Liquid Adsorption Model of Phenol Via Activated Carbon

By

Nursaaidah binti Hassim

Dissertation submitted in partial fulfillment of
the requirements for the
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Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

(Dr. Azmi Mohd, Shariff)
Main Supervisor

Universiti Teknologi PETRONAS
Tronoh, Perak
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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.

Nursaaidah binti Hassim

ABSTRACT

Every industrial process create products and waste streams that must be treated before they can be marketed (products) or safely discharged (waste). Phenol is one of the compounds found in petrochemical wastewater that have attracted public attention due to its possible link with health even at low concentration. Adsorption via activated carbon is known as one of the most efficient methods for removal of petrochemical waste from aqueous solution.

Conventionally, pilot scale evaluations on adsorption unit require huge investment; provide limited knowledge on the adsorption behavior and exposes testing personnel to hazardous environment during evaluation. Hence, prediction using adsorption mathematical model is a better option.

The objectives of this project are to develop a mathematical model which represents the behavior of the adiabatic-constant-velocity (ACV) adsorption process and to simulate dynamic concentration and temperature profiles of phenol-activated carbon adsorption using stage method and MATLAB.

The adsorption mathematical model was developed by using Freundlich isotherm based on the differential mass and heat balances for adiabatic adsorption column. Numerical method of lines (NUMOL) serves as the core mathematical solution for stage method. Equilibrium data from Abdul Hameed REHAN, Pakistan Institute of Nuclear Science and Technology (1998) were used to simulate the ACV model.

Simulation results on the concentration and temperature using the ACV model give reasonably not very accurate predictions when compared to the predicted breakthrough curves of adsorption of phenol (Frank L.Slejko, 1985). The possibilities cause of the errors was discussed. It is observed that at high temperature, the adsorbed loading tends to be lowered and mass transfer is impeded. Lastly, the simulation results show that the prediction of concentration is more sensitive to mesh size than temperature predictions.

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ABBREVIATIONS AND NOMENCLATURES

ρ_b	Bulk density
n	Isotherm constant
ε	Void fraction
v	Interstitial fluid velocity
u	Superficial velocity
T	Temperature
z	Cartesian flow direction
q	Concentration in solid phase
c	Fluid phase concentration
k	Isotherm constant
h_f	Fluid phase enthalpy
u_f	Fluid phase internal energy
u_s	Adsorbate phase internal energy

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

1.1.1 History of Adsorption

Adsorption is widely applied in many instances which are interesting both historically and contemporarily. In Sanskrit manuscripts 2 millennia ago (Weber 1984), the use of charcoal to remove odor and taste from water was recorded. Modern industrial applications began with Lowitz's discovery on decolorizing effect of charcoal on solutions (Seader and Henley, 1999). In 1900, Von Ostrejko's invention has manufactured activated carbon and made possible the Lowitz's discovery. Sorption is a general term introduced by J.W. McBain includes selective transfer to the surface, and for into the bulk of liquid. In a general sorption process, the sorbed solutes are referred to as sorbate & the sorbing agent is the sorbent (Seader and Henley, 1999). Early applications of adsorption involved only purification, for e.g.: adsorption with charred wood to improve the taste of water has been known for at least five centuries. The commercial scale bulk separation of liquid mixtures also began in 1960s, following the invention by Broughton & Greshold of the simulated moving bed for adsorptive separation.

1.1.2 Application of Liquid Adsorption in Industry

Every industrial process create products and waste streams that must be treated before they can be marketed (products) or safely discharged (waste). There are many separation techniques can be used with varying degrees of success for the control of organic chemicals in water. These include coagulation, filtration, oxidation, aeration, ion exchange and liquid phase adsorption method. However, liquid phase adsorption system is still the most efficient method for the removal of organic pollutants from wastewater (Juang et. Al., 2000). Applications of granular and powdered activated carbon to remove toxic organics have established to be effective for water and wastewater treatment. Decolorizing and drying of petroleum fractions, for example, the petrochemical effluent (raw) by fly ash coal remarked that the adsorption dose of 3-3.5% shows significant color removal and contact period of 30-40 minutes gives optimum removal (Kapadia et al, 2000). Other application of adsorption includes decolorizing crude sugar syrup and vegetable oils. For drinking water supplies, adsorption is used to remove dissolved organics, odor, taste and color from water. Since the invention of molecular sieves by Milton (1959) was capable to separate species on the basis of molecular shape, adsorption is found to be useful not only in purifying wastewater but also for bulk separating of paraffins.

