# CERTIFICATION OF APPROVAL

## Regression Analysis for Hydrocarbon Adsorption Isotherm on Activated Carbon

by

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Approved by,

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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.

NORADNIN HAFEEZA BINTI HAJI NAWAWI

# ABSTRACT

Adsorption process refers to the capability of all solid substances to attract to their surfaces molecules of gases or solutions with which they are in contact. This process is very useful for purification and separation. It is widely used in industry such as in the separation and fractionation of hydrocarbons for example adsorption of phenol using activated carbon.

Adsorption isotherm is a relationship between the partial pressure of an adsorbate gas and the surface coverage of the adsorbent at constant temperature. There are a lot of adsorption isotherms available in the literature, however not all the correlations can best fit all the data which covers wide range of the temperature and pressure found in most process situations. This project deals primarily with the regression analysis on adsorption isotherm correlation of hydrocarbon adsorption.

The objectives of this project are to identify the appropriate correlation for adsorption data and to use existing regression analysis software which can cover 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 five selected adsorption isotherms, which are Langmuir, Sips (Langmuir-Freundlich), Toth, Dubinin-Radushkevich and Dubinin-Astakhov isotherms. MATLAB programming is used for nonlinear regression of adsorption data at wide range of temperature and pressure. The data used for simulation is taken from published literature.

From the result, the best fit of adsorption isotherm data is determined by the statistical analysis using residual. The best fit adsorption isotherm is identified based on the lowest value of residual obtained. Verification of the method used is done by comparing the result with published literature.

From this study, it can be concluded the nonlinear regression tool from MATLAB can provide better selection of adsorption isotherm model of hydrocarbon adsorption systems. 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 residual. The findings of this project are useful for preliminary studies of adsorption isotherm and plays important role in the design of adsorption unit in the industry.

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## TABLE OF CONTENTS

## LIST OF FIGURES

## LIST OF TABLES

# LIST OF APPENDICES

## APPENDIX A : MODEL PARAMETERS, PHYSICAL PROPERTY DATA AND ADSORPTION DATA

## APPENDIX B : CALCULATION OF THE ADSORPTION ISOTHERM

# 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 | $kPa^{-1}$ |
| $b_0$ | Affinity constant at some reference temperature, $T_0$ | $kPa^{-1}$ |
| $E_0$ | Characteristic energy of the adsorption for reference adsorbate | J/mol |
| $M_W$ | Molecular weight | kg/mol |
| n | Parameter characterizing system heterogeneity | |
| $n_0$ | Parameter n at reference temperature, $T_0$ | |
| P | Pressure | kPa |
| $P_S$ | Saturated vapour pressure | MPa |
| q | Adsorbed amount | mol/kg |
| $q_m$ | Monolayer capacity | mol/kg |
| $q_s$ | Saturation adsorbed concentration | mol/kg |
| $q_{s,0}$ | Saturation capacity at reference temperature, $T_0$ | mol/kg |
| R | Universal gas constant | Joule/mol.K |
| T | Temperature | K |
| $T_0$ | Reference temperature | K |

| | | |
|---|---|---|
| $T_R$ | Relative temperature | K |
| t | Parameter in Toth isotherm | |
| $t_0$ | Parameter t at reference temperature, $T_0$ | |
| $\rho_A$ | Density of adsorbed phase | $kg/cm^3$ |
| $V_m$ | Liquid molar volume | $cm^3/mol$ |
| $V^*$ | Characteristic volume | $cm^3/mol$ |
| $V_R^{(0)}$ | Corresponding state function for normal fluids | |
| $V_R^{(\delta)}$ | Deviation function | |
| W | Volume of adsorbate | $cm^3/kg$ |
| $W_0$ | Maximum volume of adsorbate to occupy | $cm^3/kg$ |
| $y_i$ | response value | |
| $\hat{y}_i$ | predicted value | |
| $\theta$ | Fraction of monolayer coverage | |
| gamma | Activity coefficient | |
| $\omega_{SRK}$ | Acentric factor from the Soave-Redlich-Kwong equation of state | |
| delta $T_0$ | Ratio of surface to pore volume diffusion | |

# CHAPTER 1
# INTRODUCTION

## 1.1 Background of Study

Adsorption is a process where one or more components of a gas or liquid stream are adsorbed on the surface of a solid adsorbent. In this process, molecules, or atoms, or ions in a gas or liquid diffuse into the surface of a solid. The adsorbed solutes are referred to as adsorbate, whereas the solid material is the adsorbent. Currently, the applications of this process have expanded rapidly due to sharply rising of environmental or quality requirement. Basically, all cyclic adsorption applications rely on regenability. This is crucial for the adsorbent to be able to operate in sequential cycles with uniform performance. Regeneration can be accomplished by a thermal swing, pressure swing, and chemicals such as displacement, supercritical extraction or combination of those (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 –xylene from mixed isomers (Kent, 1995).

Adsorption isotherm relates the amount of substance adsorbed on solid adsorbent at equilibrium to the pressure or concentration of the gas or liquid phases. It plays a significant role especially during designing of an adsorption column, where adsorption isotherm is used for modeling and scale up purposes. Brunauer et al., (1940), has divided isotherms of physical adsorption into five types as shown in Figure 1.1.

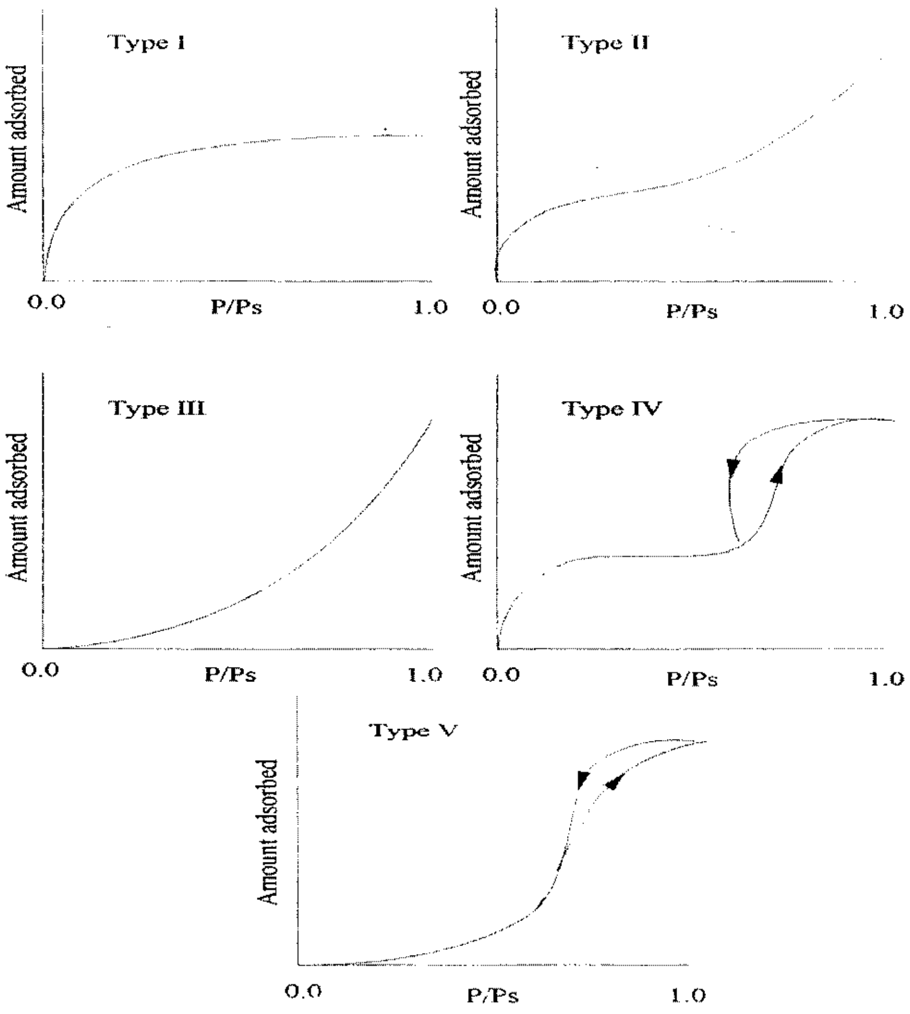

**Figure 1.1**: The five types of pure-component gas-adsorption isotherms in the classification of Brunaeur, Deming, Deming and Teller (BDDT). Source: Seader and Henley, (1998).

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 made by processes that involve the partial oxidation of a number of materials such as coconut shell, fruit nuts, coal, petroleum residue, and bones. The functional groups of an activated carbon can be increased by treating it with some oxidizing agents or decreased by exposing it to a vacuum environment at very high temperature (Do, 1998).

Regression analysis refers to the analysis of functional relationship between two or more correlated variables that is often empirically determined from data. Values of one variable when given values of the others could be predicted by using regression method. The goal of regression analysis is to determine the values of parameters for a function that cause the function to best fit a set of data observations. For this particular study, regression is performed to determine and obtain the curve fit of adsorption data which is predicted by several adsorption isotherms. The correlation which best fit the adsorption data over wide range of temperature and pressure is chosen based on regression analysis study.

Generally, the purpose of this project is to identify some of established adsorption isotherm weather it is suitable for hydrocarbon adsorption at wide range of temperature and pressure. The findings of this project are beneficial to provide guide for the determination of the best material in order for the adsorption process to occur at its maximum amount to be adsorbed. Models or correlations of adsorption equilibria from experimental data are important for the design of adsorption systems. Using the modelling, adsorber can be designed in such that it can optimize the adsorption process for continuous operation in cyclic adsorption system. Overall, the findings of this project plays important role in industrial adsorption system design.

## 1.2 Problem Statement

There are many isotherms which are useful in representing various types of adsorption equilibrium data. Nevertheless, very few are appropriate over the wide range of temperature and pressure found in most process situations. Thus, it is almost impossible to choose one single correlation to best fit all adsorption data. Currently, there are several computer software such as MATLAB, NLREG, Curve Fit and SPSS that are capable for regression purposes. However, not all are able to regress the nonlinear adsorption data which covers wide range of temperature and pressure. In addition, a suitable correlation of relevant adsorption isotherms is crucial to ensure how accurate it fits the selected adsorption data.

## 1.3 Objectives

The objectives of the project are:

i) To identify and determine the appropriate correlation for adsorption data at wide range of temperature and pressure.
ii) To use the possible software that is able to do the regression at wide range of temperature and pressure.
iii) To conduct comparison study on different types of adsorption isotherms.
iv) To compare different type of regression method from Statistical Analysing System (SAS) and MATLAB programming.

## 1.4 Scope of Study

In order to achieve the objectives, this project is focusing on single component adsorption. It will cover the study of five selected adsorption isotherms, which are Langmuir, Sips (Langmuir-Freundlich), Toth, Dubinin-Radushkevich and Dubinin-Astakhov isotherms. MATLAB programming is used for nonlinear regression of the adsorption data. The data for Octane Adsorption on Activated Carbon (M. Shariff, A., 1995) is used as a case study in order to determine the best adsorption isotherm correlation. The adsorption data is listed in A.2 of Appendix A. The comparison study is done with the results from other researcher who had used nonlinear regression tool in SAS for similar experimental data using Dubinin-Radushkevich and Dubinin-Astakhov isotherms.

# CHAPTER 2
# LITERATURE REVIEW

## 2.1 Introduction

There is a lot of relevant published literature of adsorption processes. Therefore, only a brief and concise summary of the prediction of adsorption isotherms is given in this section. These literatures are crucial during preliminary research in order to give clear overview on the direction of work on which adsorption isotherm correlation that should be focused on.

## 2.2 Adsorption Isotherm of Pure Component Equilibria

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:

$$\theta = \frac{q}{q_s} = \frac{\alpha P}{1 + \alpha P} \qquad [2.1]$$

where $\alpha$ refers to the empirical fitted constant which is dependent on temperature. This equation is beneficial and widely used in practical purposes as it fits Type 1 isotherms and the initial region of Type II isotherm.

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:

$$\theta = \alpha P^{\beta} \qquad [2.2]$$

where both α and ß are empirical fitted constant which are a function of temperature. Nevertheless, this equation does not reduce to a Henry's law limit except when ß equals to unity.

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

$$\theta = \frac{\alpha P^{\beta}}{1 + \alpha P^{\beta}} \qquad [2.3]$$

where α and ß are empirical fitted constant which are temperature dependent.

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

$$\theta = \frac{\alpha P}{1 + \alpha_1 P^{\beta}} \qquad [2.4]$$

where both α and α1 are empirical constant and depend on temperature while ß 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.

A totally different theory which is the potential theory was derived by Polanyi, (1932). 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).

