac{Q}{R_g T}\right) = b_0 \exp\left[\frac{Q}{R_g T_0} \left(\frac{T_0}{T} - 1\right)\right] \quad (3.18)$$

Where,

$b_\infty$  refers to the affinity constant at infinite temperature

$b_0$  is the affinity constant at some reference temperature  $T_0$

$Q$  is the measure of the heat of adsorption.

In the meantime, the parameter  $t$  is usually less than unity. This parameter is represented by the following empirical functional form of temperature dependence:

$$t = t_0 + \alpha \left(1 - \frac{T_0}{T}\right) \quad (3.19)$$

As mentioned previously in the Sips equation theory, the saturation capacity  $q_s$  can be either considered as constant or it may take the following temperature dependence:

$$q_s = q_{s,0} \exp \left[ \Delta T_0 \left( 1 - \frac{T}{T_0} \right) \right] \quad (3.20)$$

Where,

$q_{s,0}$  is the saturation capacity at the reference temperature  $T_0$

$\Delta T_0$  is a constant parameter.

This equation is suitable for fitting data of many adsorbates such as hydrocarbons, carbon oxides on activated carbon as well as zeolites due to its simplicity in form and its correct behaviour at low and high pressures (Do, 1998).

### 3.2.5 Dubinin-Radushkevich and Dubinin-Astakhov Isotherms

One of the most successful isotherms of this sort was proposed by Dubinin and Radushkevich, (1947). The characteristic curve was based on a Gaussian pore size distribution which is:

$$\theta = \exp \left[ - \left( \frac{\varepsilon}{\beta E_0} \right)^2 \right] \quad (3.21)$$

Where,

$E_0$  is the characteristic energy of adsorption for a reference adsorbate

$\beta$  is the scaling factor to relate the adsorbates to the reference adsorbate

$\theta$  is the fractional filling of the pore volume which is represented by

$$\theta = \frac{W}{W_0} \quad (3.22)$$

Where,

$W$  is the volume of adsorbate in micropore

$W_0$  is the maximum volume that the adsorbate can occupy.

The Dubinin-Radushkevich equation describes well many carbonaceous solids with low

degree of burn-off (Do, 1998). However, this equation does not describe the equilibrium data for carbonaceous solids resulting from a high degree of burn-off during activation because degree of heterogeneity increases.

In order to allow for the surface heterogeneity, Dubinin and Astakhov proposed the following form:

$$\theta = \exp \left[ - \left( \frac{\varepsilon}{\beta E_0} \right)^n \right] \quad (3.23)$$

Where,

$n$  refers to the surface heterogeneity.

When  $n$  equals to 2, the Dubinin-Astakhov equation reduces to the Dubinin-Radushkevich equation. The additional parameter of Dubinin-Astakhov isotherm provides flexibility in the description of wide range of micropore size distribution of many microporous solids. If the parameter  $n$  of a given system is found to be smaller than 3, the system has a broad micropore size distribution. Typical values of  $n$  for strongly activated carbon are in the range of 1.2 to 1.8 (Do, 1998).

The rearranged form of the Dubinin-Radushkevich isotherms is given as

$$\ln P = \ln P_s - \frac{\beta E_0}{RT} (-\ln \theta)^{1/2} \quad (3.24)$$

and the rearranged form for Dubinin-Astakhov is written as

$$\ln P = \ln P_s - \frac{\beta E_0}{RT} (-\ln \theta)^{1/n} \quad (3.25)$$

where,

$P$  is the adsorbate vapor pressure in MPa

$P_s$  is the saturated vapour pressure of the adsorbate in MPa

$E_0$  is the characteristic energy of the adsorption for reference adsorbate in J/mol

$T$  is isotherm temperature in K

$R$  is the universal gas constant in J/mol.K,  $\theta$  is the fractional filling of pore volume.

Substituting these equations with equation (3.22) and  $W=qV_m$ , the equations (3.26) and (3.27) are obtained for Dubinin-Radushkevich and Dubinin-Astakhov isotherms respectively:

$$q = \frac{W_0}{V_m} \exp \left[ - \left( \frac{RT \ln(p_s / p)}{\beta E_0} \right)^2 \right] \quad (3.26)$$

$$q = \frac{W_0}{V_m} \exp \left[ - \left( \frac{RT \ln(p_s / p)}{\beta E_0} \right)^n \right] \quad (3.27)$$

Where,

$W_0$  is the micropore volume in  $\text{cm}^3/\text{kg}$

$V_m$  is the liquid molar volume in  $\text{cm}^3/\text{mol}$ .

To fit the parameters of Dubinin-Radushkevich and Dubinin-Atakhov Isotherms, the adsorbed amount per unit mass,  $q$  ( $\text{mol}/\text{kg}$ ) has to be transformed into adsorbed volume per unit mass,  $W$  ( $\text{cm}^3/\text{kg}$ ).

For this transformation, the following equation is employed:

$$W = \frac{q \cdot M_w}{\rho_A} = qV_m \quad (3.28)$$

Where,

$M_w$  is molecular weight of adsorbate in  $\text{kg}/\text{mol}$ ,

$\rho_A$  is the density of adsorbed phase in  $\text{kg}/\text{cm}^3$

$V_m$  is the saturated liquid molar volume in  $\text{cm}^3/\text{mol}$ .

Since amount adsorbed,  $q$  is known, therefore the only unknown value is the saturated liquid molar volume,  $V_m$ . Firstly, the temperature of its pure component vapour pressure need to be determined. A similar technique employed by HacsKaylo and Levan, (1985), was used in this project to determine the temperature using Antoine equation. In this equation, the saturated vapour pressure is assumed as a pseudo saturated vapor pressure

which is considered to be equivalent to the equilibrium vapour pressure with the adsorbed loading at the temperature of interest.

For a known vapour pressure, the temperature is determined by this equation:

$$T = \frac{B}{A - \ln P} - C \quad (3.29)$$

Where,

A, B and C are the parameters of Antoine equation for octane.

Based on temperature evaluated using equation (3.29), the saturated molar volume can be obtained using Hankinson-Brost-Thomson (HBT) technique (Reid et. al., 1987). This technique employed the following equations:

$$V_m = V^* \times V_R^{(0)} [1 - \omega_{SRK} V_R^{(\delta)}] \quad (3.30)$$

$$V_R^{(0)} = 1 + a(1 - T_R)^{1/3} + b(1 - T_R)^{2/3} + c(1 - T_R) + d(1 - T_R)^{4/3} \quad \text{for } 0.25 < T_R < 0.95 \quad (3.31)$$

$$V_R^{(\delta)} = \frac{(e + fT_R + gT_R^2 + hT_R^3)}{(T_R - 1.00001)} \quad \text{for } 0.25 < T_R < 1.0 \quad (3.32)$$

With,

$$T_R = \frac{T}{T_C} \quad (3.33)$$

where,

$V^*$  is a characteristic volume in  $\text{cm}^3/\text{mol}$

$V_R^{(0)}$  is a corresponding state function for normal fluids

$V_R^{(\delta)}$  is a deviation function

$\omega_{SRK}$  is an acentric factor from the Soave-Redlich-Kwong equation of state

a to h are HBT constant

$T_R$  is a relative temperature.

The Antoine equation parameters and the HBT equations parameters for octane are given in Tables A.1.1 and A.1.2 of Appendix A.

## CHAPTER 4

### METHODOLOGY

#### 4.1 Introduction

There are various tools that can be used to do a research on the correlations of adsorption isotherms for Octane adsorption on activated carbon. Among the available software for this purposes are Microsoft Excel, MATLAB, and SAS. These are powerful mathematical computation tools, which also provide extensive capabilities of generating graphs. In this study, Microsoft Excel is chosen to regress the isotherms to obtain a correlation of data and achieve a curve fit with the Octane Adsorption data. The data obtained will be compared with the results from previous study.

Considering easy accessibility and capability, Microsoft Excel has been chosen as the tool for the nonlinear regression purposes. The data will then be compared to the MATLAB programming and SAS programming.

#### 4.2 The Adsorption Isotherms

About 7 adsorption Isotherms will be used in this study. Expressions for adsorption isotherm are given by the equations, (3.2) for Modified Antoine Equation Isotherm, (3.11) for Langmuir Isotherm, (3.16) for Sips Isotherm, (3.20) for Toth Isotherm, (3.26) for Dubinin-Radushkevich Isotherm and (3.27) for Dubinin-Astakhov Isotherm.

### 4.3 Data for Nonlinear Regression

The data used to determine the best adsorption isotherm is Octane Adsorption on Activated Carbon (M. Shariff, A., 1995). The data is listed in the Appendix. From the data on Octane, the pressure (kPa) and  $q$  (mol/kg) is given. Deriving from this, the unknown variable properties can be achieved. The graph of amount Adsorbed ( $q$ ) versus pressure ( $P$ ) is plotted based on the nonlinear regression data.

### 4.4 Procedure

First, the equation is determined and all parameters must be identified. This includes all possible factors needed. When all data from the equation has been set, the next step is to do a sample of the flow to identify each known and unknown variables. After all the steps in equation have been done until a result is obtained, a table is set with all the Octane data and each part of the equation in the table. The initial guess for all unknown variables is then set into the program. After all data has been introduced in the table, then the Variance is calculated. From the variance, Solver is then used to set the variance as minimal as possible, to achieve the best fit on the graph. The solver will calculate the best variable to be placed in the unknown variable to achieve the best fit.

Solver is part of a suite of commands sometimes called what-if analysis tools. With Solver, an optimal value for an equation in one cell (target cell) can be found. The Solver works with a group of cells that are related to the equation in the target cell. Solver changes the values in the changing cells specified to produce the results. Solver can be used to determine the maximum or minimum value of the cell specified, or can be set near a number specified.

When the desired variables have been determined, a graph of amount Adsorbed ( $q$ ) versus pressure ( $P$ ) is then plotted based on the nonlinear regression.

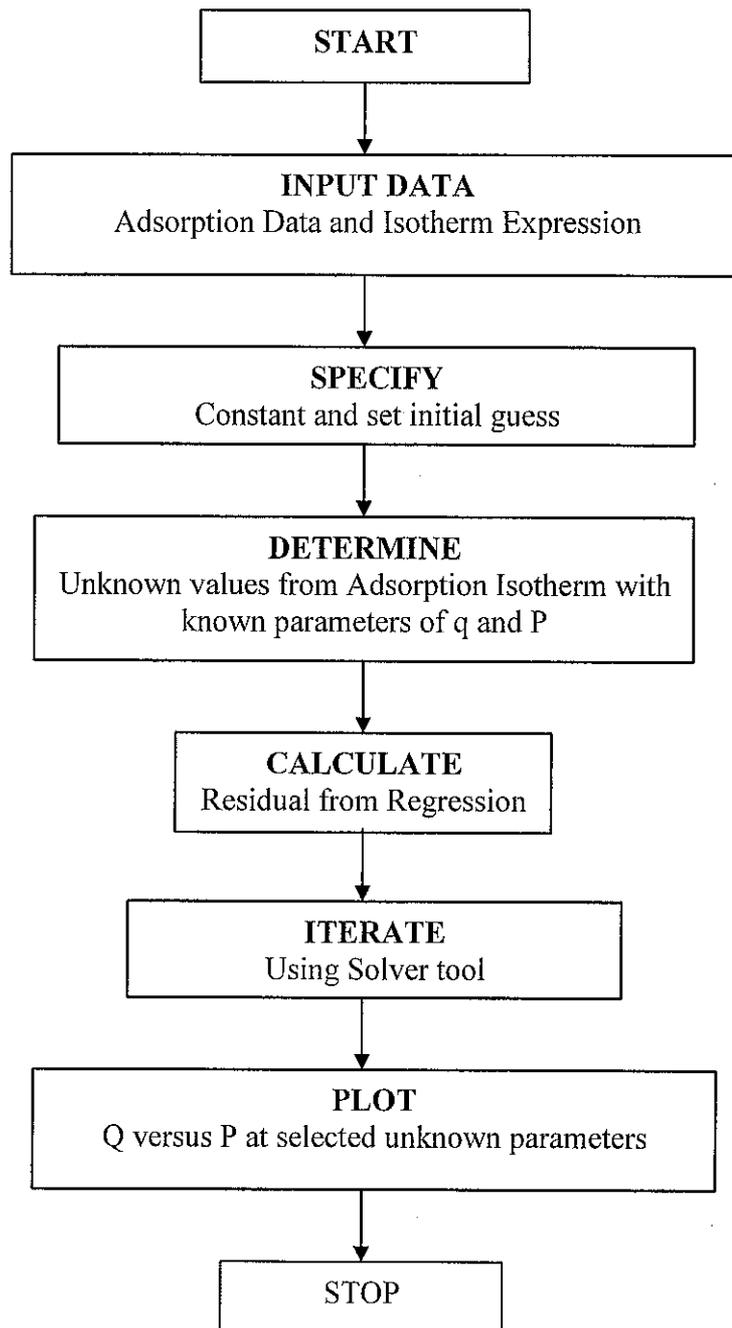


Figure 4.2 Flowchart for procedure.