1.1.3 Phenol as the Hazardous Pollutant

Phenols are widely used for the commercial production of a wide variety of resins including phenolic resins, which are used as construction materials for automobiles and appliances, epoxy resins and adhesives, and polyamide for various applications (Fang and Chen, 1997). Phenols are very soluble in water and quite flammable and they are considered as priority pollutants since they are harmful to organisms at low concentrations with ingestion of 1 g reported to be lethal, with symptoms including muscle weakness and tremors (Toxic Substances and Disease Registry's, 1999). Many of them have been classified as hazardous pollutants because of their potential harm to human health by creating an oxygen demand in receiving waters. According to IS 2490 (Part III)-1974, the concentration of phenols in the industrial effluents should not exceed 1.0 mg/l before safe discharge into the surface of water. These limits have generally been on the basis of the total phenols present in the effluent.

The demand for removal of organic compounds including phenol has been increased by increasing the industrial wastewaters. Adsorption of phenol by different adsorbents has been investigated to find the relation between adsorption capacity and adsorbent characteristics such as surface area, and pore size distribution for separation applications in the drinking water concentration range.

Roostaei and Tezel, (2004), had studied the removal of phenol from aqueous solution by adsorption using few types of adsorbents such as silica gel, HiSiv

3000, activated alumina, activated carbon, Filtrasorb-400 and HiSiv 1000. The Langmuir-Freundlich isotherm model was the best model to describe adsorption equilibrium data of phenol on the adsorbents at 25 ^{0}C, 40 ^{0}C and 55 ^{0}C. The results showed that adsorption capacity decreased with increasing temperature. Zokorski and Faust, (1978) observed the same results on the effect of temperature to the adsorption capacity of phenol on granular activated carbon at different temperatures. Sing and Rawat, (1994), stated that the rate of adsorption of phenol by fly ash was increased as the temperature increased in the range of 30 to 50 ^{0}C. Zogorski et. Al, (1976), had concluded that the removal rate of phenol on granular activated carbon tend to increase by 21% after raising the temperature of the system from 10 to 30 ^{0}C.

1.1.4 Activated Carbon as the Practical Adsorbent

Activated carbon has found wide use in liquid and gas phase applications. In water and wastewater treatment systems, activated carbon is the most preferrable used due to its large surface area and pore volume, which allows the removal of liquid-phase contaminants, including organic compounds, heavy metal ions and colors (Hseih and Teng, 2000). The adsorption capacities of carbons for the compounds to be removed are an important cost factor in applying the adsorption treatment (Ying, 1989). The adsorption capacities are significantly affected by the pore structures of activated carbon as well as the size of adsorbate. Therefore, selecting suitable carbon adsorbent to remove specific compounds is an important criterion for the treatment process (Hseih and Teng, 2000).

In particular, granular activated carbon has been used in various areas of application such as cane sugar and dextrose decolorization, wastewater treatment (COD removal, decolorization, etc.), city and industrial water treatment (odor removal), and sodium glutamate. In some cases, powdered activated carbon (PAC) is used as it has a faster adsorption rate, it was often used in the past, but disposal and handling concerns have made granular activated carbon (GAC) a more popular alternative for most applications.

The simplest system involves a fixed bed system, in which the granular carbon remains stationary in a cylindrical tank while the water flows downward through the granular medium under the force of gravity and is removed from the bottom. With the fixed bed, the spent carbon is removed after breakthrough by shutting down and draining the tank. New or reactivated carbon is added as a new batch. The trouble associated with this replacement limits the use of this type of system to situations involving very low influent concentrations and usually relatively low flows.

1.1.5 Fixed Bed Operation System

The fixed bed, columnar configuration is the most widely used arrangement for conducting adsorption operations. In the operation of a fixed bed adsorber, a degree of separation and removal is achieved that would require many steps in a batch configuration. In fact, the columnar configuration has often been modeled as a multiple stage, batch adsorption process wherein small cross-sections of the column (akin to the theoretical plates in distillation theory) function as individual batch adsorption stages. The upper most portions of the bed are constantly being contacted by fresh feed solutions, whereas the lower portions of the bed are contacted by solution containing solute not adsorbed by the upper portion. Thus, the bed becomes fully loaded (and equilibrium with the feed) at the top of the column first and then downward. This results in the formation of an adsorption front in the column which moves downward and as it emerges from the bottom, gives raise the familiar loading curve.