The adsorption isotherms of the thermodynamic approaches are derived from the Gibbs adsorption isotherm which is written as:

$$A\left(\frac{d\pi}{dinP}\right)_T = qRT \qquad [2.5]$$

where A refers to the surface area, π is the spreading pressure. This isotherm provides a general relation between spreading pressure and adsorbed phase concentration. Harkins and Jura, (1944), were the first to use the thermodynamic approach and proposed an isotherm developed from Gibbs Equation and various equations of state. The proposed isotherm is as:

$$InP_R = \beta - \frac{\alpha}{q^2} \qquad [2.6]$$

where ß is a constant and α depends on A and T.

Later, Suwanayuen and Danner, (1980), developed a model based on the concept of 'vacancy solution theory' (VST). The correlation was then simplified by using the Florry-Huggins activity coefficients, (Cochran et. al., 1985) which give an expression which have three fitted parameters. Later, the model was extended to include the temperature dependence resulting in an equation having five fitted parameters.

Concerning adsorption process in most process situations takes place in wide operating conditions, Mohd. Shariff, A., (1995), conducted study on prediction of adsorption isotherm for octane adsorption on activated carbon at various temperature and pressure by using several isotherms. The isotherms used are modified Antoine equation with linear variation of the heat of adsorption with loading (MA-2 and MA-3), Dubinin-Astakhov and Dubinin-Radushkevich isotherms. Nonlinear regressions for the experimental adsorption data were performed using SAS (Statistical Analysing System) package to determine the best fit correlation to the experimental data. Model MA-3 was the best correlation for the representation of octane adsorption isotherm measured for the whole range of temperature and relative vapor pressure up to unity.

Rusch et. al., (1997), interpreted the competitive adsorption isotherms which involve several components in terms of affinity distributions. The applicability of the regularized least-squares technique was demonstrated with a newly derived isotherm with the generalized Langmuir–Freundlich (LF) isotherm. The extended Henderson-Hasselbalch (HH) isotherm have been analyzed and showed that the underlying distribution displays a partial correlation. Meanwhile, the non-ideal competitive adsorption (NICA) isotherm may have, depending on the parameters, an affinity distribution with a varying degree of correlation. In conclusion, proper understanding of all these characteristic features of the affinity distributions might prove essential represent interesting characteristics of a competitive adsorption process for the future development of adsorption models for heterogeneous materials.

Berti et. al., (1998) discovered a new approach to describe the adsorption behaviour of liquid mixtures on solid surfaces by use of $G^{E-}$models. By incorporating the Gibbs excess energy $G^{E*}$ for this adsorbate-solid-solution, the free energy of adsorption is correlated with the respective activity coefficients of all involved components. The Wilson model was used to calculate the Gibbs excess free energy $G^{E*}$ for the evaluation purposes. The prediction of surface excess physical meaning of the Wilson interaction parameters were proved by the prediction of surface excess isotherms of binary liquid mixtures from other binary adsorption data.

Wang and Do, (1999), make the prediction of adsorption equilibrium and kinetics of hydrocarbons onto activated carbon for different micropore size distribution (MPSD). The MPSD is regarded as the source of surface heterogeneity and is described by the Lennard-Jones potential theory. The study was done on activated carbon with three different MPSDs with ethane and propane as the two model adsorbates by employing simulation using Heterogeneous Macropore Surface Diffusion model (HMSD). The result of simulation proved that MPSD is a crucial factor which affects both the multicomponent equilibria and kinetics.

Wang et. al., (2000), conducted comparison study on five kinetic models for adsorption of hydrocarbons on activated carbon. These models assume different mass transfer mechanisms within the porous carbon particle. These models are compared with the adsorption kinetics of pure as well as binary mixtures of ethane and propane on two commercial activated carbon samples under various conditions. The findings of study suggest that the role of the surface flux in the overall sorption kinetics is significant and needs to be properly addressed.

## 2.3 Concluding Remarks

There are quite a number of literatures on adsorption isotherm. This includes the overview of some important correlations or models for the prediction of adsorption equilibria. This literature review enhances the understanding of current developments of this area. It is noticed that there are few literatures which covers on the current status of the field which includes prediction of adsorption isotherm in terms of micropore size distribution, mass transfer mechanism and affinity distribution. However, there are scarce literatures on adsorption isotherm correlation for hydrocarbon adsorption process which involves wide operating conditions of temperature and pressure except the one conducted by Mohd. Shariff, A., (1995). Therefore, investigation and specific study on adsorption isotherm correlation need to be further refined concerning the importance of considering temperature and pressure in this area.

# CHAPTER 3

# THEORY

## 3.1 Introduction

According to BDDT classification, the adsorption isotherms of single component systems can be classified into five different types (Brunaeur et. al., 1940). The simplest 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 associated with 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 undesirable because the extent of adsorption is low except at high pressures. This isotherm is quite rare and associated with non-porous solids. Type IV is characterized by multilayer adsorption on a non-porous solid. On the other hand, Type V is associated with adsorption on porous solids. Hysterisis phenomenon can occur in multimolecular adsorption regions for both isotherms of types IV and V.

## 3.2 Adsorption Isotherms

Until today, there are many isotherm models that have been developed to represent adsorption isotherms for various systems. In this project, isotherms of interest are those incorporating temperature dependent term. In this entire chapter, basic theories of five selected adsorption isotherms are discussed. The isotherms include Langmuir, Sips (Langmuir-Freundlich), Toth, Dubinin-Radushkevich and Dubinin-Astakhov isotherms.

### 3.2.1 Langmuir Isotherm

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:

$$\theta = \frac{bP}{1+bP} \qquad [3.1]$$

$$b(T) = b_0 \exp\left(\frac{Q}{RT} - \frac{Q}{RT_0}\right) \qquad [3.2]$$

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 and $b_0$ is the affinity constant at the reference temperature. The isotherm equation [3.1] 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 [3.1] 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:

$$q = q_s \frac{b(T)P}{1+b(T)P} \qquad [3.3]$$

where q is amount adsorbed in mol/kg and $q_s$ is the maximum adsorbed concentration corresponding to a complete monolayer coverage.

$$q = q_s \frac{b_0 \exp(\frac{Q}{RT} - \frac{Q}{RT_0})P}{1+b_0 \exp\left(\frac{Q}{RT} - \frac{Q}{RT_0}\right)P} \qquad [3.4]$$

and

$$q_s = q_{s0} \exp(deltaT_0 * (1 - T/T_0)) \qquad [3.5]$$

where $q_{s,0}$ is the saturation capacity at the reference temperature $T_0$ while deltaT$_0$ is a constant parameter.

### 3.2.2 Sips Equation (Langmuir-Freundlich)

Sips equation is sometimes called 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:

$$q = q_s \frac{(bP)^{1/n}}{1+(bP)^{1/n}} \qquad [3.6]$$

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

$$b = b_\infty \exp\left(\frac{Q}{RT}\right) = b_0 \exp\left[\frac{Q}{RT_0}\left(\frac{T_0}{T}-1\right)\right] \qquad [3.7]$$

$$\frac{1}{n} = \frac{1}{n_0} + \alpha\left(1-\frac{T_0}{T}\right) \qquad [3.8]$$

Here, $b_\infty$ refers to 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 and $\alpha$ is a constant parameter. Meanwhile, the saturation capacity $q_s$ can be either considered as constant or it may take the following temperature dependence:

$$q_s = q_{s,0} * \exp\left[deltaT_0\left(1-\frac{T}{T_0}\right)\right] \qquad [3.9]$$

where $q_{s,0}$ is the saturation capacity at the reference temperature $T_0$ while deltaT$_0$ is a constant parameter.

The temperature dependence of Sips equation represented by Equation [3.6] 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:

$$q = q_s \frac{bP}{[1+(bp)^t]^{1/t}} \qquad [3.10]$$

where the parameters 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:

$$b(T) = b_\infty \exp\left(\frac{Q}{RT}\right) = b_0 \exp\left[\frac{Q}{RT_0}\left(\frac{T_0}{T} - 1\right)\right] \qquad [3.11]$$

where $b_\infty$ refers to the affinity constant at infinite temperature, $b_0$ is the affinity constant at some reference temperature $T_0$, and Q is the measure of the heat of adsorption. Meanwhile, the parameter t is usually less than unity. This parameter is represented by the following empirical functional form of temperature dependence:

$$t = t_0 + \alpha\left(1 - \frac{T_0}{T}\right) \qquad [3.12]$$

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:

$$q_s = q_{s,0} * \exp\left[deltaT_0\left(1-\frac{T}{T_0}\right)\right] \qquad [3.13]$$

where $q_{s,0}$ is the saturation capacity at the reference temperature $T_0$ while deltaT$_0$ is a constant parameter. Toth 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).

### 3.2.4 Dubinin-Radushkevich and Dubinin-Astakhov Isotherms

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

$$\theta = \exp\left[-\left(\frac{\varepsilon}{\beta E_0}\right)^2\right] \qquad [3.14]$$

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

$$\theta = \frac{W}{W_0} \qquad [3.15]$$

where W is the volume of adsorbate in micropore and $W_0$ 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:

$$\theta = \exp\left[-\left(\frac{\varepsilon}{\beta E_0}\right)^n\right] \qquad [3.16]$$

where parameter 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

$$InP = InP_S - \frac{\beta E_0}{RT}(-In\theta)^{1/2} \qquad [3.17]$$

and the rearranged form for Dubinin-Astakhov is written as

$$InP = InP_S - \frac{\beta E_0}{RT}(-In\theta)^{1/n} \qquad [3.18]$$

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, θ is the fractional filling of pore volume .

Substituting these equations with equation [3.15] and W=q$V_m$, the equations [3.19] and [3.20] are obtained for Dubinin-Radushkevich and Dubinin-Astakhov isotherms respectively:

$$q = \frac{W_0}{V_m} \exp\left[ -\left( \frac{RT \ln(p_s / p)}{\beta E_0} \right)^2 \right] \qquad [3.19]$$

$$q = \frac{W_0}{V_m} \exp\left[ -\left( \frac{RT \ln(p_s / p)}{\beta E_0} \right)^n \right] \qquad [3.20]$$

where the parameter $W_0$ is the micropore volume in $cm^3/kg$ and $V_m$ is the liquid molar volume in $cm^3/mol$.

To fit the parameters of Dubinin-Radushkevich and Dubinin-Atakhov Isotherms, the adsorbed amount per unit mass, q (mol/kg) has to be transformed into adsorbed volume per unit mass, W ($cm^3/kg$). For this transformation, the following equation is employed:

$$W = \frac{q.M_W}{\rho_A} = qV_m \qquad [3.21]$$

where $M_W$ is molecular weight of adsorbate in kg/mol, $\rho_A$ is the density of adsorbed phase in $kg/cm^3$ and $V_m$ is the saturated liquid molar volume in $cm^3/mol$.

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:

$$T = \frac{B}{A - \ln P} - C \tag{3.22}$$

where A, B and C are the parameters of Antoine equation for octane. Based on temperature evaluated using equation [3.22], the saturated molar volume can be obtained using Hankinson-Brobst-Thomson (HBT) technique (Reid et. al., 1987). This technique employed the following equations:

$$V_m = V^* \times V_R^{(0)} \left[1 - \omega_{SRK} V_R^{(\delta)}\right] \tag{3.23}$$

$$V_R^{(0)} = 1 + a(1 - T_R)^{1/3} + b(1 - T_R)^{2/3} + c(1 - T_R) + d(1 - T_R)^{4/3} \quad \text{for } 0.25 < T_R < 0.95 \tag{3.24}$$

$$V_R^{\delta} = \frac{\left(e + fT_R + gT_R^{2} + hT_R^{3}\right)}{\left(T_R - 1.00001\right)} \quad \text{for } 0.25 < T_R < 1.0 \tag{3.25}$$

with

$$T_R = \frac{T}{T_C} \tag{3.26}$$

where V* is a characteristic volume in cm$^3$/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, and $T_R$ 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.

## 3.3 Nonlinear Regression

There are various tools that can be utilized for nonlinear regression. Among the available software for this purpose are MATLAB, NLREG, Curve Fit and SAS programming. These are powerful mathematical computation tools, which also provide extensive capabilities of generating graphs. In this chapter, an introduction to the essential methods employed in the project which are the MATLAB and SAS programming is given.