#### 4.4.1 Solver Parameter

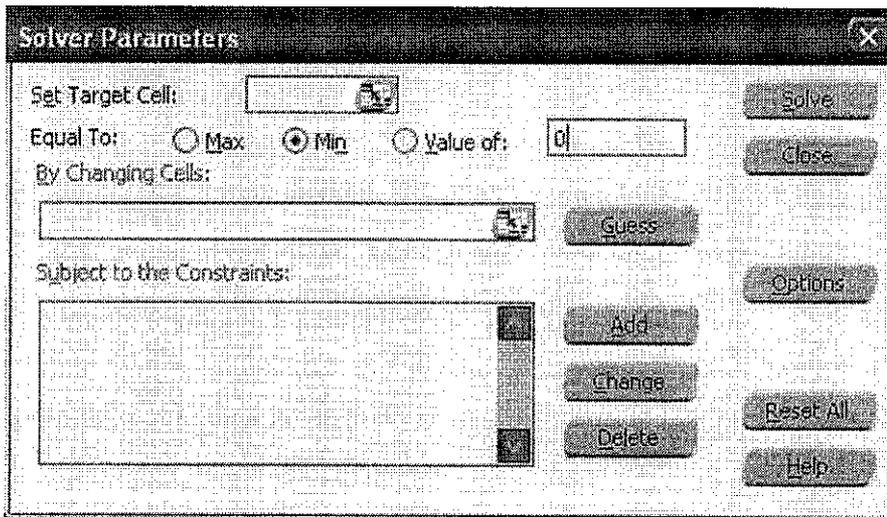


Figure 4.1 Solver Parameters

1. Set the Target Cell: target cell specifies the cell where the equation is set.
2. Identify Variables: the cell which the variables are present to be changed
3. Specify task, to set the Target cell as Maximum as possible, Minimum as possible or user specified
4. Solve button pressed then results obtained.

#### 4.5 Concluding Remarks

Microsoft Excel is used for the nonlinear regression. The correlation of adsorption equilibria is performed by fitting a single equation to the experimental data for temperatures of 308K, 328K and 348K. The unknown parameters are determined from the Variance generated, where the lowest value of variance is the best fit for the graph plotted. This method is capable of performing regression at a wide range of temperature and pressure.

## CHAPTER 5

### RESULTS AND DISCUSSION

#### 5.1 Introduction

Although the nonlinear regression is done using Microsoft Excel with simple methods, the best fit line for all selected isotherms can be identified. The best fit for each curve was calculated by minimizing the total variance obtained. The total variance is the total residual calculated. By decreasing the total variance to almost zero value, the best fit for the curve can be achieved. In this study, the results is also compared to the residual obtained from MATLAB programming and SAS programming.

#### 5.2 Adsorption Equilibria Models for Pure Components

##### 5.2.1 Modified Antoine's Equation Isotherm

For the Modified Antoine's Equation Isotherm, equations (3.2), the correlation is done for two-fitted parameters and three fitted parameters. The parameters can be determined using equations (3.4) and (3.5). The equations are to fit the data of octane adsorption. The detailed explanation is discussed previously in chapter 3.2.1. From these equations, the known parameters are the experimental data which is the amount adsorbed,  $q$  (mol/kg) and pressure,  $P$  (kPa).

### 5.2.1.1 Modified Antoine's Equation Isotherm (two fitted parameters)

The nonlinear regression was conducted to estimate the values for  $W_0$  and  $b$  and also the value of residuals. From the total of residuals, the variance has been calculated. The unknown variables are listed in table 5.1.

Table 5.1 Optimal parameters obtained by Modified Antoine's Equation Isotherm (two fitted parameters)

	$W_0$	$b$	Variance
All data	557.9030	966.6034	0.4862
Omit last data	532.0561	1043.6456	0.1980

Comparing the obtained parameters, it is noticeable that the values of variance are smaller for the regression which omits the last data, rather than the regression for all experimental data. Graph representation of the correlation using Modified Antoine's Equation Isotherm (two fitted parameters) is shown in Figure 5.1 (a) and Figure 5.1 (b) on the following page.

### Modified Antoine 2 - All Data

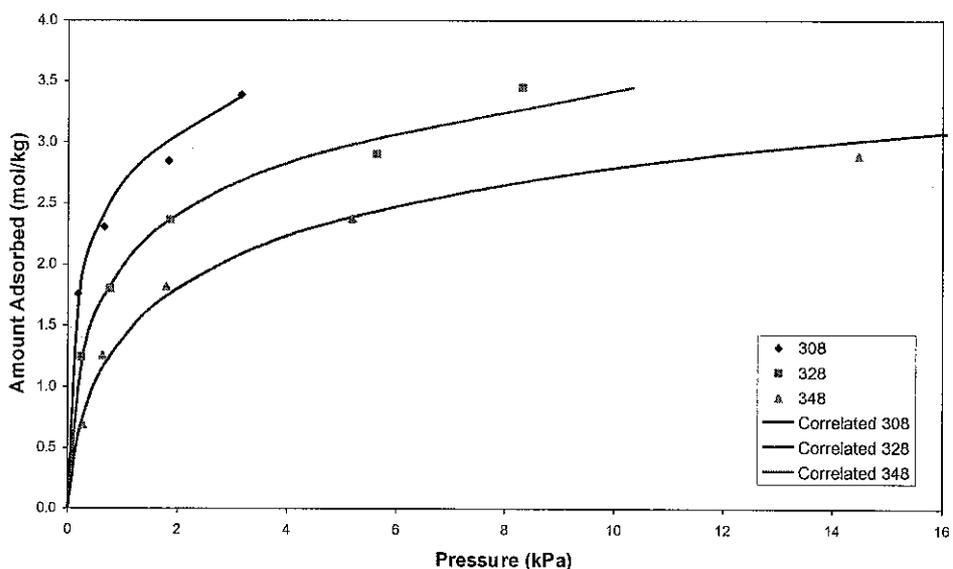


Figure 5.1 (a) Correlation using Modified Antoine's Equation Isotherm (two fitted parameters) for all experimental data points.

### Modified Antoine 2 - Omit Last Data

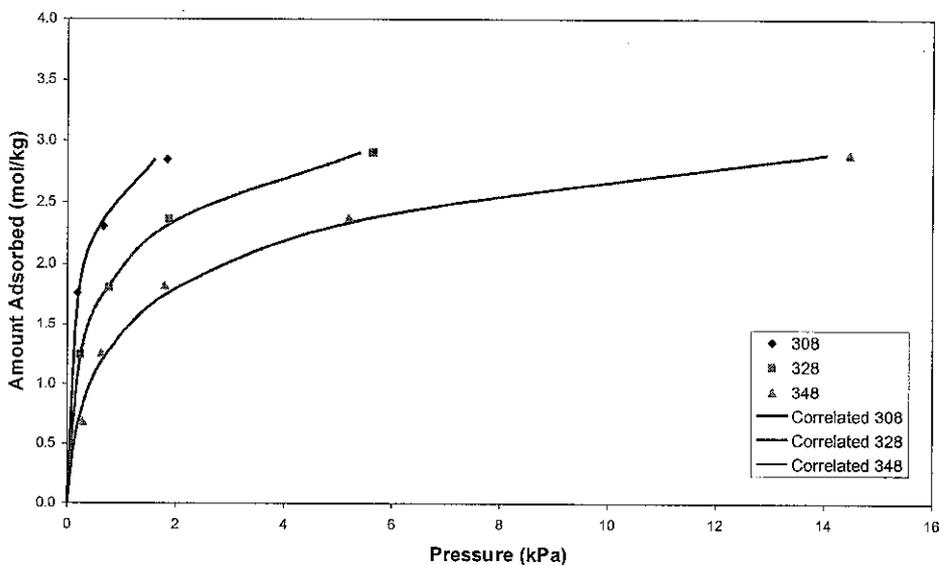


Figure 5.1 (b) Correlation using Modified Antoine's Equation Isotherm (two fitted parameters) with last data omitted experimental data points.

### 5.2.1.2 Modified Antoine's Equation Isotherm (three fitted parameters)

The nonlinear regression was conducted to estimate the values for  $W_0$ ,  $b$  and  $c$  and also the value of residuals. From the total of residuals, the variance has been calculated. The unknown variables are listed in Table 5.2 as shown below:

Table 5.2 Optimal parameters obtained by Modified Antoine's Equation Isotherm (three fitted parameters)

	$W_0$	$b$	$c$	Variance
All data	558.1111	611.5986	-26.0174	0.4719
Omit last data	528.1743	1579.2685	38.0090	0.1829

Comparing the obtained parameters, it is noticeable that the values of variance are smaller for the regression which omits the last data, rather than the regression for all experimental data. Graph representation of the correlation using Modified Antoine's Equation Isotherm (two fitted parameters) is shown in Figure 5.2 (a) and Figure 5.2 (b) on the following page.

### Modified Antoine 3 - All Data

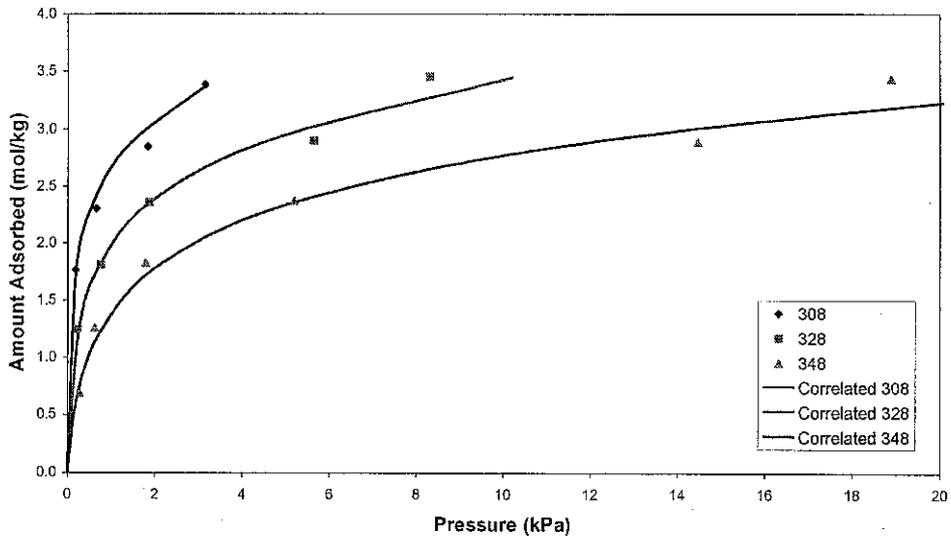


Figure 5.2 (a) Correlation using Modified Antoine's Equation Isotherm (three fitted parameters) for all experimental data points.

### Modified Antoine 3 - Omit Last Data

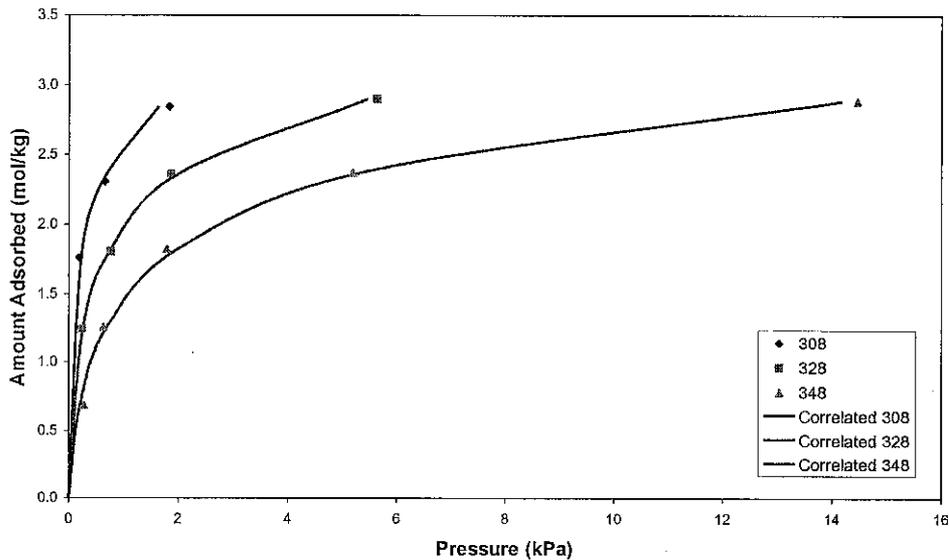


Figure 5.2 (b) Correlation using Modified Antoine's Equation Isotherm (three fitted parameters) with last data omitted experimental data points.