The standard pilot column test can be operated in either the downflow or upflow mode. If suspended solids are a concern for the full scale operation, downflow operation with backwashing capabilities to remove filtered solids is generally the best option. In an upflow mode, the solids would likely plug most distributors. The upflow operation typically generates carbon fines and, thus, gray water.

Downflow mode is generally preferred for liquid streams, unless they are susceptible to biological fouling. The column operating characteristics (e.g., surface loading rate, detention time, vertical velocity through the bed) should be similar to those expected in the full scale system. Although upflow can give superior performances in many applications, it is not widely practiced owing to the difficulty in operating fixed bed adsorption in this mode. Most adsorbers are designed for downflow loading. Upflow operation requires a special design which carefully considers the hydraulics constraints of the operation. In addition, there are operating variables, such as residence time, which can be modified to improve the performance of a downflow system. Nevertheless, for applications where the rates of adsorption are very slow (such as in the adsorption of solutes with large molecular weights), upflow loading should be considered.

The design and theory of fixed bed adsorption systems centers on establishing the shape of the breakthrough curve and its velocity through the bed. The breakthrough curve and the influence of volumetric throughput rate on the shape of the breakthrough curve is shown in Figure 1.1.

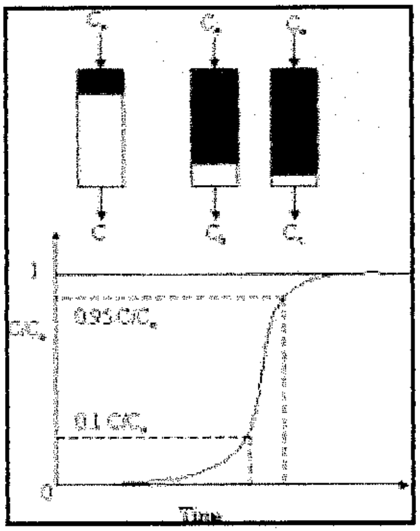


Figure 1.1: Adsorption Zone Progression in a Fixed Bed Adsorber

From figure 1.1, it was observed that the concentration of the adsorbate exists an S shaped curve in the adsorption zone with ends asymptotically approaching zero and the influent concentration C_o. The breakthrough concentration, C_b, is selected based on effluent criterion with a safety factor.

1.2 PROBLEM STATEMENT

Despite of its industrial importance, adsorption from liquid phase has been studied less extensively than adsorption in vapor phase. Until today, there was only a few numbers of published literatures on the liquid adsorption neither experimentally nor modeling .The limitation of this knowledge acquired people to do more research on liquid adsorption study but most of them preferred for the pilot tests of liquid adsorption. This kind of tests usually requires high cost and it could be reduced only if the manufacturer is given the tender of the project. Besides, the test subjected only to a specified set of operating conditions and thus provides limited knowledge on adsorption behavior. From safety factor, the personnel-in-charge also will be exposed to the hazardous during the pilot test.

With reference to the problems above, a simple liquid adsorption model will be developed to study more about the liquid phase adsorption. The study would involve the simple conditions such as using the single component adsorption isotherm by neglect some of the factors and also apply the simple adsorption system for e.g. fixed bed system. This dynamic model has the advantages compared to the pilot test in terms of cost saving and safer working environment. This initial basic model can be expanded to consider the neglected factor for more accurate prediction in adsorption process performance.

1.3 OBJECTIVE(S)

The primary objectives of the research projects are as follows:

(a) To develop a mathematical model that reasonably represents the dynamic behavior of phenol-activated carbon adsorption process

(b) To simulate dynamic concentrations and temperature profile of phenol-activated carbon adsorption process by using MATLAB

1.4 SCOPE OF STUDY

A mathematical model for fixed bed adsorption system with Freundlich isotherm as the case study was developed. The study was about the removal of phenol from aqueous solution by using activated carbon in adiabatic-constant-velocity (ACV) condition. ACV condition is generally valid when the temperature and concentration changes are small. In order to reach the equilibrium in short time, plug flow condition was applied which not considering velocity gradient.

Phenol as a single component adsorption isotherm was considered adsorbable while the solvent was assumed to be constant. In this model, the effects of concentration and temperature were evaluated and analyzed. The other factors such like mass and heat transfer resistances and axial dispersion are not considered in order to simplify the equations.

Data for simulation was taken from published literature. The results generated were compared with the theoretical predictions of typical adsorption behavior to observe its effectiveness. The associated dynamic concentration and temperature profile were simulated with MATLAB and the results area was then analyzed.