### 3.3.1 MATLAB programming

MATLAB is presently a globally available standard computational tool used widely by engineers. It is maintained and sold by The Mathworks, Inc., of Natick, Massachusetts. The MATLAB interactive environment allows managing variables, import and export data, performs calculations, generate plots, and develop and manage files. This programming uses the Newton-Raphson method for the nonlinear regression purposes. Given an equation f(x) = 0, with f(x) expandable in a Taylor series about an initial guess value $x_0$, it can be written as follows:

$$f(x) = f(x0) + f'(x_0)\,(x - x_0) + \ldots \qquad [3.27]$$

Neglecting the terms in higher powers of $(x-x_0)$ and recall that f(x) = 0, thus the following equation is obtained.

$$x = x_0 - f(x_0)/f'(x_0) \qquad [3.28]$$

or in iteration form:

$$x_{i+1} = x_i - f(x_i)/f'(x_i) \qquad [3.29]$$

There is no general convergence criterion for Newton-Raphson method (Steven and Raymond, 1998). Its convergence depends on the nature of the function and the accuracy of the initial guess. Therefore, the initial guesses obtained on basis of trial and error should be sufficiently close to the root. Using MATLAB, it is possible to develop an interactive program which the user can view the graph of equation to be solved, choose initial guess, and run a Newton-Raphson procedure to obtain the final approximation of the root (Biran and Breiner, 1996).

### 3.3.2 SAS programming

The SAS® System is a product of SAS (Statistical Analysing System) Institute, Cary North Carolina. This software system has its own language for analyzing data. This system used the NLIN (NonLINear regression) procedure by least squares. This method minimizes the sum of squares of the residuals which is the differences between the actual response value, $y_i$ and the value predicted, $\hat{y}_i$. The estimates are called least-squares estimates, and the criterion is called the error sum of squares or the residual sum of squares SSE:

$$SSE = \sum_{i=1}^{n} (y_i - \hat{y}_i)^2 \qquad [3.30]$$

with n the number of observations in the data set of experiments.

NLIN uses the Marquart method. This method is a compromise between Gauss-Newton and steepest-descent (Marquardt, 1963). If the SSE improves the iteration essentially the Gauss-Newton method is applied. However, if SSE does not improve, the steepest descent direction is used.

## 3.4 Statistical Analysis

### 3.4.1 Definition of Residual

Residual is the measure of how the fitted line deviates from the original adsorption data. Generally, residuals are calculated by using the equation [3.30] as described previously. Specifically, for the interest of the project, the residual calculation is as follows:

$$\text{Residuals} = \sqrt{\sum (\Delta q)^2} \qquad [3.31]$$

where $\Delta q$ refers to the difference between the $q_{experimental}$ from published data and $q_{correlated}$ by computation from the selected isotherms. The best fit model is indicated by the one that has the smallest residual value or approaching zero.

## 3.5 Concluding Remarks

The fundamentals of adsorption equilibria of pure component have been addressed in this chapter. A number of fundamental equations have been discussed. Although the equations are successful in describing some experimental data, not all are able to describe adsorption in wide range of temperature and pressure.

# CHAPTER 4
# METHODOLOGY

## 4.1 Introduction

Selection has been made in order to choose the possible software that is able to do the regression of adsorption isotherm correlation for hydrocarbon on adsorbents at wide range of temperature and pressure. Considering easy accessibility and capability, MATLAB have been chosen as the tool for the nonlinear regression purposes. MATLAB programming can be used to fit the adsorption data by correlating using the adsorption isotherms. The sample of MATLAB programming is listed in C.1 of Appendix C.

## 4.2 The Adsorption Isotherms

Basically there are five adsorption isotherm used in this study. Expressions for adsorption isotherm are given as the following equations: equations [3.4] for Langmuir, equation [3.6] for Sips (Langmuir-Freundlich), equation [3.10] for Toth, equation [3.19] for Dubinin-Radushkevich and equation [3.20] for Dubinin-Astakhov isotherms. These expressions are the main equations used in the programming which employed derivation as been discussed previously in Chapter 3.

## 4.3 Data for Nonlinear Regression

The data used for to determine the best adsorption isotherm correlation is Octane Adsorption on Activated Carbon (M. Shariff, A., 1995). The adsorption data is listed in A.2 of Appendix A. The data provided consists of amount adsorbed (mol/kg) and pressure (kPa) which are the known parameters for the isotherm equations.

## 4.4 Solution Procedure

A summary of computational procedure is given in Figure 4.1. Nonlinear regression from MATLAB is used for the regression analysis. The main equations for adsorption isotherm of interest are programmed using MATLAB coding. The adsorption isotherm data of octane on activated carbon from M. Shariff, (1995) are keyed in as input data. Initial guess of the unknown parameters as listed in Table 4.1 need to be specified. This is done on trial and error basis. The initial guess needs to be as close as possible to the predicted parameters to ensure the convergence of the iteration. MATLAB will conduct nonlinear regression based on Newton-Raphson iteration method. Incorporating this method, the unknown parameters for the isotherm expression are determined. Residual calculation based on equation [3.31] is done automatically by MATLAB.

**Table 4.1**: Unknown parameters for adsorption isotherm models

| **Model** | **Unknown Parameters** |
|---|---|
| Langmuir | $q_{s0}$, $b_0$, Q/RT, delta$T_o$ |
| Sips | $q_{s0}$, $b_0$, Q/RT, delta$T_o$, $n_0$, $\alpha$ |
| Toth | $q_{s0}$, $b_0$, Q/RT, delta$T_o$,, $t_0$, $\alpha$ |
| Dubinin-Radushkevich | $W_0$, $\beta E_0$ |
| Dubinin-Astakhov | $W_0$, $\beta E_0$, n |

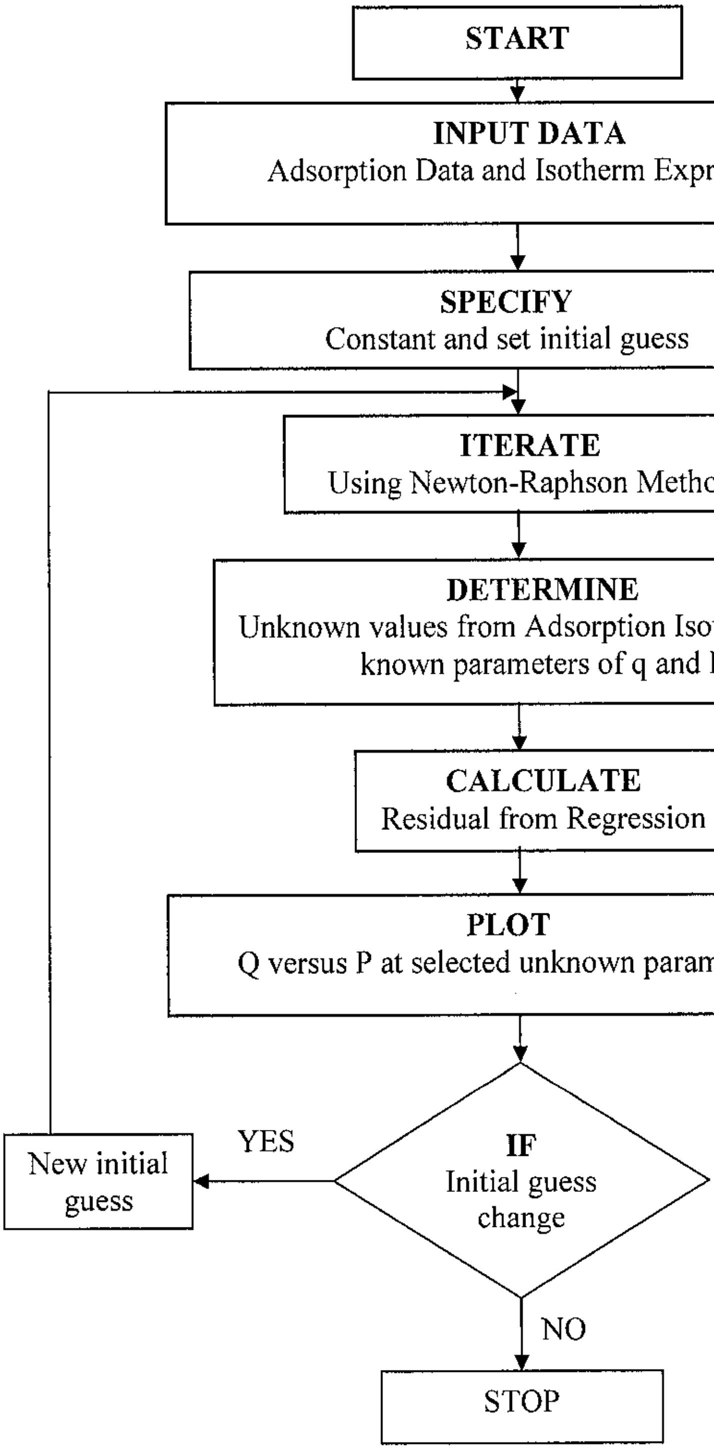

**Figure 4.1**: Flowchart for the procedure of MATLAB programming

## 4.5 Concluding Remarks

The MATLAB computer programming employed Newton-Raphson iteration for the nonlinear regression purposes. The correlation of adsorption equilibria is performed by fitting a single equation to the experimental data for all the considered temperature together. The unknown parameters are determined and the residual which is a measure of how the fitted line deviates from the original adsorption data is calculated using this programming. Most importantly, this method is capable of performing regression of adsorption data at wide range of temperature and pressure. The detail of result of the selected adsorption isotherms obtained from this programming is presented and discussed further in Chapter 5.

# CHAPTER 5

# RESULT AND DISCUSSION

## 5.1 Introduction

Through nonlinear regression by using MATLAB, the best fit line for all selected isotherm could be identified. However, it is difficult and almost impossible to select the best fit of the correlation to the adsorption data based on the graphs of the nonlinear regressions only. This is due to most of the selected isotherms in the study are showing the same trend which fit Type 1 isotherms quite satisfactorily. Therefore, there is a need to check on other criterion such as the quality of the curve fitting in order to justify the representation of the adsorption data. For this purpose, residual analysis of correlation to the adsorption data for each selected isotherms have been conducted to differentiate regression result correlated by five different isotherms.

## 5.2 Adsorptifon Equilibria For Pure Octane Adsorption

### 5.2.1 Langmuir Isotherm

For Langmuir isotherm, equations [3.3] to [3.5] are proposed to fit the data of octane adsorption. Detail explanation of this equation is as discussed previously in Chapter 3.2.1. Using these equations, the known parameters are the experimental data which are amount adsorbed, q (mol/kg) and pressure, P (kPa).

Nonlinear regression was conducted to estimate the value for $q_{s0}$, $b_0$, Q/RT and $\mathrm{deltaT}_0$ and also the value of residuals. The unknown values results are listed in Table 5.1. Comparing the obtained parameters, it is noticeable that the values of residual are smaller for regression which neglects the last data than for regression which considers all experimental data. Graphs representation of the correlation using Langmuir isotherm are shown as Figure 5.1 and Figure 5.2.

**Table 5.1:** Optimal parameters obtained by Langmuir isotherm

| | **$q_{s0}$ (mol/kg)** | **$b_0$ $(\mathrm{kPa})^{-1}$** | **$\frac{Q}{RT}$** | **$\mathrm{deltaT}_0$** | **Residual** |
|---|---|---|---|---|---|
| All data | 3.3591 | 4.6957 | 16.0444 | 0.07785 | 0.8213 |
| Omit last data | 2.9819 | 6.9316 | 16.8835 | 0.02949 | 0.3754 |

Based on the obtained parameters using Langmuir isotherm, the values of affinity constant, b for each temperature could be calculated by using equation [3.2].

**Table 5.2**: Calculated b parameter for each temperature using Langmuir isotherm

| **T (K)** | **b $(\mathrm{kPa})^{-1}$** |
|---|---|
| 308 | 4.6957 |
| 328 | 1.7653 |
| 348 | 0.7443 |

Referring to results in Table 5.2, it can be clearly seen that as temperature increases, the affinity constant decreases. At a given pressure, increase in temperature will decrease the amount to be adsorbed due to greater energy acquired by the adsorbed molecules to evaporate (Do, 1998). At 308 K, the b value is higher as the affinity of adsorbate towards surface is higher as the surface is covered more with adsorbate molecule.