### 5.2.2 Langmuir Isotherm

For Langmuir's isotherm, the equations (3.10) to (3.12) is used to correlate data to fit the data of octane adsorption. The detailed explanation is discussed previously in chapter 3.2.2. From these equations, the known parameters are the experimental data which is the amount adsorbed,  $q$  (mol/kg) and pressure,  $P$  (kPa).

The nonlinear regression was conducted to estimate the values for  $q_{s0}$ ,  $b_0$ ,  $\gamma$  and  $\Delta T_0$ , also the value of residuals. From the total of residuals, the variance has been calculated. The unknown variables are listed in Table 5.3 as shown below.

Table 5.3 Optimal parameters obtained by Langmuir Isotherm

	$q_{s0}$	$b_0$	$\gamma$	$\Delta T_0$	Variance
All data	3.3591	4.6957	16.0444	0.0779	0.6745
Omit last data	2.9819	6.9316	16.8835	0.0295	0.1409

Comparing the obtained parameters, it is noticeable that the values of variance is smaller for the regression which omits the last data, rather than the regression for all experimental data. Graph representation of the correlation using Langmuir Isotherm is shown in Figure 5.3 (a) and Figure 5.3 (b) in the following page.

### Langmuir - All Data

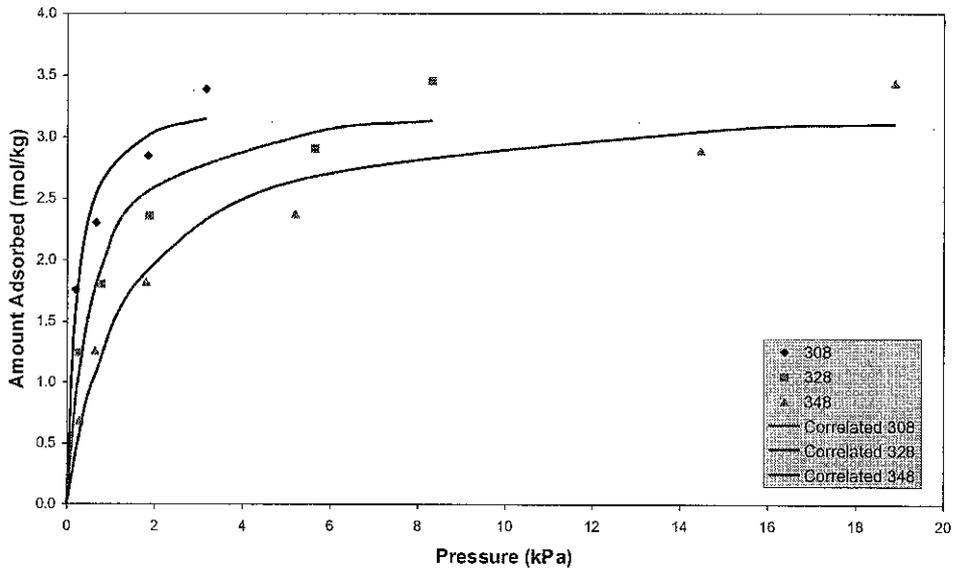


Figure 5.3 (a) Correlation using Langmuir Isotherm for all experimental data points.

### Langmuir - Omit Last Data

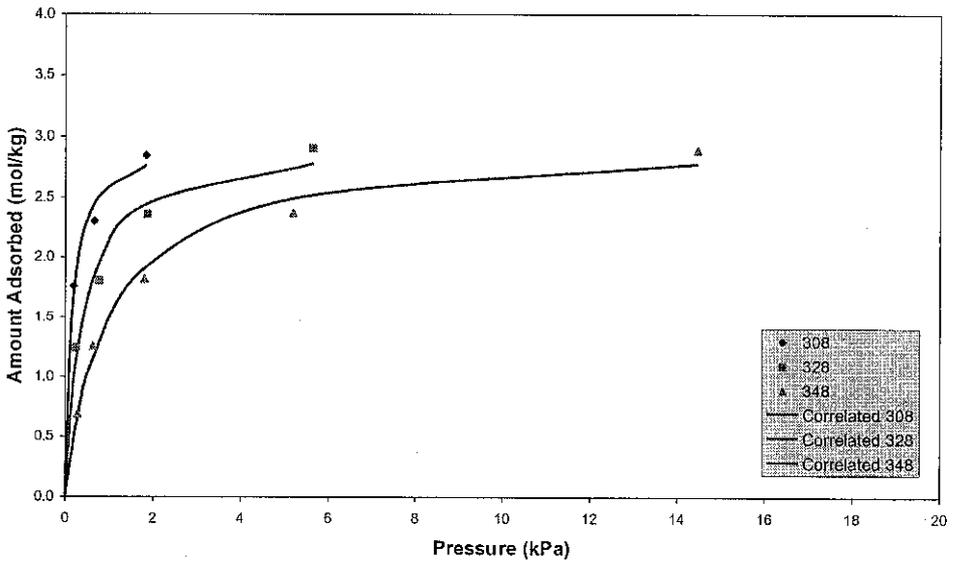


Figure 5.3 (b) Correlation using Langmuir Isotherm with last data omitted experimental data points.

### 5.2.3 Sips Isotherm

For Sips isotherm, the equations (3.13) to (3.16) is used to correlate data to fit the data of octane adsorption. The detailed explanation is discussed previously in chapter 3.2.3. From these equations, the known parameters are the experimental data which is the amount adsorbed,  $q$  (mol/kg) and pressure,  $P$  (kPa).

The nonlinear regression was conducted to estimate the values for  $q_{s0}$ ,  $b_0$ ,  $\gamma$ ,  $n_0$ ,  $\alpha$  and  $\Delta T_0$ , also the value of residuals. From the total of residuals, the variance has been calculated. The unknown variables are listed in Table 5.4 below:

Table 5.4 Optimal parameters obtained by Sips Equation Isotherm

	$q_{s0}$	$b_0$	$\gamma$	$n_0$	$\alpha$	$\Delta T_0$	Variance
All data	7.0665	0.2206	5.6988	2.7821	1.1823	1.9177	0.1830
Omit last data	5.1113	0.9689	2.9750	2.6822	3.0917	3.1609	0.0246

Comparing the obtained parameters, it is noticeable that the values of variance are smaller for the regression which omits the last data, rather than the regression for all experimental data. Graph representation of the correlation using Sips Equation Isotherm is shown in Figure 5.4 (a) and Figure 5.4 (b) in the following page.

### Sips Equation - All Data

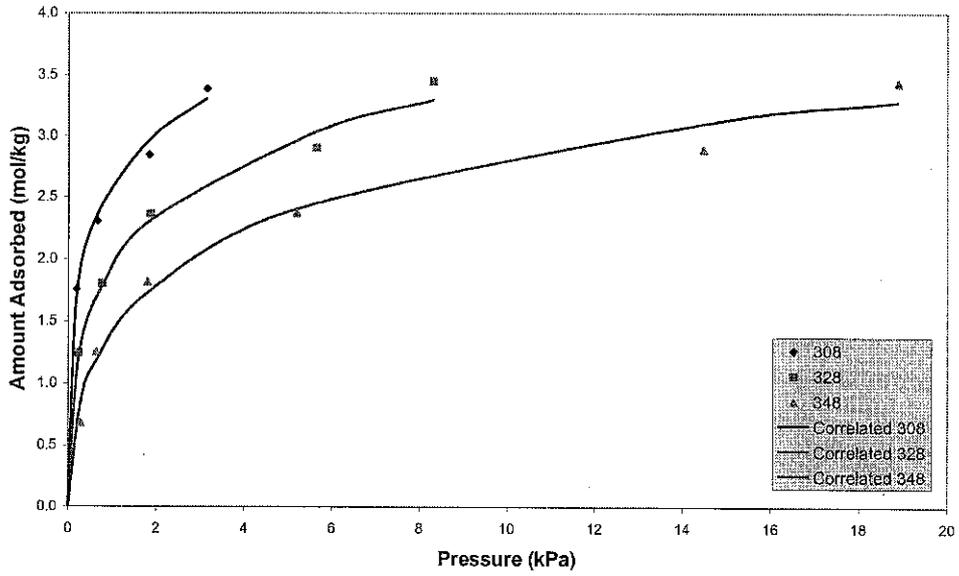


Figure 5.4 (a) Correlation using Sips Equation Isotherm for all experimental data points.

### Sips Equation - Omit Last Data

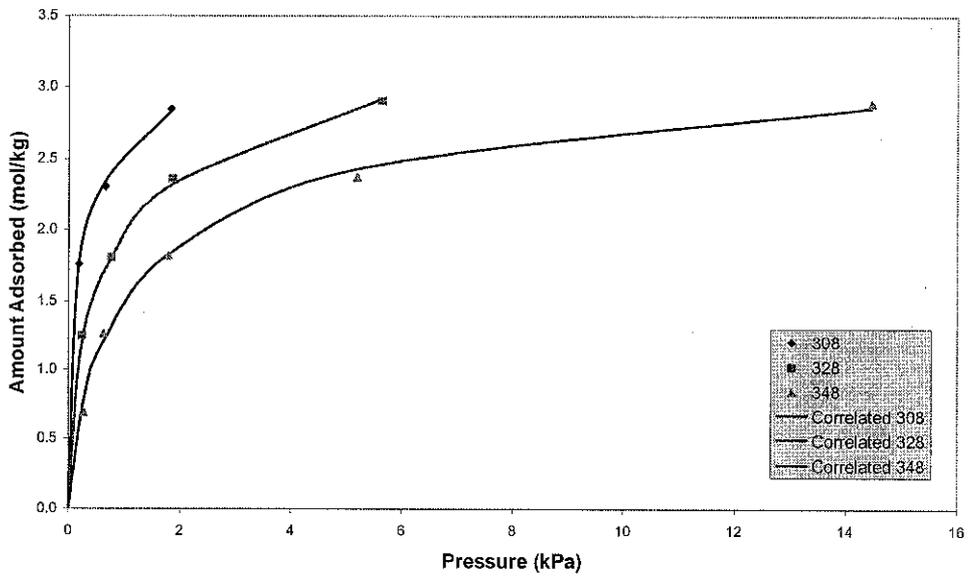


Figure 5.4 (b) Correlation using Sips Equation Isotherm with last data omitted experimental data points.

#### 5.2.4 Toth Isotherm

For Toth Equation isotherm, the equations (3.17) to (3.20) is used to correlate data to fit the data of octane adsorption. The detailed explanation is discussed previously in chapter 3.2.4. From these equations, the known parameters are the experimental data which is the amount adsorbed,  $q$  (mol/kg) and pressure,  $P$  (kPa).

The nonlinear regression was conducted to estimate the values for  $q_{s0}$ ,  $b_0$ ,  $\gamma$ ,  $t_0$ ,  $\alpha$  and  $\Delta T_0$ , also the value of residuals. From the total of residuals, the variance has been calculated. The unknown variables are listed in Table 5.5 below:

Table 5.5 Optimal parameters obtained by Toth Isotherm

	$q_{s0}$	$b_0$	$\gamma$	$t_0$	$\alpha$	$\Delta T_0$	Variance
All data	11.1651	942.2669	32.5010	0.1775	0.1356	-1.4006	0.1771
Omit last data	3.9883	30.6802	23.0108	0.0299	0.4447	0.5356	0.0299

Comparing the obtained parameters, it is noticeable that the values of variance are smaller for the regression which omits the last data, rather than the regression for all experimental data. Graph representation of the correlation using Sips Equation Isotherm is shown in Figure 5.5 (a) and Figure 5.5 (b) in the following page.