CHAPTER 2
LITERATURE REVIEW/THEORY

2.1 LITERATURE REVIEW

Much literature has been published on the use of fixed beds in use of gas adsorption. However the use of a liquid adsorption has been very little studied. Decolourization of waste water by activated carbon involves the mass transfer operation of adsorption. Adsorption uses the ability of certain substances called adsorbent, in this case activated carbon, to separate specific substances, adsorbate, from solution by concentrating these substances on their surface. The concentration difference of the adsorbate, between the surface of the adsorbent and solution causes the substance to adhere to the adsorbent's surface and thus separating it from solution. There are two types of adsorption, physical and chemical. Physical adsorption involves 'van der Waals' forces while chemical adsorption or chemisorption involves chemical interaction between the solid and adsorbate. Chemisorption uses ionic and covalent bonds in adsorption and is, therefore, a stronger method than physical adsorption.

2.1.1 Isotherm Expressions of Liquid Adsorption

Many adsorption equilibrium models have been developed to predict the types of adsorption isotherm. Liquid phase adsorption, in general, is a more complex phenomenon than gas phase adsorption. This includes the presence of solvent molecules and the formation of micelles from adsorbed molecule. For this reason, it is prudent not too attach too great a physical significance to isotherm expressions. There are various isotherm expressions used in liquid adsorption to describe the equilibrium distribution of a solute between the dissolved (liquid) and adsorbed (solid) phases. These relationships help interpret the adsorption data obtained during constant temperature tests and referred to as adsorption isotherms.

The simplest relationship between solid-phase and fluid-phase concentrations is the linear isotherm. Data that follow a linear law can be expressed by an equation similar to Henry's law.

Linear Isotherm $$q=Kc \quad \text{.....................} \quad (2.1)$$

where q is the concentration in the solid-phase, k is the isotherm constant and c is the concentration in fluid-phase. Linear isotherm is not common, but in dilute region it can be used to approximate data of many systems. Thermodynamics requires that a linear limit be approached in the Henry's law region for all isotherm equations. Henry's law limit if the fundamental test for any equilibrium relation to ensure thermodynamic consistency in the limit of low loading (LeVan, 1988).

The Langmuir isotherm equation assumes that fixed individual sites exist on the surface of the adsorbent, each of these sites being capable of adsorbing one molecule, resulting in a layer one molecule thick over the entire carbon surface. The Langmuir model also assumes that all sites adsorb the adsorbate equally.

Langmuir Isotherm $$\frac{q}{qm}=\frac{bc}{1+bc} \quad \text{...........} \quad (2.2)$$

The Fruendlich isotherm equation assumes that the adsorbent has a heterogeneous surface composed of adsorption sites with different adsorption potentials. This equation assumes that each class of adsorption site adsorbs molecules, as in the Langmuir Equation.

Freundlich Isotherm $$q=Kc^{1/n} \quad \text{............} \quad (2.3)$$

where

q: adsorption capacity (mg/g)

K: Freundlich constant (mg/g)(l/mg)$^{1/n}$

c: concentration of solute remaining in solution after adsorption is complete (at equilibrium (mg/l)

$1/n$: Freundlich constant (dimensionless)

K, n = constants that must be determined for each solute, carbon type, and temperature.

Langmuir-Freundlich Isotherm

$$\frac{q}{q_m} = \frac{bc^{1/n}}{1+bc^{1/n}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2.4)$$

The Brunauer, Emmett, and Teller (BET) equation also assumes the adsorbent surface is composed of fixed individual sites. However, the BET equation assumes that molecules can be adsorbed more than one layer thick on the surface of the adsorbent. The BET equation assumes that the energy required to adsorb the first particle layer is adequate to hold the monolayer in place.

BET Isotherm

$$\frac{q}{qm} = \frac{c/cs}{(1-c/cs)[1+(\alpha-1)(c/cs)]} \quad \ldots.. (2.5)$$

Some general rules of thumb, uses, and caveats that is helpful in isotherm interpretation are as follows:

1) A flat isotherm curve indicates a narrow Mass Transfer Zone (MTZ), meaning that the GAC generally adsorbs contaminants at a constant capacity over a relatively wide range of equilibrium concentrations. Given an adequate capacity, carbons exhibiting this type of isotherm will be very cost effective, and adsorption system design will be simplified owing to a shorter mass transfer zone

2) A steep isotherm curve indicates a wide MTZ, with the adsorption capacity increasing as equilibrium concentration increases. Carbons exhibiting this type of isotherm curve tend to be more cost effective.