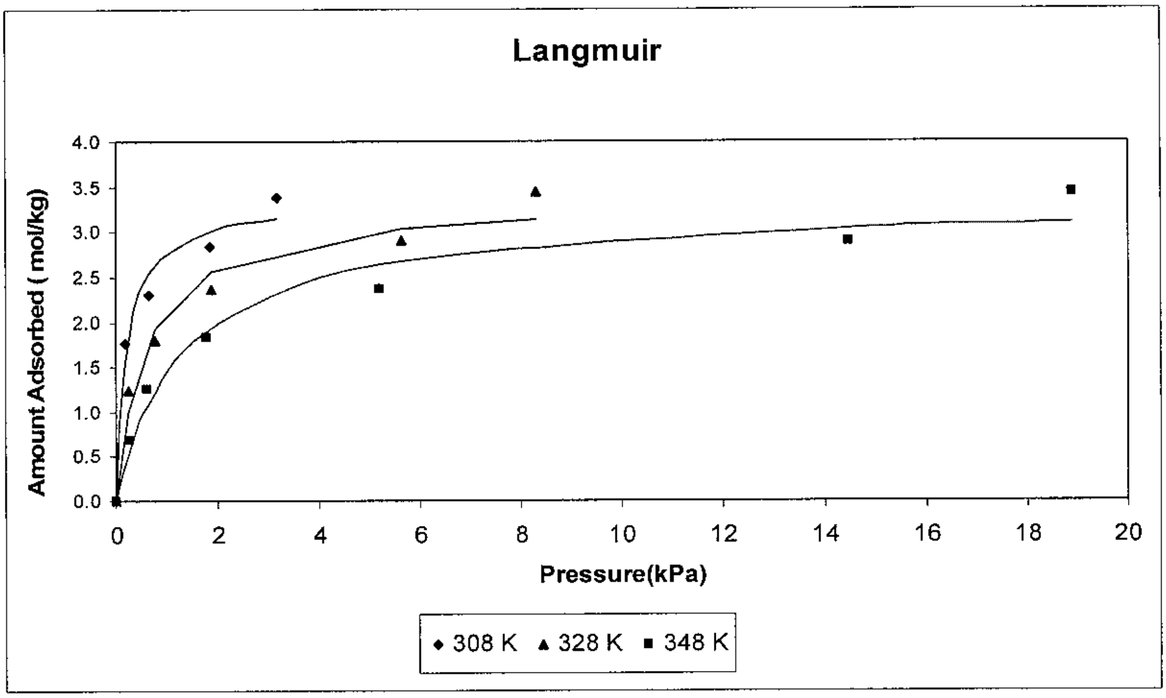

**Figure 5.1**: Adsorption isotherm correlated for all experimental data points with Langmuir isotherm

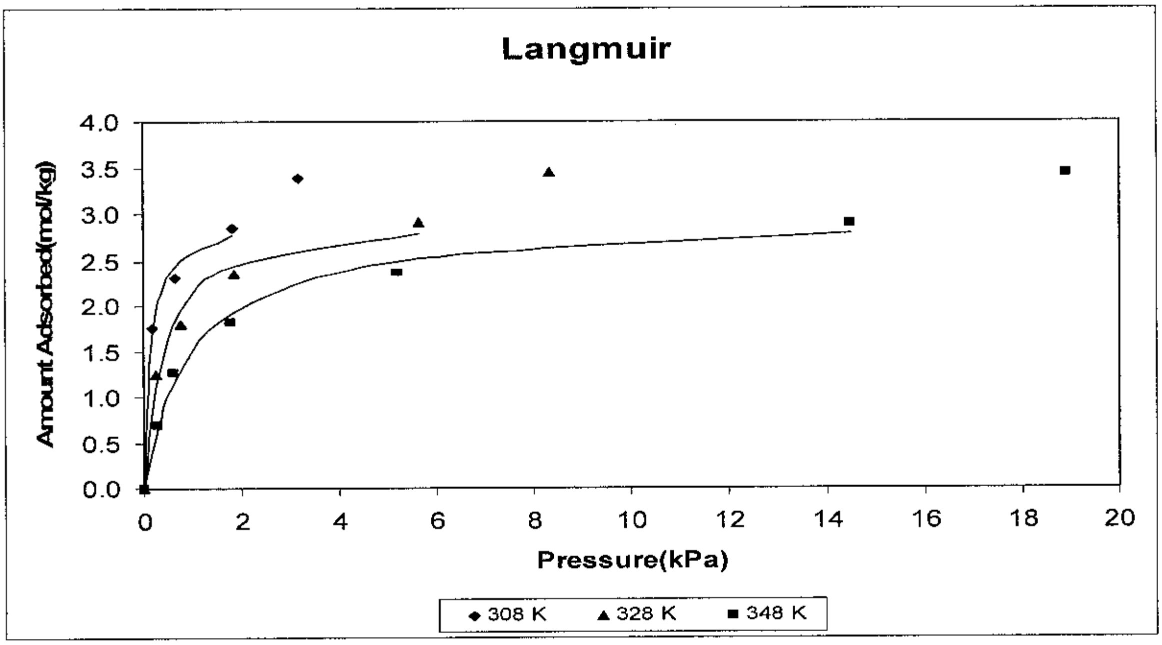

**Figure 5.2**: Adsorption isotherm correlated (omit last data) with Langmuir isotherm

### 5.2.2 Sips Equation

The temperature dependence of Sips is represented by equations [3.6] to [3.9], as derived in Chapter 3.2.2. By using nonlinear regression on the octane adsorption data, several unknown parameters could be determined. It is noticed that in Table 5.3, the residuals for both considering all experimental data and omitting the last data are especially low.

**Table 5.3**: Optimal parameters obtained by Sips equation

| | $q_{s,0}$ (mol/kg) | $b_0$ $(kPa)^{-1}$ | $\frac{Q}{RT}$ | $n_0$ | $\alpha$ | deltaT$_0$ | residual |
|---|---|---|---|---|---|---|---|
| All data | 7.1651 | 0.2044 | 14.783 | 2.8025 | 0.6677 | 0.00020 | 0.4313 |
| Omit last data | 3.6932 | 4.1706 | 18.548 | 1.7603 | 0.8195 | 0.02629 | 0.1282 |

Based on the obtained parameters using Sips equation, the values of n have been calculated for each temperature using the equation [3.8]. The results in Table 5.4 show that the n values are all greater than unity, suggesting some degree of heterogeneity of this octane/activated carbon system. As temperature increases, the parameter n decreases. This indicates that the system is less heterogenenous as temperature increases (Do, 1998).

**Table 5.4**: Calculated n parameter for each temperature using Sips equation

| T (K) | n (-) |
|---|---|
| 308 | 2.8025 |
| 328 | 2.5155 |
| 348 | 2.3064 |

By examining the plots of Figure 5.3 and Figure 5.4, it can be observed that correlation by Sips equation is very close to the experimental data.

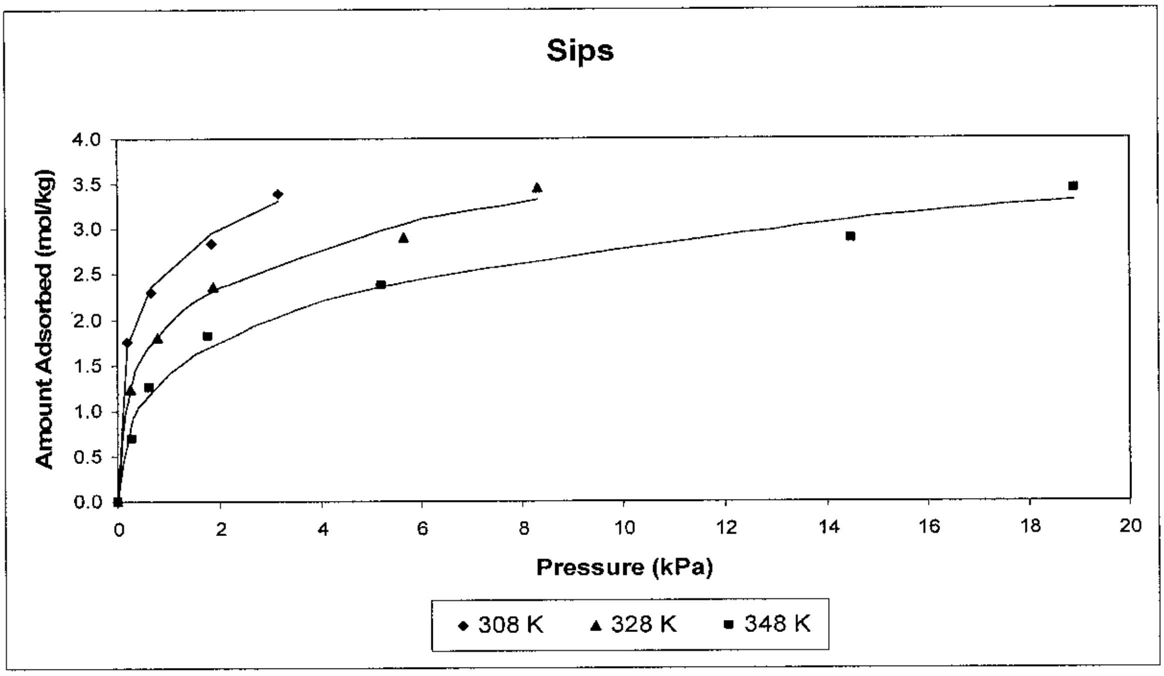

**Figure 5.3**: Adsorption isotherm correlated for all experimental data points with Sips equation

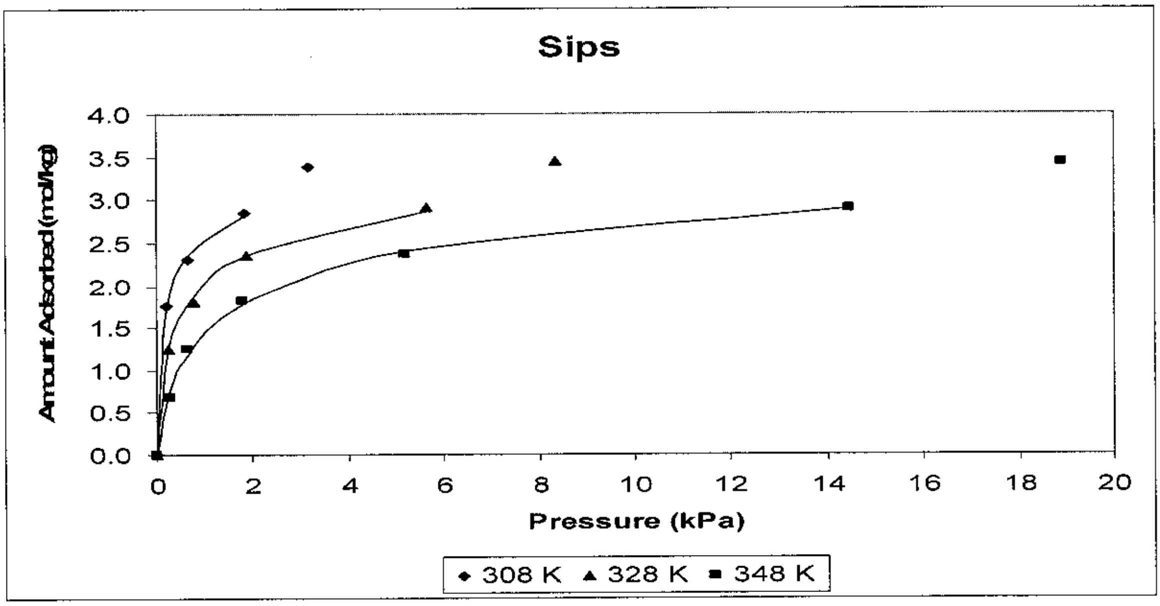

**Figure 5.4**: Adsorption isotherm correlated (omit last data) with Sips equation

### 5.2.3 Toth equation

Toth equation as introduced previously is valid for wide range of pressure. For the nonlinear regression purpose, equations [3.10] to [3.13] are used to fit the data. Detail explanation on this isotherm is available in Chapter 3.2.3. These equations are used to fit the parameters $q_{s0}$, $b_0$, Q/RT, $t_0$, $\alpha$ and deltaT$_0$ to the experimental data of q versus P.

**Table 5.5**: Optimal parameters obtained by Toth equation

| | $q_{s0}$ (mol/kg) | $b_0$ (kPa)$^{-1}$ | $\frac{Q}{RT}$ | $t_0$ | $\alpha$ | deltaT$_0$ | Residual |
|---|---|---|---|---|---|---|---|
| All data | 4.9703 | 15.734 | 16.5138 | 0.42391 | -0.02886 | -0.0123 | 0.49737 |
| Omit last data | 3.9799 | 30.6847 | 22.9909 | 0.4456 | 0.51551 | -0.0051 | 0.17303 |

The optimal parameters correlated with Toth equation is shown in Table 5.5 as above. It is observed that the curve fit give satisfactory result by looking at the small residual values for both regression on octane adsorption which considers all experimental data and omits the last data. The visualization of plot for octane isotherm correlated with Toth equation is as shown in Figure 5.5 and Figure 5.6. It can be seen that the plot using Toth equation correlation give satisfactory fit to the experimental data.