### Toth Equation - All Data

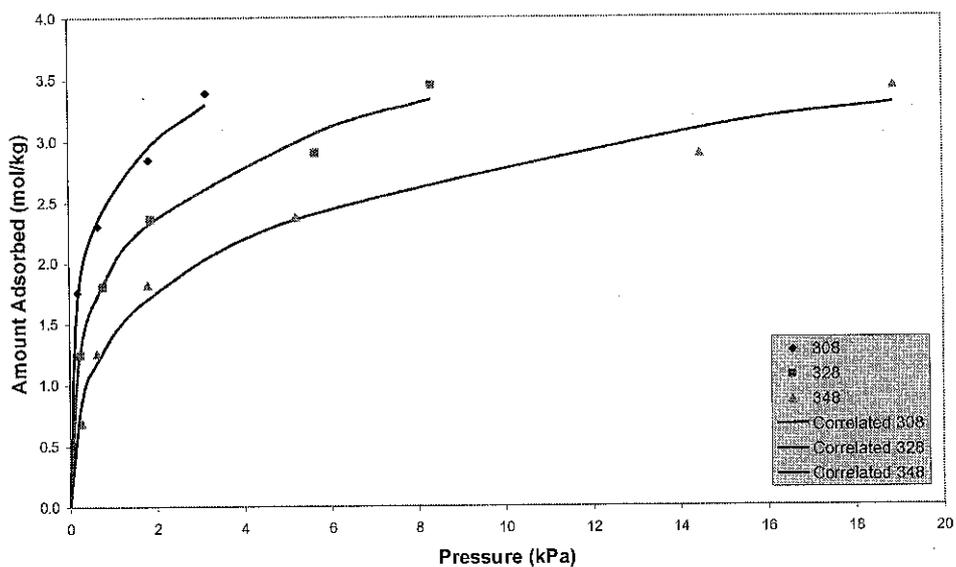


Figure 5.5 (a) Correlation using Toth Equation Isotherm for all experimental data points.

### Toth Equation - Omit Last Data

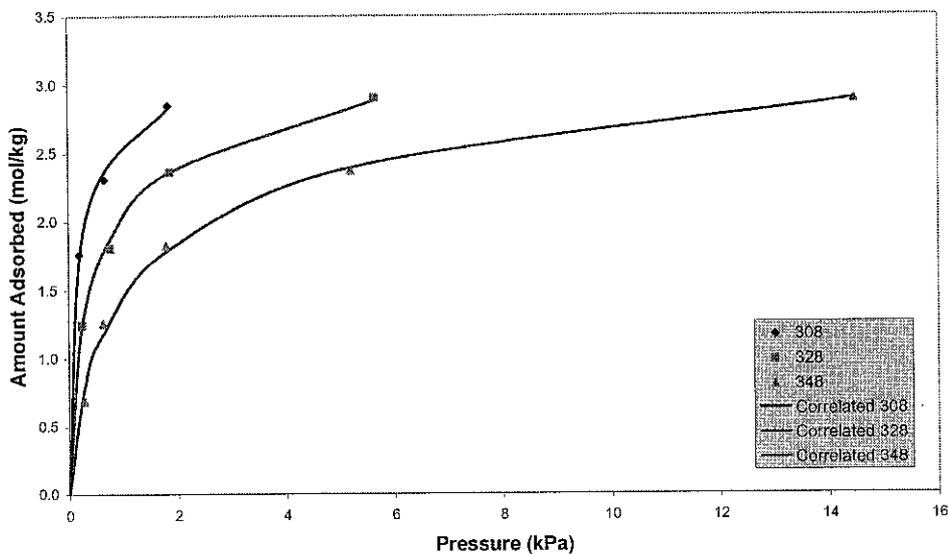


Figure 5.5 (b) Correlation using Toth Equation Isotherm with last data omitted experimental data points.

### 5.2.5 Dubinin-Radushkevich Isotherm

For Dubinin-Radushkevich isotherm, the equations (3.26) are used to correlate data to fit the data of octane adsorption. The detailed explanation is discussed previously in chapter 3.2.5. From these equations, the known parameters are the experimental data which is the amount adsorbed,  $q$  (mol/kg) and pressure,  $P$  (kPa).

The nonlinear regression was conducted to estimate the values for  $W_0$  and  $\beta E_0$ , also the value of residuals. From the total of residuals, the variance has been calculated. The unknown variables are listed in Table 5.6 below:

Table 5.6 Optimal parameters obtained by Dubinin-Radushkevich Isotherm

	$W_0$	$\beta E_0$	Variance
All data	515.5740933	9219.006097	0.8842
Omit last data	470.293077	10035.265	0.1350

Comparing the obtained parameters, it is noticeable that the values of variance are smaller for the regression which omits the last data, rather than the regression for all experimental data. Graph representation of the correlation using Dubinin-Radushkevich Isotherm is shown in Figure 5.6 (a) and Figure 5.6 (b) in the following page.

### Dubinin-Radushkevich - All Data

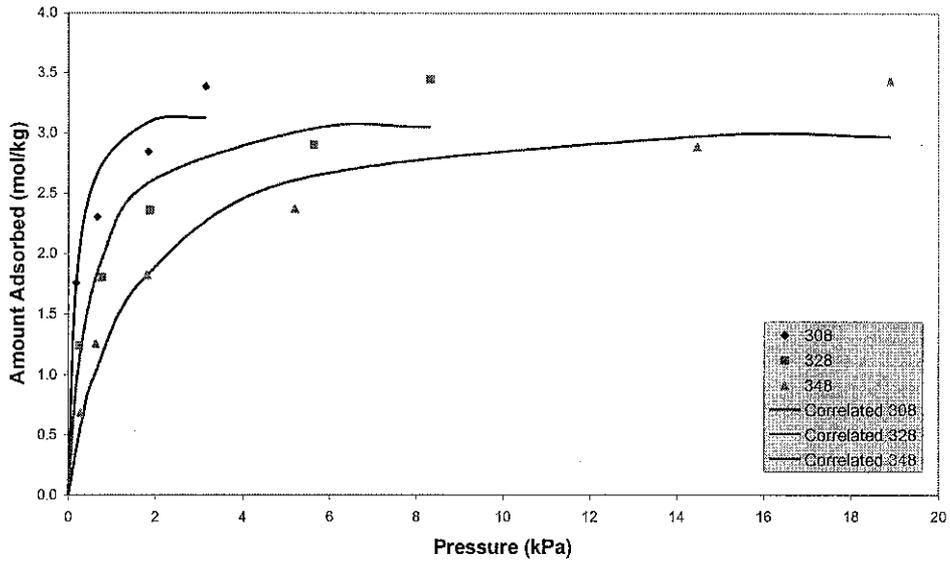


Figure 5.6 (a) Correlation using Dubinin-Radushkevich Isotherm for all experimental data points.

### Dubinin-Radushkevich - Omit Last Data

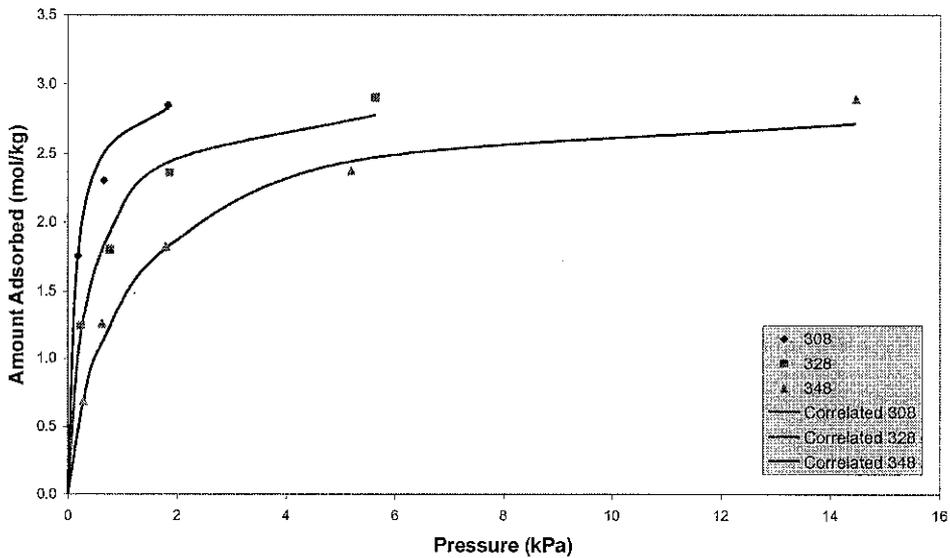


Figure 5.6 (b) Correlation using Dubinin-Radushkevich Isotherm with last data omitted experimental data points.

### 5.2.6 Dubinin-Astakhov Isotherm

For Dubinin-Astakhov isotherm, the equations (3.27) are used to correlate data to fit the data of octane adsorption. The detailed explanation is discussed previously in chapter 3.2.6. From these equations, the known parameters are the experimental data which is the amount adsorbed,  $q$  (mol/kg) and pressure,  $P$  (kPa).

The nonlinear regression was conducted to estimate the values for  $W_0$ ,  $\beta E_0$  and  $n$  also the value of residuals. From the total of residuals, the variance has been calculated. The unknown variables are listed in Table 5.7 below:

Table 5.7 Optimal parameters obtained by Dubinin-Astakhov Isotherm

	$W_0$	$\beta E_0$	$n$	Variance
All data	565.8466	9308.6190	1.0411	0.2369
Omit last data	497.5933	10017.3680	1.5145	0.0554

Comparing the obtained parameters, it is noticeable that the values of variance are smaller for the regression which omits the last data, rather than the regression for all experimental data. Graph representation of the correlation using Dubinin-Astakhov Isotherm is shown in Figure 5.7 (a) and Figure 5.7 (b) in the following page.

### Dubinin-Astakhov - All Data

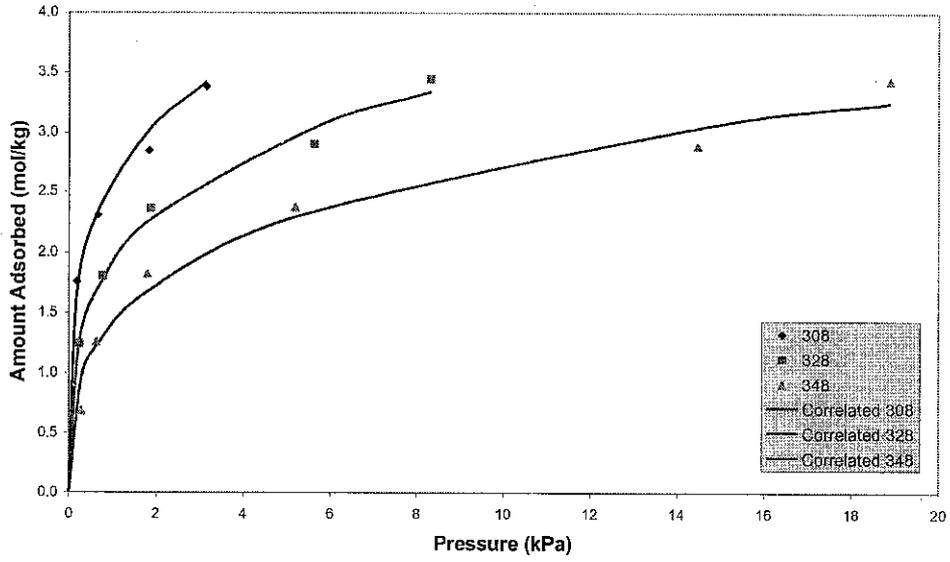


Figure 5.7 (a) Correlation using Dubinin-Astakhov Isotherm for all experimental data points.

### Dubinin-Astakhov - Omit Last Data

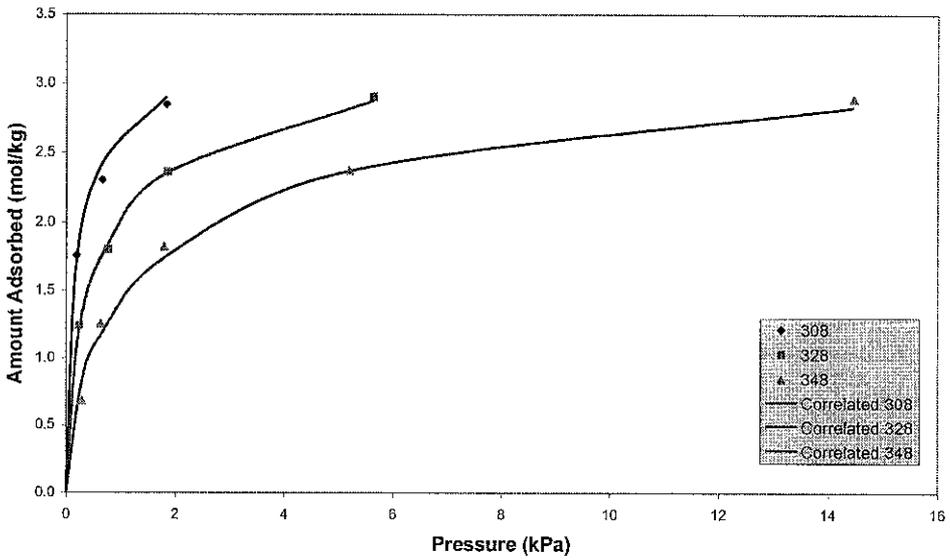


Figure 5.7 (b) Correlation using Dubinin-Astakhov Isotherm with last data omitted experimental data points.