3) A change in isotherm slope generally occurs for wastes that contain several compounds with variable adsorption capacities. An inflection point occurs when one compound is preferentially adsorbed over another and desorption occurs, so that the preferentially adsorbed compound can utilize sites previously used by less adsorbable.

If the liquid is a homogeneous binary mixture, it is customary to designate one component as the solute, and the other component as the solvent. The assumption is then made that the change in concentration of the liquid mixture in contact with a

2.1.2 Commercial Adsorbents

Many adsorbents have been developed in the form of small pellets, beads or granules ranging from about 0.1 mm to 12mm in size. The choice of adsorbents for practical separation depends on the requirement for adequate adsorptive capacity. A particle with many fine pores can have up to 50% of total particle volume. There are a number of adsorbents such as activated carbon, silica gel, activated alumina and molecular sieves zeolites. Activated carbon can be produced from a number of agricultural commodities. Among these are hardwoods, grain hulls, corn cobs, and nut shells (Young, 1996). Zeolites are crystalline networks of alumino-silicates with the general stoichiometric unit cell formula $M_{x/m}[(AlO_2)_x(SiO_2)_y]z\ H_2O$ where M is the cation with valence m, z is the number of water molecules in each unit cell, and x and y are integers such that $y/x \geq 1$ (Seader and Henley, 1998). Water is adsorbed more strongly on molecular sieves than alumina or silica gel, but the ultimate capacity of silica gel is generally higher. Therefore, it acts as a useful desiccant where high capacity is required at low temperature.

Any solid has some tendency to adsorb fluid medium onto their surface, however only some solid materials have the selective adsorption capacity to adsorbate molecules. The adsorbate may be organic compound, color, odor, moisture etc. Keller (1995) lists the four most common adsorption processes in terms of their estimated annual sales, along with their characteristics, applications and disadvantages (Table 2.1).

Table 2.1 Characteristics of Different Adsorbent

Type	Characteristics	Use	Disadvantages
Activated Carbon	Hydrophobic, favors organics over water	Removal of organic pollutants	Difficult to regenerate
Zeolites	Hydrophillic, polar, regular channels	Air separation, dehydration	Low total capacity
Silica gel	High capacity, hydrophillic	Drying gas streams	Trace removal not effective
Activated alumina	High capacity, hydrophiilic	Drying gas streams	Trace removal not effective

The identification of characteristics of adsorbate requires relative molecular mass, solubility of adsorbate, concentration relative to solubility limits, polarity of adsorbate and temperature of solution .The selection of adsorbent for optimum efficiency requires a study of adsorption isotherm data, selection of optimum activity level, physical requirements of adsorption system, cost analysis and consideration of thermal reactivation.

2.1.3 Adsorption Dynamic Model

Most basic fixed-bed adsorption models developed are for dilute single adsorbate isothermal systems. According to Leavitt (1962), the bed approaches isothermal by readily conducting the heat generated through the bed wall. However, most reasonably accurate adsorption modeling requires the inclusion of heat effect. Most works done includes heat effect by treating the adsorption system as adiabatic or taking into account heat loss through wall. Ruthven (1984) has compiled various analytical and numerical solutions for fixed bed adsorption systems, which mostly use 'equilibrium theory' to analyze the system behavior. He commented that the complexity of the dynamic behavior of an adsorption column is directly related to the number of components and nature of the system since these factors determine the number of transition or mass transfer zones and the difficulty of most dynamic adsorption behavior lies in the role played by the adsorption process itself. Ultimately, it must also be determined whether the adsorption is relatively fast or slow as compared to the gas phase transport.

Numerical method known as 'method of characteristic' proposed by Acrivos (1956) is important to solve dynamic model using equilibrium theory for both isothermal and adiabatic fixed-bed adsorption. A more value added "film model" was introduced by Giorgio and Rebecca (1999) to simplify numerical calculations of multicomponent adsorption in batch and fixed-bed adsorber which is based on difffusional mass transfer on a resistance film. On top of that, Lee, Porter and McKay (2000) have developed modified bed depth service time (BDST) and empty bed residence time (EBRT) models to predict performance of fixed-bed adsorption units which systems requires a long period of time to reach equilibrium. These models are based on an expression to correlate the residence time in the adsorption bed with the time-dependent fraction degree of the saturation of the bed.