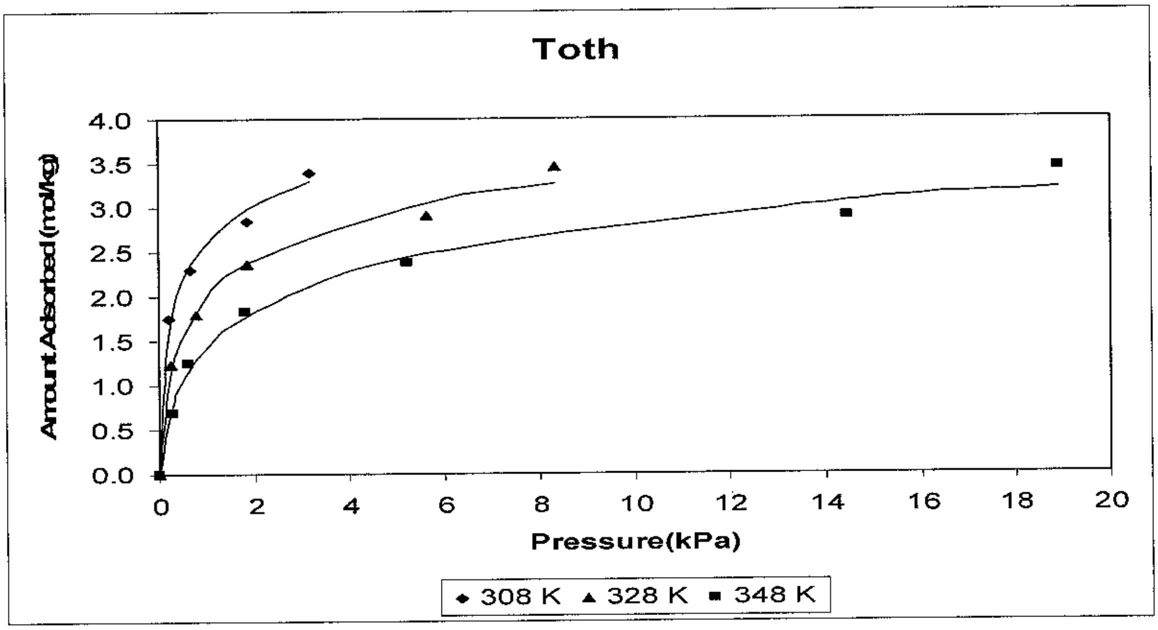

**Figure 5.5**: Adsorption isotherm correlated for all experimental data points with Toth equation

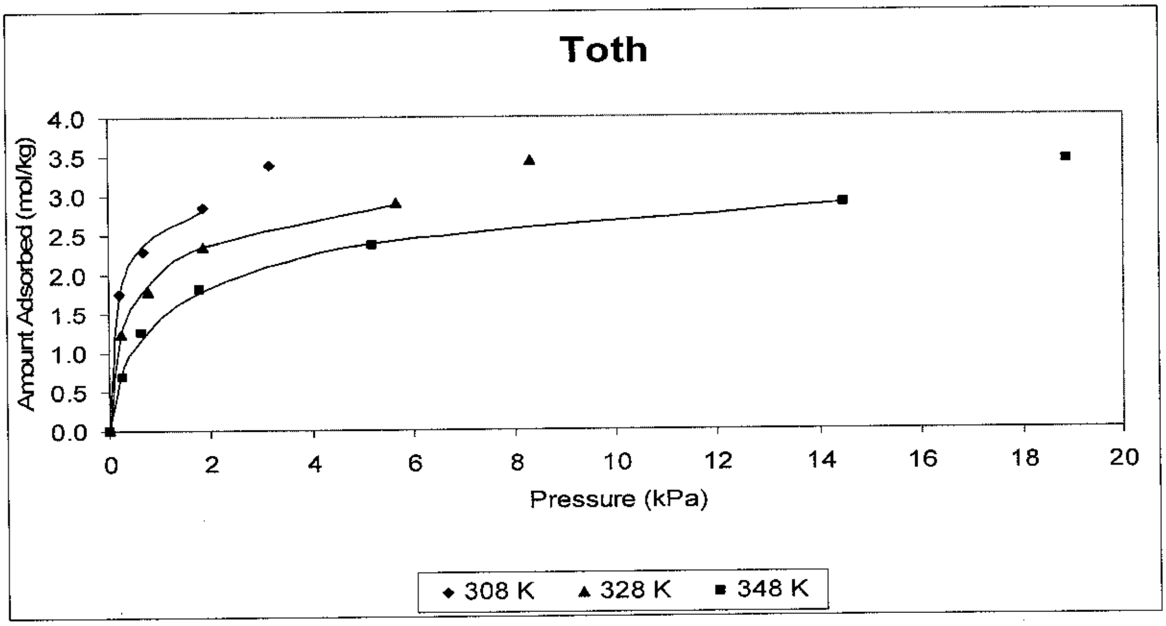

**Figure 5.6**: Adsorption isotherm correlated (omit last data) with Toth equation

Based on the optimum parameters obtained, value of t is determined for each temperature using equation [3.12]. The parameter t for each temperature is tabulated in Table 5.6. From the result, it is noticed for all temperature, the calculated t parameters are less that unity. The more parameter t deviates from unity, the more heterogeneous is the system (Do, 1998). However, for this particular case this could not be proven as the difference of parameter t for different temperature are very small or negligible.

**Table 5.6**: Calculated t parameter for each temperature using Toth equation

| **T (K)** | **t (-)** |
|---|---|
| 308 | 0.4239 |
| 328 | 0.4222 |
| 348 | 0.4206 |

### 5.2.4 Dubinin-Astakhov Isotherm

The isotherm equation of the Dubinin-Astakhov isotherm is equation [3.20]. Further explanation on derivation of this equation is described in Chapter 3.2.4. The equation requires transformation of amount of adsorbed, q (kg/mol) into the adsorbed volume, W ($cm^3/kg$). The calculation of Vapour Pressure, $P_s$ and Saturated Liquid Volume, $V_s$ were explained prior in Chapter 3.2.4. Sample calculation incorporating HBT and Lewis method is listed in Appendix B.1.1 whereas the calculated values of adsorbed volume, W, are given in B.1.2 of Appendix B. By utilizing the optimization of nonlinear regression, the value of fitted parameters, $W_0$, $\beta E_0$ and n are estimated. The results are tabulated in table 5.7 whereas the plots are presented as Figure 5.7 and Figure 5.8.

**Table 5.7:** Optimal parameters obtained by Dubinin-Astakhov isotherm

| | **$W_0$ ($cm^3/kg$)** | **$\beta E_0$ (J/mole)** | **n** | **Residual** |
|---|---|---|---|---|
| All data | 534.0748 | 9982.0489 | 1.066 | 0.6339 |
| Omit last data | 471.569 | 10500.6084 | 1.588 | 0.3377 |

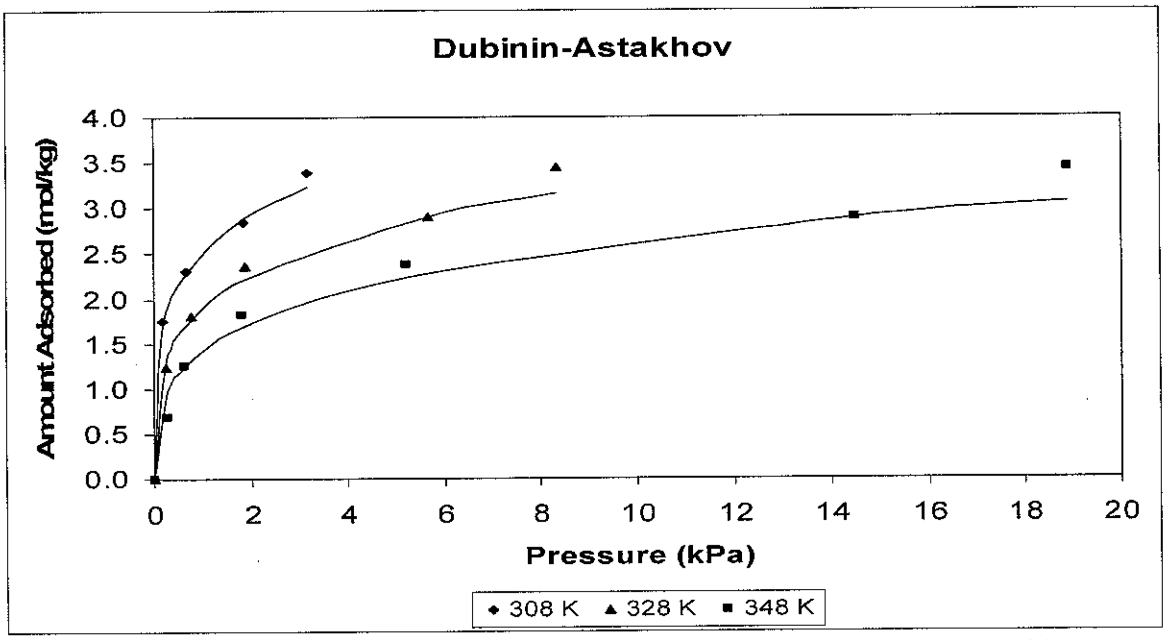

**Figure 5.7**: Adsorption isotherm correlated for all experimental data points with Dubinin-Astakhov isotherm

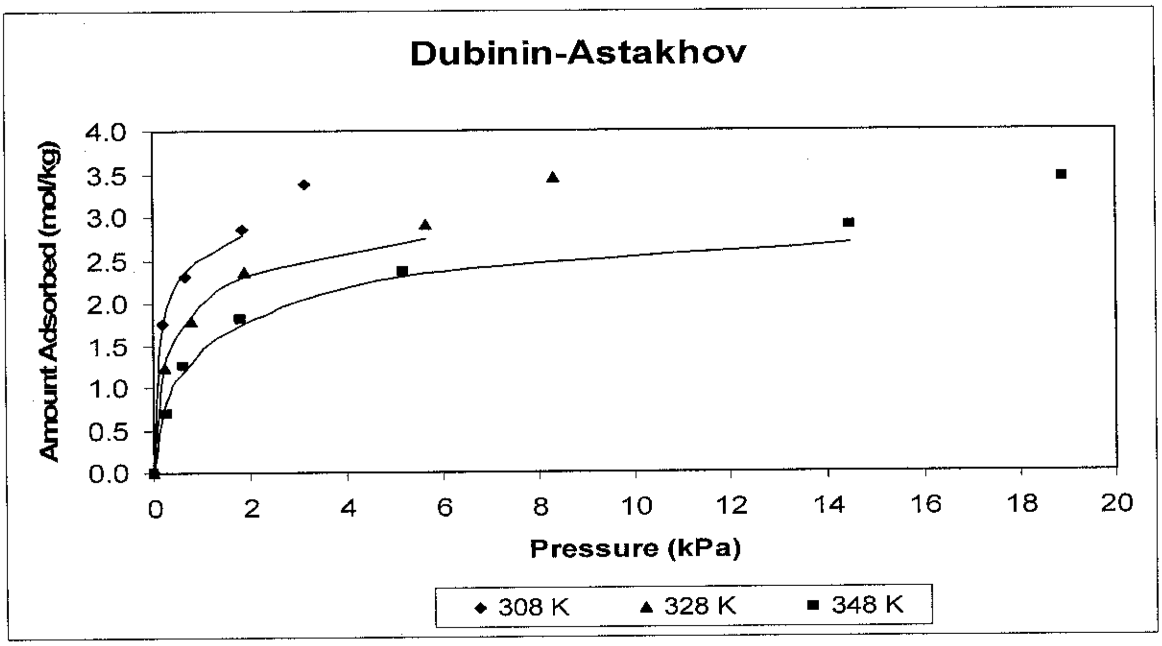

**Figure 5.8**: Adsorption isotherm correlated (omit last data) with Dubinin-Astakhov isotherm

### 5.2.5 Dubinin-Radushkevich Isotherm

The main equation used for nonlinear regression predicted by Dubinin-Radushkevich isotherm is equation [3.19]. The derivation of this equation is available in Chapter 3.2.4.

It is observed that the isotherm equation is similar to the Dubinin-Astakhov Isotherm equation except for n equals to 2 in this equation. Therefore, there are only two fitted parameters in this equation which are $W_0$ and $ßE_0$. The result of correlation using this isotherm is tabulated in Table 5.8 whereas the graphs are plotted as Figure 5.9 and Figure 5.10. It is observed that, the residual value for correlation using all experimental data is above unity indicating a quite poor fit.