### **5.3 Comparison of result from Excel with MATLAB and SAS Programming**

Comparison study is conducted on the Modified Antoine's Equation models using two different methods, which are Excel and SAS Programming, while the other Isotherms models are conducted between Excel and MATLAB programming. This is essential to verify and prove the effectiveness of result obtained using the Excel with both MATLAB and SAS programming.

The adsorption data used for the simulation is Octane Adsorption on Activated Carbon (Mohd. Shariff, A., 1995). In the study, the isotherms models that are considered are Modified Antoine isotherm (both two and three fitted parameters). The comparison for MATLAB programming is considered for Langmuirs isotherm, Sips Isotherms, Toths Isotherms, Dubinin-Radushkevich Isotherms and Dubinin-Astakhov Isotherms from the study of Regression Analysis for Hydrocarbon Adsorption Isotherm on Activated Carbon (Haji Nawawi, N., 2004).

The comparison is presented in terms of visualization graphs and optimal parameters obtained by the selected isotherms obtained. The parameters include all the unknown parameters and calculated variance for each isotherms. By comparison, the best approach for each correlated isotherm can be determined.

#### **5.3.1 Comparison between SAS programming with Excel**

From the study done on the correlation of Modified Antoine's Law using Microsoft Excel and SAS (Statistical Analysis Software), it can be clearly seen that the difference in the unknown values is very small and almost identical. When the graph is plotted, the lines are covering each other.

The only difference noticed is in the Variance acquired from both software, where the Variance in SAS programming is much smaller compared to Excel software. It is not logic that the difference is quite big, as the unknown parameters are almost the same. Thus it is concluded that the variance is calculated differently in both cases and the difference in Variance is void.

The SAS programming use least-squares criterion method while the Excel software uses the Solver method to achieve the desired results. The methods used in both programs are totally different and the form of producing results is dependent on many factors. However, the results are almost the same, thus ensuring that both methods are capable of producing reliable results.

From the observation, it can be concluded that the best approach is by using Microsoft Excel as it is far easier to conduct and faster. Tables 5.8 and 5.9 show the difference between SAS programming with Excel programming for All Data and Omit Last Data, and for Modified Antoine's Equation (both two and three fitted parameters).

Table 5.8 Comparison Data for Modified Antoine's Equation (2 fitted Parameters)

		$W_0$	B	Variance
All Data	Excel	557.9030	966.6034	0.4862
	SAS	558.7201	968.4543	0.0323
Omit Last Data	Excel	532.0561	1043.6456	0.1980
	SAS	532.7982	1045.5245	0.0165

Table 5.9 Comparison Data for Modified Antoine's Equation (3 fitted Parameters)

		$W_0$	b	C	Variance
All Data	Excel	558.1111	611.5986	-26.0174	0.4719
	SAS	558.9610	612.5515	-26.0805	0.0314
Omit Last Data	Excel	528.1743	1579.2685	38.0090	0.1829
	SAS	528.9215	1574.2011	37.5131	0.0122

### 5.3.2 Comparison between MATLAB programming with Excel

The study of comparison between MATLAB programming with Microsoft Excel is done using Langmuir's Isotherm, Sips Isotherms, Toth Isotherms, Dubinin-Radushkevich Isotherm and Dubinin-Ashtakov Isotherm.

MATLAB programming use Newton-Raphson method for the non-linear purposes while Excel is using the solver tool to get the required variables. The Variance obtained from Excel is slightly lower than the variance obtained from MATLAB software. This can be seen both in the tables and graphs that the difference in values shows the slightly lower in Excel compared to MATLAB programming.

From observation of all the isotherms, it can be concluded that the best approach is by using Microsoft Excel, based on the smaller variance from both programs and the time used to regress.

Tables 5.10 to 5.14 in the next page show the difference between MATLAB programming with Excel programming for All Data and Omit Last Data.

Table 5.10 Comparison Data for Langmuir's Isotherm

		$q_{s0}$	$b_0$	gamma	$\Delta T_0$	Variance
All Data	Excel	3.3591	4.6957	16.0444	0.0779	0.6745
	MATLAB	3.3591	4.6957	16.0444	0.07785	0.8213
Omit Last Data	Excel	2.9819	6.9316	16.8835	0.0295	0.1409
	MATLAB	2.9819	6.9316	16.8835	0.02949	0.3754

From table 5.10, there is no difference in the variable data obtained from both Excel and MATLAB programming. The simulation was run a few times in Excel to ensure the results taken are precise. However, the Variance obtained is different, showing that the Variance in Excel is lower. This might happen due to different programs

where the method is different. it can be concluded that, based on the lower variance, Excel is a better approach in predicting the variables.

Table 5.11 Comparison Data for Sips Isotherm

		$q_{s0}$	$b_0$	gamma	$n_0$	A	$\Delta T_0$	Variance
All data	Excel	7.0665	0.2206	5.6988	2.7821	1.1823	1.9177	0.1830
	MATLAB	7.1651	0.2044	14.783	2.8025	0.6677	0.00020	0.4313
Omit Last data	Excel	5.1113	0.9689	2.9750	2.6822	3.0917	3.1609	0.0246
	MATLAB	3.6932	4.1706	18.548	1.7603	0.8195	0.02629	0.1282

Table 5.11 in the previous page shows the comparison data for Sips Isotherm, where it is observed that there is a big difference in both methods of regression. This can be observed in  $b_0$ , gamma, alpha and  $\Delta T_0$  values. Although the values of variables are different, the plotted graph shows similar lines, with little differences. Since the Variance value is smaller using Excel, it can be concluded that Excel is the best approach for predicting the variables.

The plotted graph can be seen in Figure 5.8 (a) and 5.8 (b). The graph shows identical lines for both Excel and Sips.

### Sips Equation - All Data

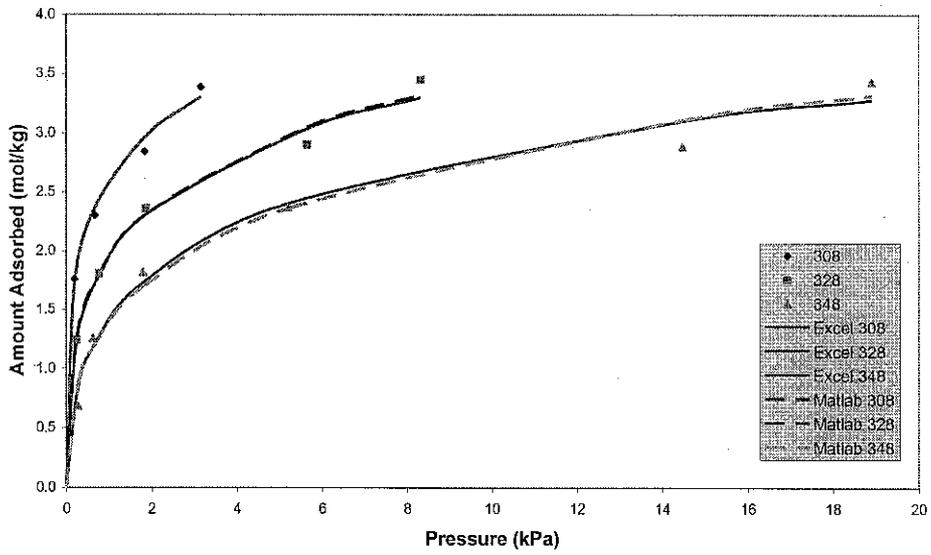


Figure 5.8 (a) Comparison of graphs for Sips Isotherm with All Data Points

### Sips Equation - Omit Last Data

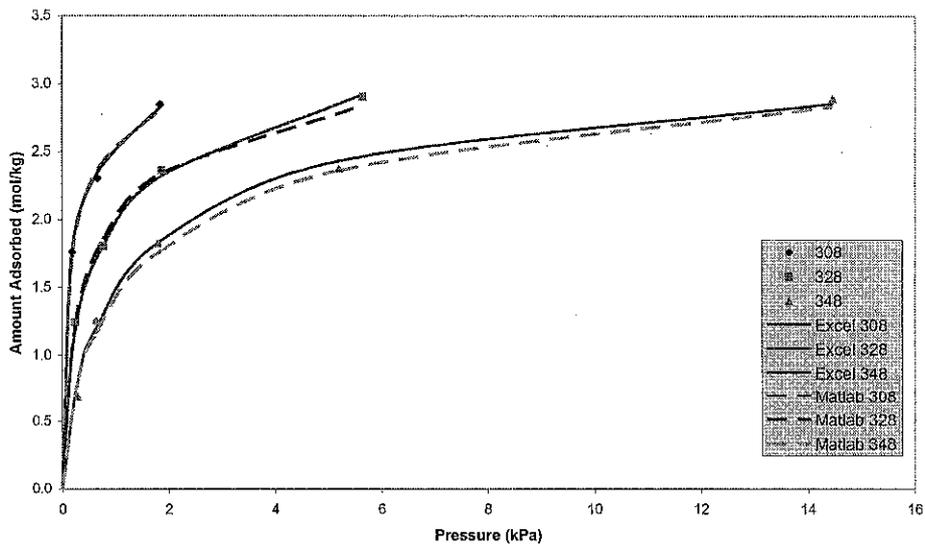


Figure 5.8 (b) Comparison of graphs for Sips Isotherm with Last Data Points Omitted

Table 5.12 Comparison Data for Toth Isotherm

		$q_{s0}$	$b_0$	gamma	$t_0$	A	$\Delta T_0$	Variance
All Data	Excel	5.3762	23.6913	11.7858	-2.1388	0.3715	-0.7201	0.2179
	MATLAB	4.9703	15.734	16.5138	0.42391	-0.02886	-0.01227	0.4974
Omit	Excel	3.9883	30.6802	23.0108	0.0299	0.4447	0.5356	0.0299
Last Data	MATLAB	3.9799	30.6847	22.9909	0.4456	0.51551	-0.00507	0.1730

Table 5.12 shows the comparison data for Toth Isotherm, where it is observed that there is some small difference in both methods of regression. This can be observed in the  $t_0$ , alpha and  $\Delta T_0$  values. The difference in values can be observed in Figure 5.9 where the curve line for MATLAB is slightly different from the curve line for Excel. This is only applied for the study of All data, whereas the curve for both MATLAB and Excel is identical. Since the Variance value is smaller using Excel, it can be concluded that Excel is the best approach for predicting the variables.

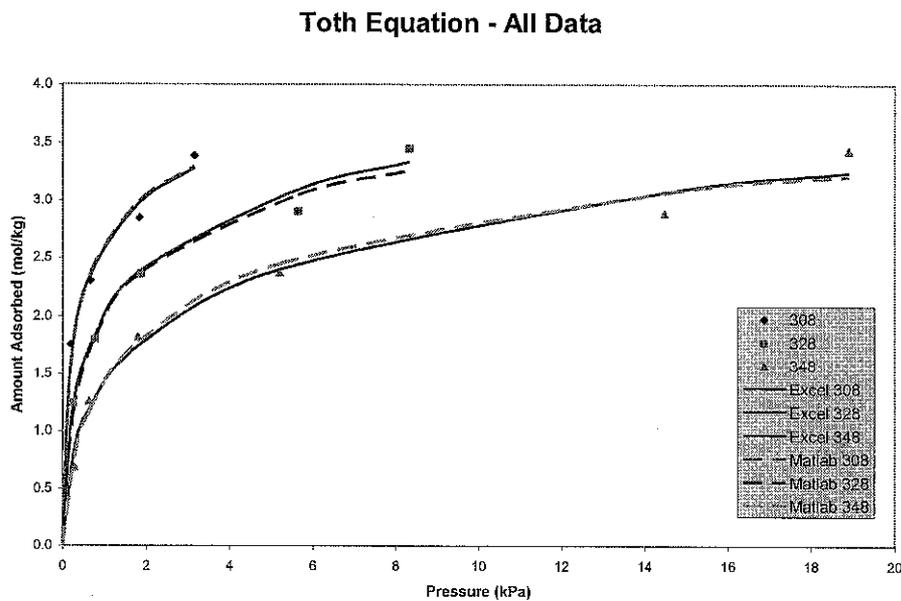


Figure 5.9 Comparison of graphs for Toth Isotherm with All Data Points

Table 5.13 Comparison Data for Dubinin-Radushkevich Isotherm

		$W_0$	$\beta E_0$	Variance
All data	Excel	515.5740933	9219.006097	0.8842
	MATLAB	492.1483	9619.9101	1.0099
Omit Last Data	Excel	470.293077	10035.265	0.1350
	MATLAB	452.0577	10445.7569	0.4319

Table 5.13 shows the comparison data for Dubinin-Radushkevich Isotherm, in which the difference is quite small. Although the differences is quite small, as the graph was plotted, the curve line was slightly lower than the line obtained from Excel.