2.1.4 Numerical Solutions

Analytical solutions can be used to predict fixed-bed performance if the adsorption equilibrium relationship is of certain type and the adsorbate uptake follows a particular mechanism. In contrast, numerical solution represent a more versatile approach since their use is not limited by the type of adsorption isotherm expression, adsorbate uptake mechanism or the initial and boundary conditions.

Historically speaking, finite difference method is perhaps the most widely used method for solving single species fixed bed adsorption (Tien, 1994). He also commented that although the method is inferior, it is conceptually simple and can be easily applied to both single and multi-component calculation. Chok (2002) has used the finite difference approach to approximate concentration and temperature at each stage and the results were ascertained with the theoretical predictions.

The widespread use of orthogonal collocation method for solving ordinary and partial differential equation in engineering applications including fixed-bed adsorption calculations. Crittenden et al. (1980) compared their results with their earlier results from the finite difference method and found that collocation method superior in terms of stability, accuracy and execution time. On the other hand, Mohd Shariff (1995) has used stage method as the basis of the process dynamic modeling and parameters investigated at each stage are approximated using the numerical method of lines (NUMOL).

2.2 THEORY

2.2.1 Macroscopic Conservation of Fluid Phase

In most cases, adsorption is carried out in fixed bed mode. Material and energy balances are needed to describe and model the adsorption process. If the flow is assumed to be one-dimensional (along the direction of the bed's axis), based on a unit cross-sectional area, then the general equation below, *Rate of Net Adsorbate Input Associated with Mass Flow*

$$(u_s c_b)_z - (u_s c_b)_{z+\Delta z} \tag{2.7}$$

Rate of Adsorbate Efflux

(a) Due to Axial Dispersion

$$-\left(E\varepsilon \frac{\partial c}{\partial z} \right)_z + \left(E\varepsilon \frac{\partial c}{\partial z} \right)_{z+\Delta z} \tag{2.8}$$

(b) Due to Uptake by Pellet

$$(\Delta z)\frac{(1-\varepsilon)}{(4/3)a3}N \tag{2.9}$$

Rate of Accumulation of Adsorbate Mass

$$\Delta z(1-\varepsilon)(\Delta c/\Delta t) \tag{2.10}$$

For the limiting situations $\Delta z \to 0$, the result obtained from applying above equations is

$$\left(E\varepsilon \frac{\partial c}{\partial z} \right) + \frac{\partial}{\partial z}(u_s c_b) + \varepsilon \frac{\partial c}{\partial z} + (1-\varepsilon)\frac{3N}{4\pi a^3} = 0 \tag{2.11}$$

For the case study, the model was developed by assuming the velocity of the fluid flow through the column is constant, there being no heat losses through the wall. The differential mass and energy balances for an element of the adsorption bed were developed by considering the system having two components but with only phenol adsorbed on the activated carbon. The material and energy balances were written according to the macroscopic conservation,

$$\boxed{\text{Rate of input} - \text{Rate of Output} = \text{Rate of accumulation}}$$

The mass balance given by

$$\varepsilon v C_A \pi r^2 \,|_z - \varepsilon v C_A \pi r^2 \,|_{z+\Delta z} = \frac{\partial}{\partial t}\left[\rho_b q_A + \varepsilon C_A\right]\pi r^2 \Delta z \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.12)$$

The energy balance given by

$$\varepsilon v h_f \pi r^2 \,|_z - \varepsilon v h_f \pi r^2 \,|_{z+\Delta z} = \frac{\partial}{\partial t}\left[\rho_b u_s + \varepsilon u_f\right]\pi r^2 \Delta z \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.13)$$

Where ρ_b is the bulk density of the adsorbent bed. The above equations were written by assuming the activated carbon and the adsorbed phenol are stationary. The notations are simplified and heat capacity is assumed to be constant,

$$h_f = C_A \cdot C_f (T - T_{ref}) \ldots\ldots\ldots\ldots\ldots (2.14)$$

$$u_f = h_f - P_T = h_f - C_A RT \ldots\ldots\ldots (2.15)$$

$$u_s = C_s + q_A \cdot C_w (T - T_{ref}) - \int_0^{qA} \lambda_A . dq_A \ldots\ldots\ldots\ldots\ldots (2.16)$$