**Table 5.8**: Optimal parameters obtained by Dubinin-Radushkevich isotherm

| | **$W_0$ ($cm^3$/kg)** | **$ßE_0$ (J/mole)** | **Residual** |
|---|---|---|---|
| All data | 492.1483 | 9619.9101 | 1.0099 |
| Omit last data | 452.0577 | 10445.7569 | 0.4319 |

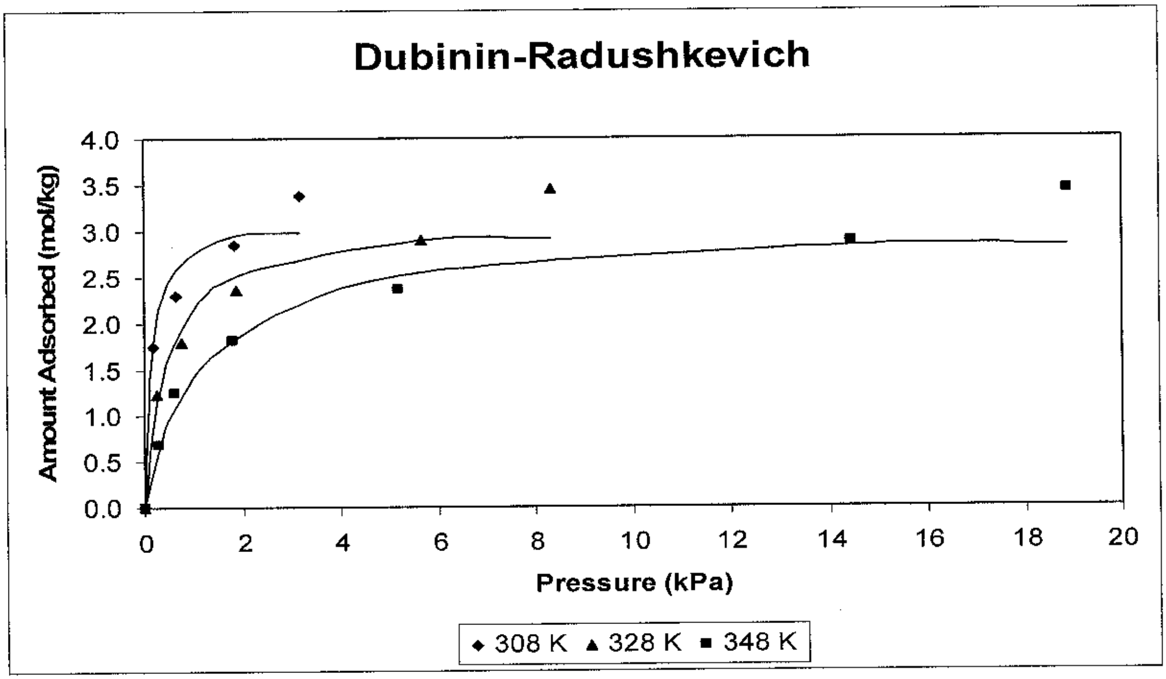

**Figure 5.9**: Adsorption isotherm correlated for all experimental data points with Dubinin-Radushkevich isotherm

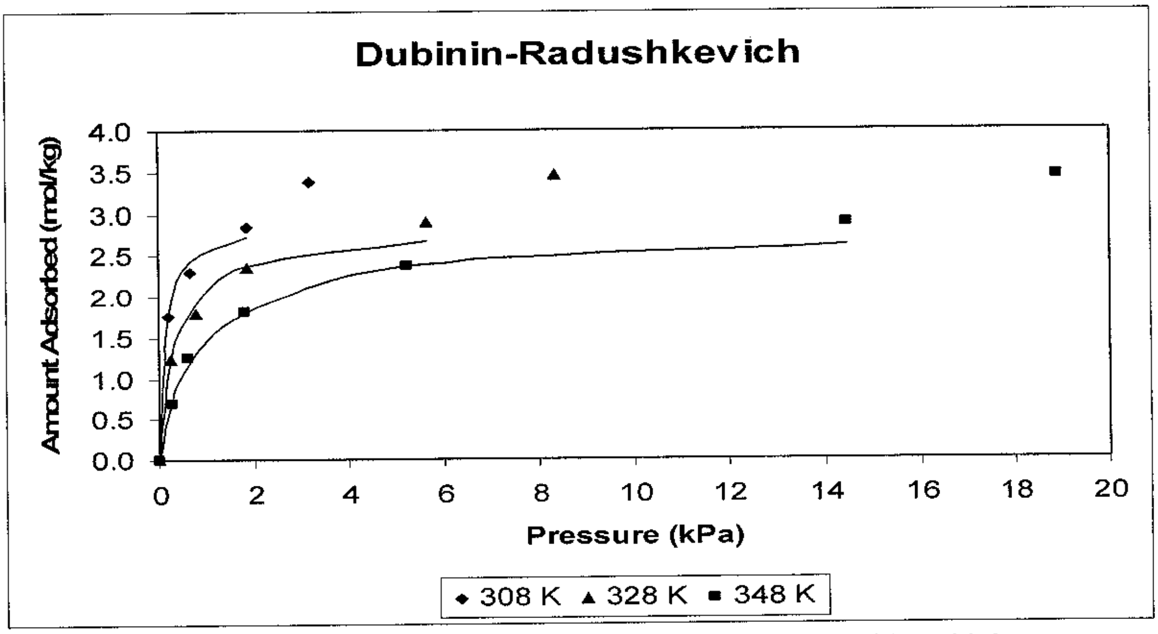

**Figure 5.10**: Adsorption isotherm correlated (omit last data) with Dubinin-Radushkevich isotherm

### 5.2.6 Comparison of Result from MATLAB and SAS Programming

Comparison study is conducted on several isotherms models of using two different methods which are the MATLAB and SAS programming. This is vital to verify and prove the effectiveness of result obtained using MATLAB as compared to SAS programming. The adsorption data used for simulation is Octane Adsorption on Activated Carbon (Mohd. Shariff, A., 1995). In this study, the isotherms models to be considered are the Dubinin-Astakhov and Dubinin-Radushkevich isotherms which are obtained by omitting the last experimental data points for all temperatures.

The comparison is presented in terms of visualization graphs and optimal parameters obtained by this two different method. The plot of graphs by Dubinin-Astakhov and Dubinin-Radushkevich isotherms are shown in Figure 5.11 and Figure 5.12 respectively. In these graphs, plots of amount adsorbed versus pressure using both approaches are represented in one graph for the ease of comparison study.

From the visualization of Figure 5.11 and Figure 5.12, it can be observed that the trend for nonlinear regressions using both MATLAB and SAS programming is very identical to each other with only slight differences. Nevertheless, through graph visualization only, one cannot predict the best approach between the two for the correlated isotherms.

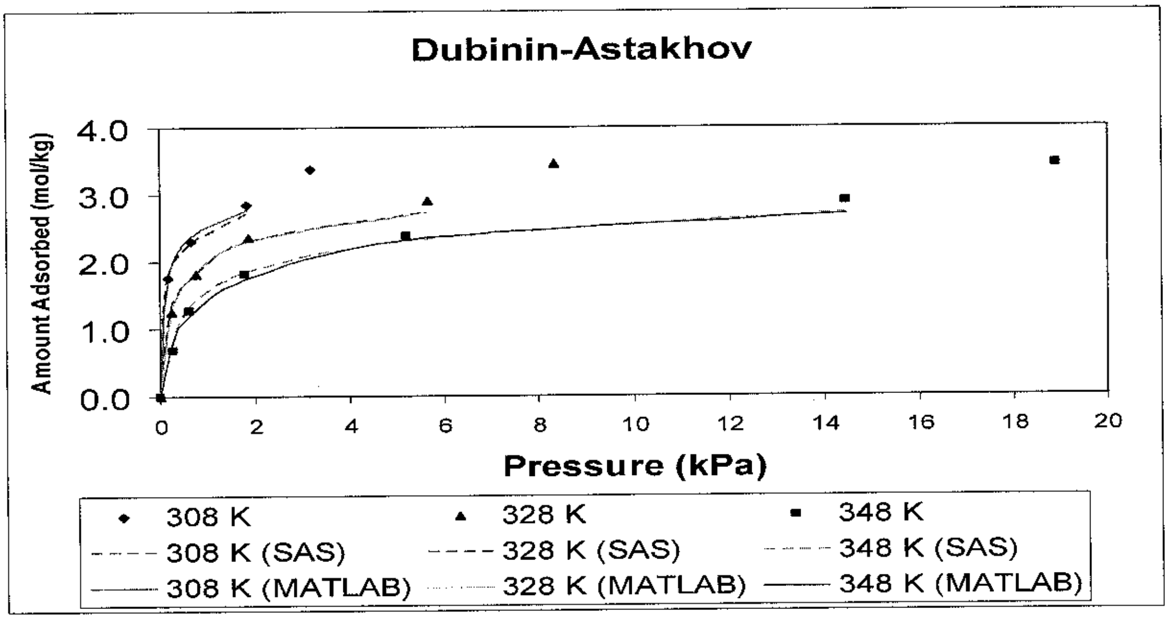

**Figure 5.11**: Octane adsorption isotherm correlated with Dubinin-Astakhov isotherm by using MATLAB and SAS programming

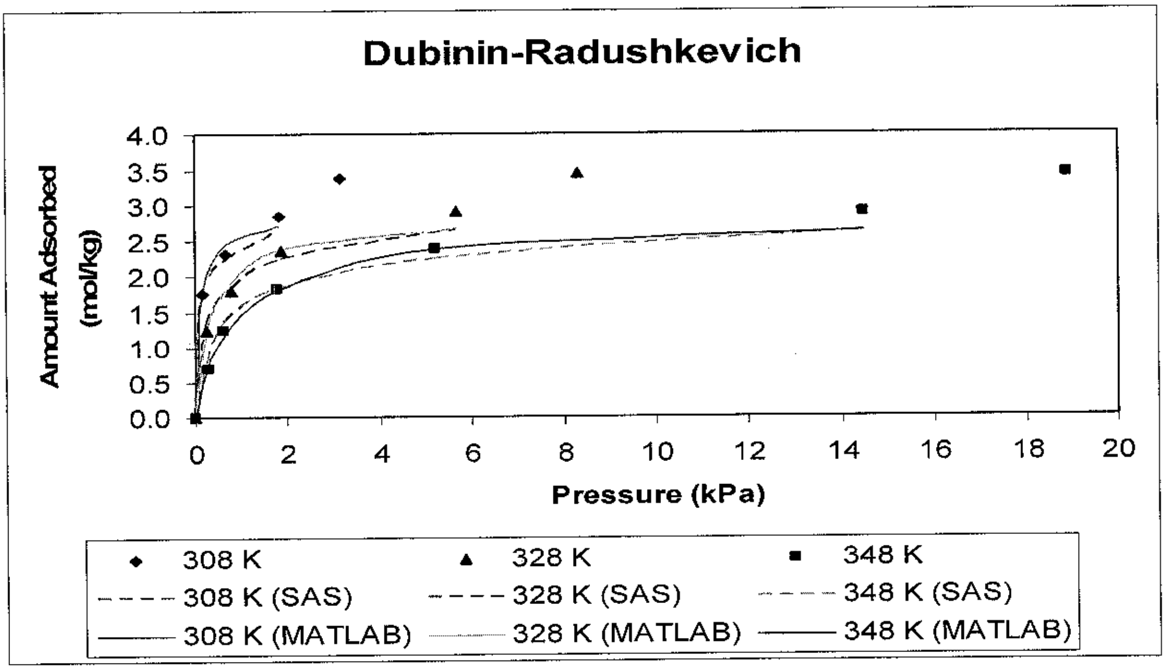

**Figure 5.12**: Octane adsorption isotherm correlated with Dubinin-Radushkevich isotherm by using MATLAB and SAS programming

The optimal parameters obtained by Dubinin-Astakhov and Dubinin-Radushkevich isotherms obtained are tabulated in Table 5.9 for the former and Table 5.10 for the latter. The parameters include the unknown parameters and calculated residuals for each isotherm which are obtained using nonlinear regression. By comparing the residuals, the best approach for each correlated isotherm models can be determined.

**Table 5.9**: Optimal parameters obtained by Dubinin-Astakhov isotherm obtained using MATLAB and SAS programming

| **Programming** | **$W_0$ ($cm^3/kg$)** | **$\beta E_0$ (J/mole)** | **n** | **Residual** |
|---|---|---|---|---|
| SAS | 502.1312 | 9785.6326 | 1.5525 | 0.3043 |
| MATLAB | 471.5690 | 10500.6084 | 1.5880 | 0.3378 |

**Table 5.10**: Optimal parameters obtained by Dubinin-Radushkevich isotherm obtained using MATLAB and SAS programming

| **Programming** | **$W_0$ ($cm^3/kg$)** | **$\beta E_0$ (J/mole)** | **Residual** |
|---|---|---|---|
| SAS | 497.5587 | 9455.2504 | 0.50694 |
| MATLAB | 452.0577 | 10445.7569 | 0.43200 |

Inspection of optimal parameters for Dubinin-Astakhov isotherm for both MATLAB and SAS programming shows a slight difference. For instance, the value of n for SAS programming is 1.5525 whereas for MATLAB programming, the value is 1.5880. This difference may incur due to different approach used by both programming. SAS programming use least-squares criterion while MATLAB programming use Newton-Raphson for nonlinear regression purposes. The calculated residuals for SAS programming show smaller value as compared to MATLAB programming. Thus, it can be concluded that SAS programming is a better approach for predicting octane adsorption isotherm correlated with Dubinin-Astakhov isotherm.