The plotted graph can be seen in Figure 5.10 (a) and 5.10 (b).

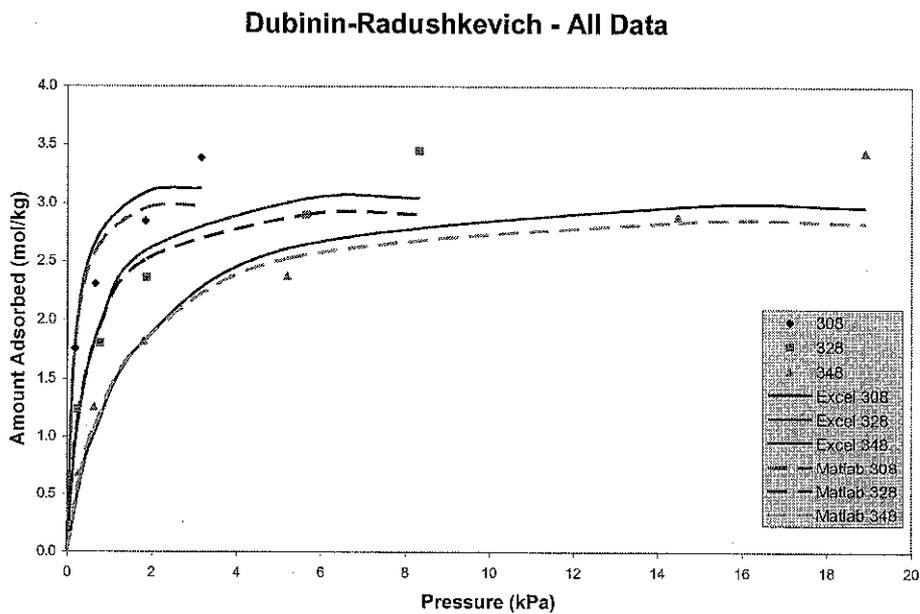


Figure 5.10 (a) Comparison of graphs for Dubinin-Radushkevich Isotherm with All Data Points

### Dubinin-Radushkevich - Omit Last Data

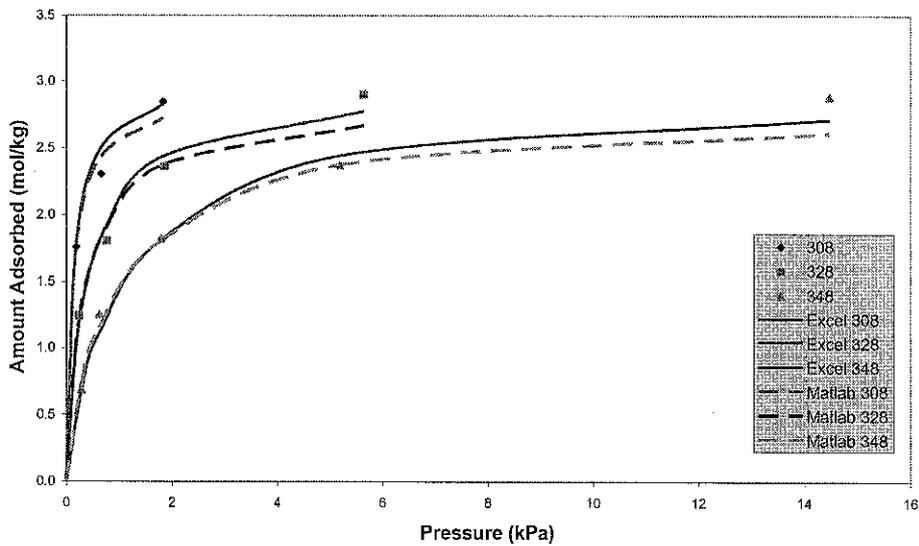


Figure 5.10 (b) Comparison of graphs for Dubinin-Radushkevich Isotherm with Last Data Points Omitted

Table 5.14 Comparison Data for Dubinin-Astakhov Isotherm

		$W_0$	$\beta E_0$	N	Variance
All data	Excel	565.8466	9308.6190	1.0411	0.2369
	MATLAB	534.0748	9982.0489	1.066	0.6339
Omit Last Data	Excel	497.5933	10017.3680	1.5145	0.0554
	MATLAB	471.569	10500.6084	1.588	0.3377

Table 5.14 shows the comparison data for Dubinin-Astakhov Isotherm, in which the difference is quite small. Although the difference is quite small, as the graph was plotted, the curve line was slightly lower than the line obtained from Excel.

The plotted graph can be seen in Figure 5.11 (a) and 5.11 (b).

### Dubinin-Astakhov - All Data

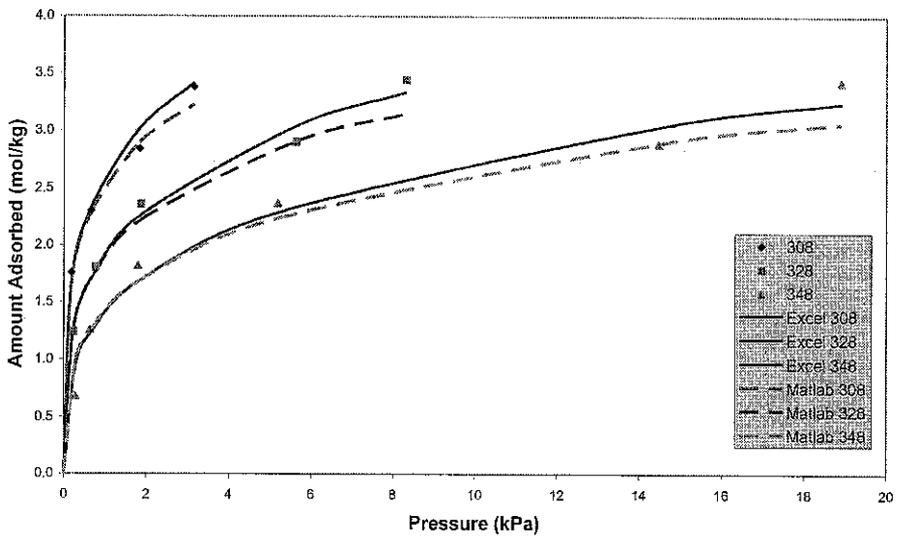


Figure 5.11 (a) Comparison of graphs for Dubinin-Astakhov Isotherm with All Data Points

### Dubinin-Astakhov - Omit Last Data

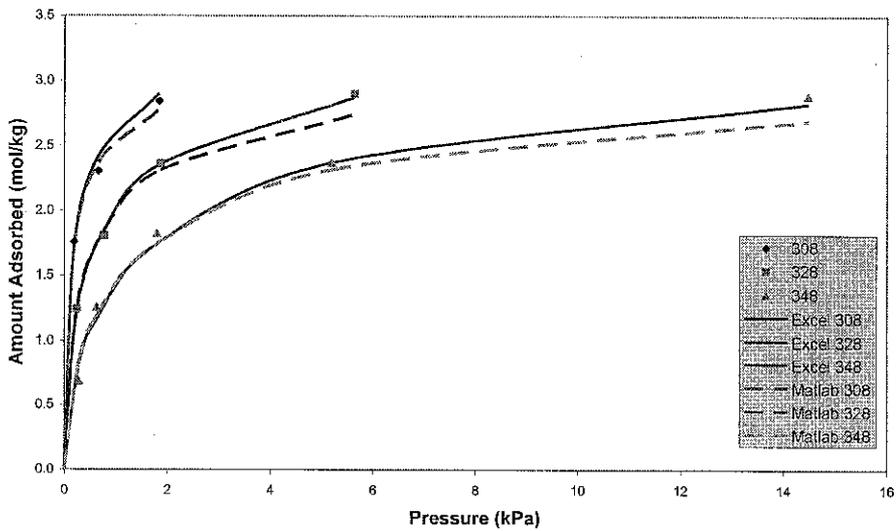


Figure 5.11 (b) Comparison of graphs for Dubinin-Astakhov Isotherm with Last Data Points Omitted

## 5.4 Concluding Remarks

The results of unknown variables for each isotherm showed some significant differences between the regression techniques used by all software, namely Excel, MATLAB and SAS. The data obtained from All Data and Omit Last Data also shows some significant difference, although it is from the same software.

The values of Variance show that Microsoft Excel gives smaller values than the values from MATLAB. This shows that Excel is a better approach to fit the correlation to the adsorption data, because in order to fit the best correlation, the variance must be equal or near zero. Between the data for all data points and Last data neglected, the data for last data neglected is much more reliable as the Variance is much smaller. This indicates the best fit for correlation of adsorption for the Isotherms.

Lastly, it can be concluded that Sips Equation has the best fit for correlation of octane adsorption on activated carbon, as it gives the smallest variance and it fits well the type 1 adsorption Isotherm shape. This is then followed by Toth's Equation, Dubinin-Astakhov Equation, Dubinin-Radushkevich, Langmuir Equation, Modified Antoine 2 and lastly Modified Antoine 3. Summary of Variance obtained for all Isotherms is tabulated in Table 5.15

Table 5.15 Summary of Variance

Isotherm	All Data	Omit Last Data
Modified Antoine 2	0.4862	0.1980
Modified Antoine 3	0.4719	0.1829
Langmuir	0.6748	0.1409
Sips	0.1830	0.0246
Toth	0.1771	0.0299
Dubinin-Radushkevich	0.8842	0.1350
Dubinin-Astakhov	0.2369	0.0554

## CHAPTER 6

### CONCLUSIONS AND RECOMMENDATIONS

#### 6.1 Conclusions

In this study, several isotherms have been selected (namely Modified Antoine's Equation, Langmuir, Sips (Langmuir-Freundlich), Toth, Dubinin-Radushkevich and Dubinin-Atakhov) isotherms to be fit and correlate of adsorption data on activated carbon. These isotherms are all temperature dependent and most suitable for Type I adsorption isotherm. The study done will cover the wide range of temperature and pressure.

Microsoft Excel has been chosen for the nonlinear regression of adsorption data, based on the simple functions and reliable calculations. The published data of pure octane adsorption on activated carbon at 308K, 328K and 348K was used to focus on single component adsorption for various temperature and pressure.

From the observation, there was none of the adsorption isotherm models that would accurately correlate the octane adsorption data over a wide range of temperature and pressure. The comparison done between all the isotherms in this study confirms this and it was concluded that Sips Isotherm has the least Variance, thus making it the closest fit to the adsorption data.

All values of variance gave a very small difference from the given data of octane adsorption. This shows that all the isotherms gives the best fit of correlation to adsorption data. There was two data from each isotherm: all data points, and omit last

data points. It was concluded that the data for omit last data points gave the best fit, compared to all data because of the smaller variance obtained.

Comparison study on Microsoft Excel with SAS and MATLAB programming has been done to determine the best approach for obtaining nonlinear regressions. Based on the findings, it can be concluded that SAS programming gives better results than of Microsoft Excel, because of the smaller variance. Microsoft Excel on the other hand is much better than MATLAB, because of the smaller variance.

Finally, it can be concluded that for nonlinear regression, the best approach is Microsoft Excel, since it can provide better fit for the adsorption isotherm of hydrocarbon adsorption. This program can give output faster than any other programs, and the regression is done easily, due to the user friendliness of the program.

## **6.2 Recommendations**

The adsorption isotherm correlation on activated carbon has been conducted for octane adsorption, it would be better if the study was conducted with other sets of adsorption data, like water adsorption, in the future to validate the efficiency of the method used and to clarify the outcome.

From the conclusion, the study proves that Microsoft Excel is best used to fit the correlation of type 1 isotherms. Future work can include testing the model for Type II and above.

The correlation of modified Antoine's equation has been done with two and three fitted parameters only in this study. To check if the program is good, future work can also include more than three parameters for the Modified Antoine Equation.