Dividing equations 2.12 and 2.13 by $\pi r^2 \Delta z$ and letting Δz approach zero, gave

$$\frac{\partial(\rho_b q_A)}{\partial t} + \frac{\partial(\varepsilon C_A)}{\partial t} + \frac{\partial(\varepsilon v C_A)}{\partial z} = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.17)$$

$$\frac{\partial(\rho_b u_s)}{\partial t} + \frac{\partial(\varepsilon u_f)}{\partial t} + \frac{\partial(\varepsilon v h_f)}{\partial z} = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.18)$$

Freundlich isotherm is used as the equilibrium relations for the model. The ideal Freundlich isotherm is

$$q = Kc^{1/n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.19)$$

2.2.2 Finite Volume Element Analysis

The adsorption column considered in this project is a cylindrical column mounted vertically. Based on the assumptions stated earlier, the mathematical model, i.e. material and energy balances are derived from the finite volume element approach.

The figure 2.2 below shows the configuration used in deriving macroscopic conservation equation above.

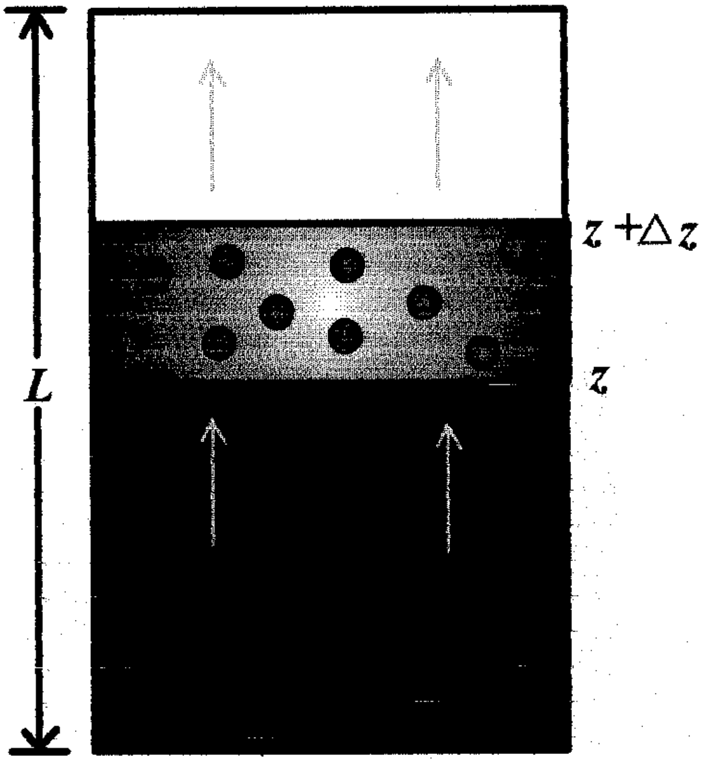


Figure 2.2: Finite Volume Element in an Adsorption Column

2.2.3 Numerical Method of Lines (NUMOL)

Since parameters of interest vary with time and space along the bed as adsorption proceeds, i.e. involve more than one independent variable, it can be modeled by partial differential equations (PDE). As per the general material and energy balances stated earlier, the PDE is can be classified as parabolic differential equations. In NUMOL, the PDE is converted into sets ordinary differential equations (ODE) by discretizing only the spatial derivative using the finite difference method and leaving the time derivative unchanged. Consider the following PDE, it is transformed to ODE by using central difference for spatial derivative.

$$\alpha \frac{\partial^2 u}{\partial x^2} = \frac{\partial u}{\partial t} \quad \text{.................................} \quad (2.20)$$

$$\Rightarrow \frac{du_i}{dt} = \frac{\alpha}{\Delta x^2}(u_{i+1} - 2u_1 + u_{i-1}) \quad \text{..........} \quad (2.21)$$

The total number of ODE is the same as the number of stages divided along the spatial direction. The complete set of simultaneous differential equations must be integrated forward in time starting with the initial condition specified. NUMOL is considered as a method that gives stable solutions for parabolic partial differential equations.

2.2.4 Stage Method

In stage method, the adsorption bed is divided into several equal stages or segments. The differential material and energy balances are incorporated with specific isotherm are then used to approximate concentration and temperature at each stage. Within the stage, the concentration and temperature is assumed constant at any position. As a result, the more stages the bed is divided into, the more accurate the prediction will be generated by stage method. The dynamic model developed is solved with respect to time and position simultaneously for each stage.