For isotherms correlated with Dubinin-Radushkevich, the graph obtained shows identical trend for nonlinear regressions using both MATLAB and SAS programming. It is observed that the plot differs slightly at the middle range of temperature and approach towards almost the same value at higher temperature. Since it is difficult to interpret the differences between these two approaches using graph, inspection in terms of optimal parameters obtained is conducted.

According to Table 5.10, the optimal parameters of adsorption isotherm correlation using Dubinin-Radushkevich isotherm for both MATLAB and SAS programming show slight differences. For example, the value of $W_0$ for SAS programming is 497.5587 $cm^3/kg$ whereas for MATLAB programming, the value is 452.0577 $cm^3/kg$. Meanwhile, the calculated residuals for SAS programming show higher value as compared to MATLAB programming. Thus, it can be concluded that MATLAB programming is a better approach for predicting octane adsorption isotherm correlated with Dubinin-Radushkevich isotherm.

As stated earlier, this difference may incur due to different approach used by both programming. MATLAB programming employed Newton-Raphson procedure meanwhile SAS programming used the least-square criterion by incorporating Marquart method. According to Steven and Raymond, (1998), there is no general convergence criterion for Newton-Raphson method. For both programming method, their convergence depends on the nature of the function and the accuracy of the initial guess.

## 5.3 Concluding Remarks

### 5.3.1 Comparison of the Different Isotherms

The result of unknown parameters obtained for each isotherm showed significant differences between regression performed by considering all experimental data with that omitting the last data point for all temperatures. Overall, the values of residual for all the selected isotherms give satisfactory fit to the experimental data. Nevertheless, results show that the residual of regression which neglect the last data point is smaller as compared to the one which take all data into consideration. This indicates that a better fit of the correlation to the adsorption data can be obtained by neglecting the saturated data point.

Finally, it may be concluded that Sips equation is the best correlation for the representation of octane adsorption on activated carbon for the whole temperature and pressure. Sips equation describes well the type 1 adsorption isotherm shape, which a typical of adsorption in microporous solids (Do, 1998). This equation gives the smallest value of residual, thus is the best fit of the adsorption data. The residual of each equation is as tabulated in Table 5.11.

**Table 5.11:** Residual for every isotherm

| **Isotherm** | **Adsorption Data** | **Residual** |
|---|---|---|
| Langmuir | All data | 0.8213 |
| | Omit last data | 0.3754 |
| Sips | All data | 0.4313 |
| | Omit last data | 0.1282 |
| Toth | All data | 0.4974 |
| | Omit last data | 0.1730 |
| Dubinin-Astakhov | All data | 0.6339 |
| | Omit last data | 0.3377 |
| Dubinin-Radushkevich | All data | 1.0099 |
| | Omit last data | 0.4319 |

### 5.3.2 Comparison of Result from MATLAB and SAS Programming

From the comparison study of conducted on several isotherms models of using two different approaches which are MATLAB and SAS programming, the best method for obtaining nonlinear regression is determined. It can be observed that the trend for both methods is very identical to each other with only slight differences. It can be concluded that SAS programming is a better approach for predicting octane adsorption isotherm correlated with Dubinin-Astakhov isotherm. On the other hand, MATLAB programming is a better approach for predicting octane adsorption isotherm correlated with Dubinin-Radushkevich isotherm. This is based on the smaller residuals obtained indicating a better fit. However, further investigation by using other set of adsorption data need to be conducted to verify these findings.

# CHAPTER 6

# CONCLUSIONS AND RECOMMENDATIONS

## 6.1 Conclusions

In this study, five isotherms have been selected to fit and correlate the adsorption data of octane adsorption on activated carbon. The selected isotherms are Langmuir, Sips (Langmuir-Freundlich), Toth, Dubinin-Radushkevich and Dubinin-Astakhov isotherms. These isotherms are all those incorporating temperature dependence and suitable for Type 1 adsorption isotherm. This is crucial as this study focused on correlation of isotherm which covers wide range of temperature and pressure.

MATLAB software is chosen for the nonlinear regression of adsorption data based on its easy accessibility and capabilities. The published data of pure octane adsorption on activated carbon at 308 K, 328 K and 348 K are used due to its relevance to the study which focused on single component adsorption for various temperature and pressure.

There is no single adsorption isotherm model that would accurately correlate the octane isotherm data over the whole range of temperature and pressure. Comparison study is conducted based on the result on different adsorption isotherms to check how well the data is fitted. It may be concluded that Sips equation is the best correlation for the representation of octane adsorption on activated carbon for the whole temperature and pressure considered in this study. This equation give the smallest value of residual, thus was the best fit of the adsorption data.

Overall, the values of residual for all the selected isotherms give satisfactory fit to the experimental data. Nevertheless, results show that the residual of regression which neglect the last data point was smaller as compared to the one which took all data into consideration. This indicates that a better fit of the correlation to the adsorption data could be obtained by neglecting the saturated data point.

Comparison study on two methods namely MATLAB and SAS programming shows almost identical results with slight differences. The difference is due to the difference in the statistical method used for the regression analysis. Based on the residuals, SAS programming is a better method for prediction of octane adsorption isotherm correlated with Dubinin-Astakhov isotherm whereas MATLAB programming is a better approach for correlation of octane adsorption isotherm with Dubinin-Radushkevich isotherm.

From this study, it can be concluded the nonlinear regression using MATLAB programming can provide better fit for adsorption isotherm of hydrocarbon adsorption. This method is capable for fitting adsorption data which covers wide range of temperature and pressure. The outcome and findings of this project is not only useful for preliminary studies of adsorption isotherm, but it also plays important role in the adsorption system design for industrial application.

## 6.2 Recommendations for Future Work

The regression analysis on adsorption isotherm correlation has been conducted for octane adsorption on activated carbon. Since the nonlinear regression was carried out on only one set of published data, it is recommended that further study need to be conducted using other set of adsorption data in order to justify on the effectiveness of method and to verify the findings.

The findings of project prove that the optimization using MATLAB programming method can be used to correlate various adsorption isotherms. However, the project focused only on Type 1 adsorption isotherm. Therefore, to prove that the method could be used widely, it is proposed to test this method on other type of adsorption isotherm.

Result of the project signifies values fit satisfactorily for all selected adsorption isotherms at 303 K, 328 K and 348 K. In the real process, a low pressure steam at $110^0$C or $115^0$C would be used. The correlation determined in this study can be used to predict the adsorption equilibria at these higher temperatures by extrapolation. To confirm and prove the predicted results, regression analysis needs to be conducted on adsorption data which covers wider range of temperature.

# CHAPTER 7

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# APPENDIX A

## MODEL PARAMETERS,
## PHYSICAL PROPERTY DATA
## AND
## ADSORPTION DATA

## A.1 Model Parameters for Adsorption Isotherm

Source: Reid et. al., (1987).

### Table A.1.1: Parameters for Antoine equation of Octane

| Antoine Equation Constants | |
|---|---|
| A | 7.00811 |
| B | 3113.08 |
| C | -64 |

### Table A.1.2: Parameters for Hankinson-Brobst-Thomson (HBT)

| HBT Constants | |
|---|---|
| a | -1.52816 |
| b | 1.43907 |
| c | -0.81446 |
| d | 0.190454 |
| e | -0.296123 |
| f | 0.386914 |
| g | -0.0427258 |
| h | -0.0480645 |

| HBT Parameters | |
|---|---|
| $\omega_{SRK}$ (-) | 0.3998 |
| V* (cm3/mol) | 490.4 |
| $T_C$ (K) | 568.83 |

## A.2 Adsorption data for Adsorption Equilibria of Octane on Activated Carbon

### Table A.2.1 Adsorption equilibria of octane on activated carbon at 308K

| Pressure (kPa) | Amount adsorbed (mol/kg) |
|---|---|
| 0.1856 | 1.7574 |
| 0.6599 | 2.3038 |
| 1.8353 | 2.8455 |
| 3.1551 | 3.3863 |

### Table A.2.2 Adsorption equilibria of octane on activated carbon at 328K

| Pressure (kPa) | Amount adsorbed (mol/kg) |
|---|---|
| 0.2416 | 1.2413 |
| 0.7686 | 1.8029 |
| 1.8666 | 2.3608 |
| 5.6437 | 2.9013 |
| 8.3228 | 3.4490 |

### Table A.2.3 Adsorption equilibria of octane on activated carbon at 348K

| Pressure (kPa) | Amount adsorbed (mol/kg) |
|---|---|
| 0.2796 | 0.6852 |
| 0.6291 | 1.2555 |
| 1.7940 | 1.8207 |
| 5.1955 | 2.3722 |
| 14.4682 | 2.8874 |
| 18.8949 | 3.4326 |

# APPENDIX B

## CALCULATION OF THE ADSORPTION ISOTHERM

## B.1 Calculation of Adsorbed Volume for Octane Adsorption Equilibria

### B.1.1 Sample Calculation Adsorbed Volume, W ($cm^3/kg$) for Octane Adsorption Equilibria using Lewis' Method

Calculation of adsorption equilibria for octane on activated carbon at 308 K
Pressure, P = $1.86 X 10^{-4}$ MPa
Amount adsorbed, q = 1.7574 mol/kg

**1. Calculation of reduced temperature**

$$T = \frac{B}{A - \ln P} - C$$

substitute
A = 7.00811
B = 3113.08
C = -64
P = $1.86 X 10^{-4}$

$\therefore$ T = 263.5561 K

$$T_R = \frac{T}{T_C}$$

substitute
T = 263.5561 K
$T_C$ = 568.83 K

$\therefore$ Reduced temperature, $T_R$ = <u>0.4633</u>

**2. Calculation of saturated molar volume, $V_m$**

for $0.25 < T_R < 0.95$

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

substitute
$T_R$ = 0.4633
a = -1.52816
b = 1.43907
c = -0.81446
d = 0.190454

$\therefore V_R^{(0)} = 0.3545$

for $0.25 < T_R < 1.0$

$$V_R^{\delta} = \frac{\left(e + fT_R + gT_R^{2} + hT_R^{3}\right)}{\left(T_R - 1.00001\right)}$$

substitute

$T_R = 0.4633$
$e = -0.296123$
$f = 0.386914$
$g = -0.0427258$
$h = -0.0480645$

$V_R^{(\delta)} = 0.2437$

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

substitute

$V^* = 490.4$
$V_R^{(0)} = 0.3545$
$\omega_{SRK} = 0.3998$
$V_R^{(\delta)} = 0.2437$

$\therefore$ Saturated molar volume, $V_m$ = <u>156.8914 cm$^3$/mol</u>

### 3. Calculation of adsorbed volume, W

$$W = \frac{q.MW}{\rho_A} = qV_m$$

substitute

$q = 1.7574$
$Vm = 156.8914$

$\therefore$ Adsorbed volume, W = <u>275.7210 cm$^3$/kg</u>

### B.1.2 Calculation of Adsorbed Volume for Octane Adsorption Equilibria using Lewis' Method

| Experimental Data | | | Calculated Parameters | | | | | |
|---|---|---|---|---|---|---|---|---|
| T | P | q | T | $T_R$ | $V_R^{(0)}$ | $V_R^{(\infty)}$ | $V_m$ | W |
| (K) | (Mpa) | (mol/kg) | (K) | (-) | (-) | (-) | ($cm^3$/mol) | ($cm^3$/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 | 3.449 | 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 |