## CHAPTER 7

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## APPENDIX A :

EXCEL CALCULATION OF ADSORBED  
VOLUME FOR OCTANE ADSORPTION  
EQUILIBRIA USING LEWIS METHOD

## Appendix A

### Calculation of Adsorbed Volume for Octane Adsorption Equilibria Using Lewis Method

Sample Calculation of Adsorption equilibria for octane on activated carbon at 308K

Pressure, P = 1.86E-04

Amount Adsorbed, q = 1.7574 mol/Kg

#### Reduced Temperature

$$T = (B/(A-\ln P)) - C$$

where

$$A = 7.00811$$

$$B = 3113.08$$

$$C = -64$$

$$P = 1.86E-04$$

$$T = 263.5836114 \text{ K}$$

$$T_R = T/T_C$$

where

$$T_C = 568.83 \text{ K}$$

$$T_R = 0.463378534$$

#### Saturated molar Volume, $V_m$

for  $0.25 < T_R < 0.95$

$$V_R^{(0)} = 1 + a(1-T_R)^{1/3} + b(1-T_R)^{2/3} + c(1-T_R) + d(1-T_R)^{4/3}$$

where

$$T_R = 0.463378534$$

$$a = -1.52816$$

$$b = 1.43907$$

$$c = -0.81446$$

$$d = 0.190454$$

$$V_R^{(0)} = 0.354475888$$

for  $0.25 < T_R < 1.0$

$$VR^{(6)} = (e+fT_R+gT_R^2+hT_R^3)/(T_R-1.00001)$$

where

$$\begin{aligned} T_R &= 0.463378534 \\ e &= -0.296123 \\ f &= 0.386914 \\ g &= -0.0427258 \\ h &= -0.0480645 \end{aligned}$$

$$VR^{(6)} = 0.243727184$$

$$V_m = V^*(V_R^{(0)}[1-\omega_{SRK}VR^{(6)}])$$

where

$$\begin{aligned} V^* &= 490.4 \\ V_R^{(0)} &= 0.354475888 \\ \omega_{SRK} &= 0.3998 \\ VR^{(6)} &= 0.243727184 \end{aligned}$$

$$V_m = 156.8961256 \text{ cm}^3/\text{mol}$$

**Adsorbed volume, W**

$$\begin{aligned} W &= qMW/\rho_A \\ &= qV_m \end{aligned}$$

where

$$\begin{aligned} q &= 1.7574 \\ V_m &= 156.8961256 \end{aligned}$$

$$W = 275.7292512 \text{ cm}^3/\text{kg}$$

Experimental Data		Calculated Parameters						
T (K)	P (MPa)	q (mol/kg)	T (K)	T <sub>R</sub> (-)	V <sub>R</sub> <sup>(g)</sup> (-)	V <sub>R</sub> <sup>(b)</sup> (-)	V <sub>m</sub> (cm <sup>3</sup> /mol)	W (cm <sup>3</sup> /kg)
308	1.86E-04	1.7574	263.5561	0.4633	0.3545	0.2437	156.8914	275.7210
	6.60E-04	2.3038	281.2189	0.4944	0.3608	0.2395	160.0036	368.6162
	1.84E-03	2.8455	297.9139	0.5237	0.3672	0.2354	163.1176	464.1511
	3.16E-03	3.3863	307.8410	0.5412	0.3711	0.2329	165.0571	558.9328
328	2.42E-04	1.2413	266.9872	0.4694	0.3557	0.2429	157.4823	195.4827
	7.69E-04	1.8029	283.5549	0.4985	0.3617	0.2389	160.4288	289.2370
	1.87E-03	2.3608	298.2115	0.5243	0.3673	0.2353	163.1747	385.2229
	5.64E-03	2.9013	319.4778	0.5616	0.3760	0.2300	167.4221	485.7416
	8.32E-03	3.4490	327.8904	0.5764	0.3796	0.2278	169.1981	583.5642
348	2.80E-04	0.6852	268.9392	0.4728	0.3564	0.2424	157.8213	108.1391
	6.29E-04	1.2555	280.4969	0.4931	0.3606	0.2397	159.8728	200.7203
	1.79E-03	1.8207	297.5146	0.5230	0.3670	0.2355	163.0410	296.8487
	5.20E-03	2.3722	317.7546	0.5586	0.3752	0.2304	167.0653	396.3123
	1.45E-02	2.8874	340.8680	0.5992	0.3854	0.2245	172.0569	496.7970
	1.89E-02	3.4326	347.6009	0.6111	0.3886	0.2227	173.6015	595.9045

Table A Calculation of Adsorbed Volume for Octane Adsorption Equilibria Using Lewis Method

APPENDIX B :  
EXCEL CALCULATION OF THE ADSORPTION  
ISOTHERM

B1 : MODIFIED ANTOINE EQUATION WITH TWO FITTED  
PARAMETERS

B2 : LANGMUIR'S ISOTHERM

B3 : DUBININ-RADUSHKEVICH ISOTHERM

## Appendix B1

### Modified Antoine (two fitted parameters) $W_0, b$

$$\ln p_1 = A' - B' / (C' + T)$$

with;

$$\begin{aligned} A' &= A + \ln(w_1/w_0) \\ B' &= B + b * (1 - (w_1/w_0)) \\ C' &= C \end{aligned}$$

Where:

A, B and C are Antoine Constants for Octane

$$\begin{aligned} A &= 7.00811 \\ B &= 3113.08 \\ C &= -64 \end{aligned}$$

$p_1$  = vapour pressure of Octane (MPa)

$w_1$  = adsorbed volume of octane per unit mass adsorbant (cm<sup>3</sup>/kgC)

$w_0$  = pore volume per unit mass adsorbant (cm<sup>3</sup>/kgC)

**$w_0$  and  $b$  to be predicted**

$$w = 275.7210$$

#### All Data

$$\begin{aligned} w_0 &= 557.9030 \\ b &= 966.6034 \\ T &= 308 \\ \ln p_1 &= -8.413016146 \end{aligned}$$

#### Omit Last Data

$$\begin{aligned} w_0 &= 532.0561 \\ b &= 1043.6456 \end{aligned}$$

All Data		Experimental Data						Calculated Parameters					
T (K)	P (kPa)	P (Mpa)	lnP	W (cm <sup>3</sup> /kg)	g (mol/kg)	lnP	P (Mpa)	P (kPa)	residual	SS			
308	0.1856	1.856E-04	-8.5919	275.7210	1.7574	-8.4589	2.1201E-04	0.2120	-0.1330	0.0177			
	0.6599	6.599E-04	-7.3234	368.6162	2.3038	-7.5089	5.4818E-04	0.5482	0.1855	0.0344			
	1.8353	1.835E-03	-6.3005	464.1511	2.8455	-6.6001	1.3602E-03	1.3602	0.2995	0.0897			
	3.1551	3.155E-03	-5.7587	558.9328	3.3863	-5.7413	3.2107E-03	3.2107	-0.0175	0.0003			
	0.2416	2.416E-04	-8.3282	195.4827	1.2413	-8.2110	2.7164E-04	0.2716	-0.1172	0.0137			
328	0.7686	7.686E-04	-7.1709	289.2370	1.8029	-7.2040	7.4362E-04	0.7436	0.0330	0.0011			
	1.8666	1.867E-03	-6.2836	385.2229	2.3608	-6.2875	1.8594E-03	1.8594	0.0038	0.0000			
	5.6437	5.644E-03	-5.1772	485.7416	2.9013	-5.3959	4.5349E-03	4.5349	0.2187	0.0478			
	8.3228	8.323E-03	-4.7888	583.5642	3.4490	-4.5705	1.0353E-02	10.3530	-0.2183	0.0476			
	0.2796	2.796E-04	-8.1822	108.1391	0.6852	-8.3380	2.3924E-04	0.2392	0.1559	0.0243			
348	0.6291	6.291E-04	-7.3712	200.7203	1.2555	-7.1547	7.8116E-04	0.7812	-0.2165	0.0469			
	1.794	1.794E-03	-6.3233	296.8487	1.8207	-6.1770	2.0767E-03	2.0767	-0.1463	0.0214			
	5.1955	5.196E-03	-5.2600	396.3123	2.3722	-5.2812	5.0862E-03	5.0862	0.0213	0.0005			
	14.4682	1.447E-02	-4.2358	496.7970	2.8874	-4.4422	1.1770E-02	11.7697	0.2064	0.0426			
	18.8949	1.889E-02	-3.9689	595.9045	3.4326	-3.6557	2.5843E-02	25.8431	-0.3132	0.0981			
variance:										0.4862			

Table B1.1 Calculation for All Data Parameters

Omit Last Data

Experimental Data

Calculated Parameters

T (K)	P (kPa)	P (Mpa)	lnP	W (cm <sup>3</sup> /kg)	g (mol/kg)	lnP	P (Mpa)	P (kPa)	residual	SS
308	0.1856	1.856E-04	-8.5919	275.7210	1.7574	-8.4685	2.0999E-04	0.2100	-0.1234	0.0152
	0.6599	6.599E-04	-7.3234	368.6162	2.3038	-7.4313	5.9241E-04	0.5924	0.1079	0.0116
	1.8353	1.835E-03	-6.3005	464.1511	2.8455	-6.4328	1.6079E-03	1.6079	0.1323	0.0175
	0.2416	2.416E-04	-8.3282	195.4827	1.2413	-8.2859	2.5205E-04	0.2520	-0.0423	0.0018
328	0.7686	7.686E-04	-7.1709	289.2370	1.8029	-7.1975	7.4844E-04	0.7484	0.0266	0.0007
	1.8666	1.867E-03	-6.2836	385.2229	2.3608	-6.1978	2.0340E-03	2.0340	-0.0859	0.0074
	5.6437	5.644E-03	-5.1772	485.7416	2.9013	-5.2191	5.4125E-03	5.4125	0.0418	0.0018
	0.2796	2.796E-04	-8.1822	108.1391	0.6852	-8.4747	2.0869E-04	0.2087	0.2925	0.0856
348	0.6291	6.291E-04	-7.3712	200.7203	1.2555	-7.2167	7.3419E-04	0.7342	-0.1545	0.0239
	1.794	1.794E-03	-6.3233	296.8487	1.8207	-6.1615	2.1091E-03	2.1091	-0.1618	0.0262
	5.1955	5.196E-03	-5.2600	396.3123	2.3722	-5.1855	5.5969E-03	5.5969	-0.0744	0.0055
	14.4682	1.447E-02	-4.2358	496.7970	2.8874	-4.2655	1.4044E-02	14.0444	0.0297	0.0009

variance:

0.1980

Table B1.2 Calculation for Omit Last Data Parameters

## Appendix B2

### Langmuir Isotherm,

$$\Theta = bP/(1+bP)$$

$$b(T) = b_0 \exp((Q/RT)-(Q/RT_0))$$

where

$\Theta$  = fraction coverage

$b$  = affinity constant

$P$  = pressure

$R$  = gas constant

$Q$  = heat of adsorption

$T$  = temperature

$T_0$  = reference temperature

$b_0$  = affinity constant

$$q = q_s(b(T)P/(1+b(T)P))$$

$$q_s = q_{s0} \exp(\Delta T_0^*(1-T/T_0))$$

where

$q_{s0}$  = saturation capacity at reference temperature  $T_0$

$\Delta T_0$  = constant parameter

$\gamma$  =  $Q/RT_0$

$q_{s0}$ ,  $b_0$ ,  $\gamma$  and  $\Delta T_0$  to be predicted

$$q = q_s(b(T)P/(1+b(T)P))$$

where

all data		omit last data			
$q_{s0}$	=	3.3591	$q_{s0}$	=	2.9819
$b_0$	=	4.6957	$b_0$	=	6.9316
$\gamma$	=	16.0444	$\gamma$	=	16.8835
$\Delta T_0$	=	0.0779	$\Delta T_0$	=	0.0295

$$b(T) = b_0 \exp((Q/RT)-(Q/RT_0))$$

$$T_0 = 308$$

<b>All Data</b>							
<b>Experimental Data</b>				<b>Calculated Parameters</b>			
T	P	q	b	q <sub>s</sub>	q	residual	SS
(K)	(kPa)	(mol/kg)	(kPa) <sup>-1</sup>	(mol/kg)	(mol/kg)		
308	0.1856	1.7574	4.6957	3.3591	1.5643	0.1931	0.0373
	0.6599	2.3038	4.6957	3.3591	2.5396	-0.2358	0.0556
	1.8353	2.8455	4.6957	3.3591	3.0099	-0.1644	0.0270
	3.1551	3.3863	4.6957	3.3591	3.1467	0.2396	0.0574
328	0.2416	1.2413	1.7653	3.3422	0.9993	0.2420	0.0586
	0.7686	1.8029	1.7653	3.3422	1.9241	-0.1212	0.0147
	1.8666	2.3608	1.7653	3.3422	2.5641	-0.2033	0.0413
	5.6437	2.9013	1.7653	3.3422	3.0373	-0.1360	0.0185
	8.3228	3.4490	1.7653	3.3422	3.1292	0.3198	0.1023
348	0.2796	0.6852	0.7426	3.3253	0.5718	0.1134	0.0129
	0.6291	1.2555	0.7426	3.3253	1.0589	0.1966	0.0387
	1.794	1.8207	0.7426	3.3253	1.8996	-0.0789	0.0062
	5.1955	2.3722	0.7426	3.3253	2.6409	-0.2687	0.0722
	14.4682	2.8874	0.7426	3.3253	3.0422	-0.1548	0.0240
	18.8949	3.4326	0.7426	3.3253	3.1041	0.3285	0.1079
							variance:

Table B2.1 Calculation for All Data Parameters

<b>Omit Last Data</b>							
<b>Experimental Data</b>				<b>Calculated Parameters</b>			
T	P	q	b	q <sub>s</sub>	q	residual	SS
(K)	(kPa)	(mol/kg)	(kPa) <sup>-1</sup>	(mol/kg)	(mol/kg)		
308	0.1856	1.7574	6.9316	2.9819	1.6778	0.0796	0.0063
	0.6599	2.3038	6.9316	2.9819	2.4470	-0.1432	0.0205
	1.8353	2.8455	6.9316	2.9819	2.7646	0.0809	0.0065
328	0.2416	1.2413	2.4759	2.9762	1.1140	0.1273	0.0162
	0.7686	1.8029	2.4759	2.9762	1.9510	-0.1481	0.0219
	1.8666	2.3608	2.4759	2.9762	2.4468	-0.0860	0.0074
	5.6437	2.9013	2.4759	2.9762	2.7775	0.1238	0.0153
348	0.2796	0.6852	0.9955	2.9705	0.6468	0.0384	0.0015
	0.6291	1.2555	0.9955	2.9705	1.1439	0.1116	0.0124
	1.794	1.8207	0.9955	2.9705	1.9043	-0.0836	0.0070
	5.1955	2.3722	0.9955	2.9705	2.4892	-0.1170	0.0137
	14.4682	2.8874	0.9955	2.9705	2.7777	0.1097	0.0120
						variance:	0.1409

Table B2.2 Calculation for Omit Last Data Parameters

## Appendix B3

### Dubinin-Radushkevich Isotherm

$$\Theta = \exp(-\text{power}((\varepsilon/\beta E_0), 2))$$

$$\varepsilon = R \cdot T \cdot \ln(P_0/p)$$

$$\Theta = W/W_0$$

$$W = q \cdot vM$$

$$q_s = W_0/V_m$$

$$R = 8.3142$$

$$q = q_s \cdot \exp(-\text{power}((\varepsilon/\beta E_0), 2))$$

where

$E_0$  = characteristic energy of adsorption for a reference adsorbate

$B$  = scaling factor  
fractional filling of pore

$\Theta$  = volume

$W_0$  and  $\beta E_0$  to be predicted

all data

$$W_0 = 515.5740933$$

$$\beta E_0 = 9219.006097$$

omit last  
data

$$W_0 = 470.293077$$

$$\beta E_0 = 10035.265$$

All Data		Experimental Data					Calculated Parameter S				
T (K)	P (kPa)	q (mol/kg)	$\gamma_m$ (gm <sup>3</sup> /mol)	$P_0$ (kPa)	$q_0$	$\epsilon$	q (mol/kg)	residual	SS		
308	0.1856	1.7574	156.8914	3.1815	3.2862	7276.4747	1.7625	-0.0051	0.0000		
	0.6599	2.3038	160.0036	3.1815	3.2223	4028.1475	2.6622	-0.3584	0.1285		
	1.8353	2.8455	163.1176	3.1815	3.1608	1408.7964	3.0878	-0.2423	0.0587		
	3.1551	3.3863	165.0571	3.1815	3.1236	21.3379	3.1236	0.2627	0.0690		
	0.2416	1.2413	157.4823	8.3637	3.2739	9665.7086	1.0906	0.1507	0.0227		
328	0.7686	1.8029	160.4288	8.3637	3.2137	6509.7197	1.9519	-0.1490	0.0222		
	1.8666	2.3608	163.1747	8.3637	3.1596	4089.9928	2.5951	-0.2343	0.0549		
	5.6437	2.9013	167.4221	8.3637	3.0795	1072.7182	3.0381	-0.1368	0.0187		
	8.3228	3.4490	169.1981	8.3637	3.0472	13.3685	3.0472	0.4018	0.1615		
	0.2796	0.6852	157.8213	19.1890	3.2668	12235.1676	0.5613	0.1239	0.0154		
348	0.6291	1.2555	159.8728	19.1890	3.2249	9888.8694	1.0205	0.2350	0.0552		
	1.794	1.8207	163.0410	19.1890	3.1622	6856.8997	1.8186	0.0021	0.0000		
	5.1955	2.3722	167.0653	19.1890	3.0861	3780.2791	2.6084	-0.2362	0.0558		
	14.4682	2.8874	172.0569	19.1890	2.9965	817.0335	2.9731	-0.0857	0.0073		
	18.8949	3.4326	173.6015	19.1890	2.9699	44.6881	2.9698	0.4628	0.2142		
variance:									0.8842		

Table B3.1 Calculations for All Data Parameters

Omit Last Data		Experimental Data						Calculated Parameter S			
T (K)	P (kPa)	q (mol/kg)	V/m (cm <sup>3</sup> /mol)	P <sub>b</sub> (kPa)	q <sub>s</sub>	ε	q (mol/kg)	residual	SS		
308	0.1856	1.7574	156.8914	3.1815	2.9976	7276.4747	1.7719	-0.0145	0.0002		
	0.6599	2.3038	160.0036	3.1815	2.9393	4028.1475	2.5019	-0.1981	0.0392		
	1.8353	2.8455	163.1176	3.1815	2.8832	1408.7964	2.8269	0.0186	0.0003		
	0.2416	1.2413	157.4823	8.3637	2.9863	9665.7086	1.1810	0.0603	0.0036		
328	0.7686	1.8029	160.4288	8.3637	2.9315	6509.7197	1.9246	-0.1217	0.0148		
	1.8666	2.3608	163.1747	8.3637	2.8821	4089.9928	2.4410	-0.0802	0.0064		
	5.6437	2.9013	167.4221	8.3637	2.8090	1072.7182	2.7771	0.1242	0.0154		
	0.2796	0.6852	157.8213	19.1890	2.9799	12235.1676	0.6740	0.0112	0.0001		
348	0.6291	1.2555	159.8728	19.1890	2.9417	9888.8694	1.1140	0.1415	0.0200		
	1.794	1.8207	163.0410	19.1890	2.8845	6856.8997	1.8085	0.0122	0.0001		
	5.1955	2.3722	167.0653	19.1890	2.8150	3780.2791	2.4426	-0.0704	0.0050		
	14.4682	2.8874	172.0569	19.1890	2.7334	817.0335	2.7153	0.1721	0.0296		
variance:									0.1350		

Table B3.2 Calculations for Omit Last Data

APPENDIX C :  
COMPARISON DATA OF THE ADSORPTION  
ISOTHERM FOR SIPS ISOTHERM

## Appendix C

### Comparison Data : Sips Equation

$$q = q_s * \text{power}((b * P), (1/n)) / (1 + \text{power}((b * P), (1/n)))$$

$$b = b_0 * \text{EXP}(Q/RT - Q/RT_0)$$

$$1/n = (1/n_0) + \alpha * (1 - (T_0/T))$$

$$q_s = q_{s0} * \text{exp}(\text{delta}T_0 * (1 - (T/T_0)))$$

where

$b_0$  = affinity constant

$T_0$  = reference temperature

$n_0$  = parameter n

$\text{delta}T_0$  = constant parameter

$q_s$  = saturation capacity

$\alpha$  = constant parameter

$\text{gamma} = Q/RT_0$

$q_{s0}$ ,  $b_0$ ,  $\text{gamma}$ ,  $n_0$ ,  $\alpha$  and  $\text{delta}T_0$  to be predicted

	Excel		MATLAB	
	all data	omit last data	all data	omit last data
$q_{s0}$	7.0665	5.1113	7.1651	3.6932
$b_0$	0.2206	0.9689	0.2044	4.1706
$\text{gamma}$	5.6988	2.9750	14.7830	18.0000
$\text{delta}T_0$	1.9177	3.1609	0.0002	0.2629
$n_0$	2.7821	2.6822	2.8025	1.7603
$\alpha$	1.1823	3.0917	0.6677	0.8195

$$T_0 = 308$$

All Data		Experimental Data			Excel			MATLAB		
T (K)	P (kPa)	q (mol/kg)	b (kPa) <sup>-1</sup>	q <sub>s</sub> (mol/kg)	1/n	q (mol/kg)	b (kPa) <sup>-1</sup>	q <sub>s</sub> (mol/kg)	1/n	q (mol/kg)
308	0.1856	1.7574	0.2206	7.0665	0.3594	1.7013	0.2044	7.1651	0.3568	1.7004
	0.6599	2.3038	0.2206	7.0665	0.3594	2.3563	0.2044	7.1651	0.3568	2.3539
	1.8353	2.8455	0.2206	7.0665	0.3594	2.9642	0.2044	7.1651	0.3568	2.9622
	3.1551	3.3863	0.2206	7.0665	0.3594	3.3036	0.2044	7.1651	0.3568	3.3027
	0.2416	1.2413	0.1559	6.2391	0.4315	1.2193	0.0830	7.1650	0.3975	1.2502
328	0.7686	1.8029	0.1559	6.2391	0.4315	1.7834	0.0830	7.1650	0.3975	1.7973
	1.8666	2.3608	0.1559	6.2391	0.4315	2.3077	0.0830	7.1650	0.3975	2.3121
	5.6437	2.9013	0.1559	6.2391	0.4315	3.0333	0.0830	7.1650	0.3975	3.0464
	8.3228	3.4490	0.1559	6.2391	0.4315	3.2946	0.0830	7.1650	0.3975	3.3194
	0.2796	0.6852	0.1146	5.5086	0.4953	0.8478	0.0374	7.1649	0.4336	0.8710
348	0.6291	1.2555	0.1146	5.5086	0.4953	1.1773	0.0374	7.1649	0.4336	1.1777
	1.794	1.8207	0.1146	5.5086	0.4953	1.7273	0.0374	7.1649	0.4336	1.6949
	5.1955	2.3722	0.1146	5.5086	0.4953	2.4025	0.0374	7.1649	0.4336	2.3605
	14.4682	2.8874	0.1146	5.5086	0.4953	3.0975	0.0374	7.1649	0.4336	3.1077
	18.8949	3.4326	0.1146	5.5086	0.4953	3.2750	0.0374	7.1649	0.4336	3.3127

Table C Comparison Calculation for All Data Parameters

**Omit Last Data**

Experimental Data		Excel				MATLAB				
T (K)	P (kPa)	q (mol/kg)	b (kPa) <sup>-1</sup>	q <sub>s</sub> (mol/kg)	1/h	q (mol/kg)	b (kPa) <sup>-1</sup>	q <sub>s</sub> (mol/kg)	1/h	q (mol/kg)
308	0.1856	1.7574	0.9689	5.1113	0.3728	1.7650	4.1706	3.6932	0.5681	1.7125
	0.6599	2.3038	0.9689	5.1113	0.3728	2.3431	4.1706	3.6932	0.5681	2.3634
	1.8353	2.8455	0.9689	5.1113	0.3728	2.8288	4.1706	3.6932	0.5681	2.8092
	0.2416	1.2413	0.8081	4.1629	0.5613	1.1888	1.3917	3.6307	0.6181	1.2260
328	0.7686	1.8029	0.8081	4.1629	0.5613	1.8049	1.3917	3.6307	0.6181	1.8531
	1.8666	2.3608	0.8081	4.1629	0.5613	2.3205	1.3917	3.6307	0.6181	2.3359
	5.6437	2.9013	0.8081	4.1629	0.5613	2.9180	1.3917	3.6307	0.6181	2.8370
	0.2796	0.6852	0.6883	3.3904	0.7282	0.7848	0.5268	3.5692	0.6623	0.7835
348	0.6291	1.2555	0.6883	3.3904	0.7282	1.1940	0.5268	3.5692	0.6623	1.1596
	1.794	1.8207	0.6883	3.3904	0.7282	1.8251	0.5268	3.5692	0.6623	1.7513
	5.1955	2.3722	0.6883	3.3904	0.7282	2.4297	0.5268	3.5692	0.6623	2.3585
	14.4682	2.8874	0.6883	3.3904	0.7282	2.8549	0.5268	3.5692	0.6623	2.8316

Table C Comparison Calculation for Omit Last Data Parameters