## B.2 Calculation of Residuals

### B.2.1 Calculation of Residuals for Isotherms Comparison of Octane Adsorption Equilibria (for all experimental data)

| Experimental Data | | Langmuir | | Sips | | Toth | | Dubinin-Astakhov | | Dubinin-Radushkevich | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| T (K) | q (mol/kg) | q (mol/kg) | $(\Delta q)^2$ | q (mol/kg) | $(\Delta q)^2$ | Q (mol/kg) | $(\Delta q)^2$ | q (mol/kg) | $(\Delta q)^2$ | q (mol/kg) | $(\Delta q)^2$ |
| 308 | 1.7574 | 1.5643 | 0.0373 | 1.7004 | 0.0032 | 1.5587 | 0.0395 | 1.6671 | 0.0082 | 1.7702 | 0.0002 |
| | 2.3038 | 2.5395 | 0.0556 | 2.354 | 0.0025 | 2.3618 | 0.0034 | 2.2825 | 0.0005 | 2.5812 | 0.0770 |
| | 2.8455 | 3.0098 | 0.0270 | 2.9623 | 0.0136 | 2.9902 | 0.0209 | 2.8923 | 0.0022 | 2.9531 | 0.0116 |
| | 3.3863 | 3.1467 | 0.0574 | 3.3028 | 0.0070 | 3.2906 | 0.0092 | 3.2311 | 0.0241 | 2.9817 | 0.1637 |
| 328 | 1.2413 | 0.9993 | 0.0586 | 1.2501 | 0.0001 | 1.1285 | 0.0127 | 1.2904 | 0.0024 | 1.1387 | 0.0105 |
| | 1.8029 | 1.9241 | 0.0147 | 1.7972 | 0.0000 | 1.8050 | 0.0000 | 1.7659 | 0.0014 | 1.9406 | 0.0190 |
| | 2.3608 | 2.564 | 0.0413 | 2.312 | 0.0024 | 2.3711 | 0.0001 | 2.2242 | 0.0187 | 2.5173 | 0.0245 |
| | 2.9013 | 3.0373 | 0.0185 | 3.0462 | 0.0210 | 3.0451 | 0.0207 | 2.9074 | 0.0000 | 2.9032 | 0.0000 |
| | 3.449 | 3.1292 | 0.1023 | 3.3192 | 0.0168 | 3.2594 | 0.0360 | 3.1538 | 0.0871 | 2.9087 | 0.2919 |
| 348 | 0.6852 | 0.5718 | 0.0129 | 0.8709 | 0.0345 | 0.7707 | 0.0073 | 0.9770 | 0.0851 | 0.6186 | 0.0044 |
| | 1.2555 | 1.0589 | 0.0387 | 1.1776 | 0.0061 | 1.1572 | 0.0097 | 1.2412 | 0.0002 | 1.0700 | 0.0344 |
| | 1.8207 | 1.8995 | 0.0062 | 1.6946 | 0.0159 | 1.7690 | 0.0027 | 1.6760 | 0.0209 | 1.8162 | 0.0000 |
| | 2.3722 | 2.6409 | 0.0722 | 2.3602 | 0.0001 | 2.4449 | 0.0053 | 2.2411 | 0.0172 | 2.5243 | 0.0231 |
| | 2.8874 | 3.0422 | 0.0240 | 3.1072 | 0.0483 | 3.0632 | 0.0309 | 2.8960 | 0.0001 | 2.8398 | 0.0023 |
| | 3.4326 | 3.1041 | 0.1079 | 3.3122 | 0.0145 | 3.2109 | 0.0491 | 3.0668 | 0.1338 | 2.8349 | 0.3572 |
| | | residuals | **0.8212** | residuals | **0.4314** | Residuals | **0.4974** | residuals | **0.6339** | Residuals | **1.0099** |

### B.2.2 Calculation of Residuals for Isotherms Comparison of Octane Adsorption Equilibria (neglecting the last data)

| Experimental Data | | Langmuir | Sips | Toth | Dubinin-Astakhov | Dubinin-Radushkevich | | Dubinin-Astakhov | | Dubinin-Radushkevich | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| T (K) | q (mol/kg) | q (mol/kg) | $(\Delta q)^2$ | q (mol/kg) | $(\Delta q)^2$ | q (mol/kg) | $(\Delta q)^2$ | q (mol/kg) | $(\Delta q)^2$ | q (mol/kg) | $(\Delta q)^2$ |
| 308 | 1.7574 | 1.6778 | 0.0063 | 1.7125 | 0.0020 | 1.7005 | 0.0032 | 1.7194 | 0.0014 | 1.7736 | 0.0003 |
| | 2.3038 | 2.4469 | 0.0205 | 2.3634 | 0.0036 | 2.3618 | 0.0034 | 2.3690 | 0.0043 | 2.4349 | 0.0172 |
| | 2.8455 | 2.7646 | 0.0065 | 2.8092 | 0.0013 | 2.8198 | 0.0007 | 2.7743 | 0.0051 | 2.7214 | 0.0154 |
| 328 | 1.2413 | 1.1140 | 0.0162 | 1.2280 | 0.0002 | 1.2308 | 0.0001 | 1.2461 | 0.0000 | 1.2193 | 0.0005 |
| | 1.8029 | 1.9510 | 0.0219 | 1.8628 | 0.0036 | 1.8748 | 0.0052 | 1.8408 | 0.0014 | 1.9109 | 0.0117 |
| | 2.3608 | 2.4468 | 0.0074 | 2.3545 | 0.0000 | 2.3609 | 0.0000 | 2.3106 | 0.0025 | 2.3766 | 0.0002 |
| | 2.9013 | 2.7774 | 0.0154 | 2.8679 | 0.0011 | 2.8802 | 0.0004 | 2.7424 | 0.0252 | 2.6718 | 0.0527 |
| 348 | 0.6852 | 0.6468 | 0.0015 | 0.7820 | 0.0094 | 0.7764 | 0.0083 | 0.8351 | 0.0225 | 0.7264 | 0.0017 |
| | 1.2555 | 1.1439 | 0.0125 | 1.1624 | 0.0087 | 1.1751 | 0.0065 | 1.1884 | 0.0045 | 1.1540 | 0.0103 |
| | 1.8207 | 1.9042 | 0.0070 | 1.7676 | 0.0028 | 1.7793 | 0.0017 | 1.7399 | 0.0065 | 1.8020 | 0.0003 |
| | 2.3722 | 2.4892 | 0.0137 | 2.3975 | 0.0006 | 2.3923 | 0.0004 | 2.3169 | 0.0031 | 2.3737 | 0.0000 |
| | 2.8874 | 2.7776 | 0.0121 | 2.8945 | 0.0001 | 2.8936 | 0.0000 | 2.6937 | 0.0375 | 2.6113 | 0.0762 |
| | | residuals | **0.3754** | residuals | **0.1826** | residuals | **0.1730** | residuals | **0.3377** | residuals | **0.4319** |

### B.2.3 Calculation of Residuals for MATLAB and SAS programming Comparison of Octane Adsorption Equilibria (neglecting the last data)

| Experimental Data | | MATLAB programming | | | | SAS programming | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Dubinin-Astakhov | | Dubinin-Radushkevich | | Dubinin-Astakhov | | Dubinin-Radushkevich | |
| T (K) | q (mol/kg) | q (mol/kg) | $(\Delta q)^2$ | q (mol/kg) | $(\Delta q)^2$ | q (mol/kg) | $(\Delta q)^2$ | q (mol/kg) | $(\Delta q)^2$ |
| 308 | 1.7574 | 1.7194 | 0.0014 | 1.7736 | 0.0003 | 1.7753 | 0.0003 | 1.7827 | 0.0006 |
| | 2.3038 | 2.3690 | 0.0043 | 2.4349 | 0.0172 | 2.2574 | 0.0022 | 2.2151 | 0.0079 |
| | 2.8455 | 2.7743 | 0.0051 | 2.7214 | 0.0154 | 2.7090 | 0.0186 | 2.6209 | 0.0505 |
| 328 | 1.2413 | 1.2461 | 0.0000 | 1.2193 | 0.0005 | 1.2942 | 0.0028 | 1.3406 | 0.0099 |
| | 1.8029 | 1.8408 | 0.0014 | 1.9109 | 0.0117 | 1.8119 | 0.0001 | 1.8120 | 0.0001 |
| | 2.3608 | 2.3106 | 0.0025 | 2.3766 | 0.0002 | 2.3009 | 0.0036 | 2.2508 | 0.0121 |
| | 2.9013 | 2.7424 | 0.0252 | 2.6718 | 0.0527 | 2.7426 | 0.0252 | 2.6489 | 0.0637 |
| 348 | 0.6852 | 0.8351 | 0.0225 | 0.7264 | 0.0017 | 0.7499 | 0.0042 | 0.8242 | 0.0193 |
| | 1.2555 | 1.1884 | 0.0045 | 1.1540 | 0.0103 | 1.3054 | 0.0025 | 1.3488 | 0.0087 |
| | 1.8207 | 1.7399 | 0.0065 | 1.8020 | 0.0003 | 1.8245 | 0.0000 | 1.8206 | 0.0000 |
| | 2.3722 | 2.3169 | 0.0031 | 2.3737 | 0.0000 | 2.3039 | 0.0047 | 2.2493 | 0.0151 |
| | 2.8874 | 2.6937 | 0.0375 | 2.6113 | 0.0762 | 2.7185 | 0.0285 | 2.6244 | 0.0692 |
| | | residuals | **0.3377** | residuals | **0.4319** | residuals | **0.3043** | residuals | **0.5069** |

# APPENDIX C

## COMPUTER PROGRAMS

## C.1 Sample of MATLAB Programming

```
%       This program is used to determine the parameters of Dubinin-Radushkevich
%       Isotherm to fit the adsorption data of adsorption isotherm of
%       Octane on Activated Carbon
%       Based on the parameters, this program is used to calculate the residuals and
%       plot the best fit line for all temperatures
%
%       ISOTHERM EXPRESSIONS:
%       1.      Dubinin-Radushkevich
%               q       = qs*exp[-(A/BE0)^2]
%               A       = RT*log(P0/P)
%               qs      = W0/vM(T)
%               The parameter array:
%               a(1)    = W0
%               a(2)    = BE0
%       where;
%       q is the amount adsorbed in mol/kg
%       qs is the saturation amount adsorbed
%       R is the gas constant
%       T is the temperature
%       P is the pressure in kPa
%       E0 is the characteristic energy of adsorption
%       B is the scaling factor
%       P0 is the vapor pressure
%       W0 is the specified micropore volume
%       vM is the liquid molar volume
        clear all
        clc
        clf
        global T0 T
        global P0 vM
        fdata           = {'DR'};

 % USER SUPPLY SECTION
        k_selection     = 1;

        T0              = 308;
        T               = [308 328 348];
        P0              = [3.1815       8.3637   19.189];
        vM              = [156.8914 160.0036 163.1176 157.4823 160.4288 163.1747  167.4221
        157.8213 159.8728 163.0410 167.0653 172.0569];
        newpath = 'C:\data';
        fname           = {'octane2_308.dat' 'octane2_328.dat' 'octane2_348.dat'};
        tol             = 1e-5;
        max             = 1000;

        f               = fdata{k_selection};
        path(path,newpath)
```

```
        for i=1:length(T)
        eval(['load ' fname{i}]);
        n1                          = find(fname{i}=='.');
        if ~isempty(n1);
        n2                          = length(fname{i});
        fname{i}(n1:n2)  = [];
        end;
        p{i}                        = eval([fname{i} '(:,1)']);
        cmu{i}           = eval([fname{i} '(:,2)']);
        end

        switch f
        case 'DR'
        a                = input('Enter the initial guess [W0(cm3/kg)  BE0(J/mole)] = ');
        end

% INITIAL GUESS BEFORE THE OPTIMIZATION IS STARTED
        k        = 1;
        while k
        guesst(f,a,p,cmu);
        iyes     = input('Do you wish to further change the guessing parameters? = ','s');
        if iyes=='y' | iyes=='Y' | iyes=='yes' | iyes=='Yes';
        switch f
        case 'DR'
        a        = input('Enter the initial guess [W0(cm3/kg)  BE0(J/mole)] = ');
        end
        else
        k        = 0;
        end
        end

% START THE OPTIMIZATION & KEEP CHECK ON THE CPUTIME
        start_time = cputime;
        k        = 1;

% START THE OPTIMIZATION LOOP
        options(1)       = 0;
        options(2)       = tol;
        options(3)       = tol;
        options(14)      = max;

% CALL THE OPTIMIZATION ROUTINE FMINS
        [a_optimal,options]        = fmins('residt',a,options,[],f,p,cmu);

% PLOTTING THE RESULTS
        figure(2)
        for i=1:length(T)
                cmu1{i} = feval(f,a_optimal,p{i},i);
                plot(p{i},cmu{i},'o',p{i},cmu1{i},'k-')
```

```
        hold on
        end
        xlabel('Pressure');
        ylabel('Amount adsorbed');
        title([f ' isotherm']);
        grid;

% DISPLAY THE RESULTS ON COMMAND WINDOWS
        disp(' RESULTS');
        disp(['The reference temperature T0 = ', num2str( T0 ) ]);
        switch f
        case 'DR'
                disp(['W0          = 'num2str(a_optimal(1)) ]);
                disp(['BE0         = 'num2str(a_optimal(2)) ]);
        end

% EVALUATION OF THE RESIDUAL
        Residual          = sqrt(residt(a_optimal,f,p,cmu));
        cpu                       = cputime - start_time;

% THIS IS THE CPU TIME
        disp(['Residual = ',num2str(Residual),';
        Number of iteration       = ',num2str(options(10)),';
        CPU                       = ',num2str(cpu),' sec']);

%--------------------------------
% THIS IS THE END OF THE PROGRAM
%--------------------------------
```