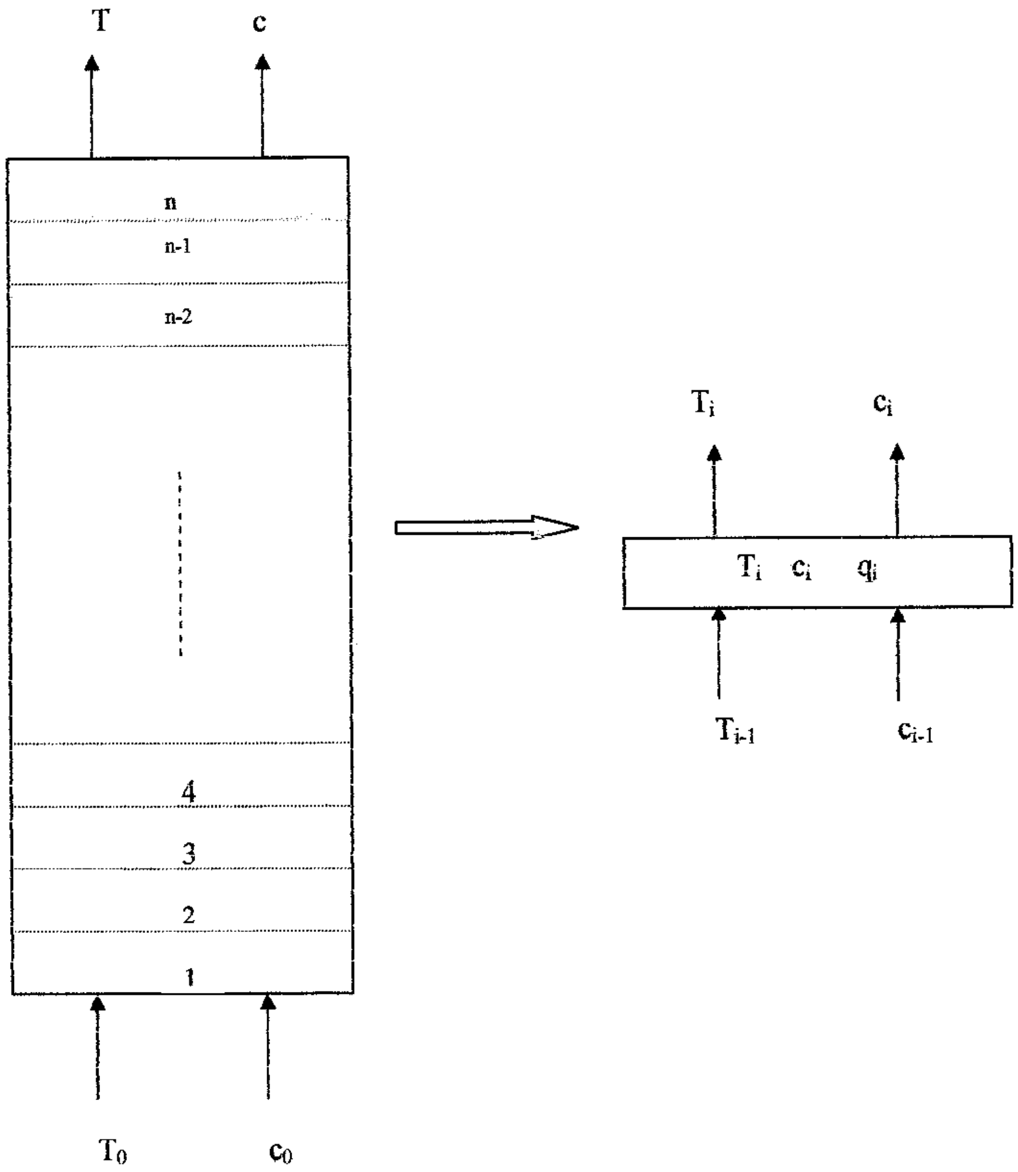


Figure 2.3: Stage i of Adsorption Bed

CHAPTER 3

METHADOLOGY/PROJECT WORK

3.1 PROCEDURE IDENTIFICATION

3.1.1 Procedures

The management of the project can be classified into two steps:

(a) Development of mathematical model

(b) Simulate the model using MATLAB

The following is the procedure to be undertaken:

1. Identify the characteristics of adsorption system to be modeled
2. Make reasonable assumptions
3. Determine the equilibrium data
4. Determine initial and boundary conditions
5. Develop dynamic mathematical model using material and energy balance
6. Solve model numerically using MATLAB
7. Generate and analyze relevant graphs
8. Compare graph with the theory (experimental result from literature)

3.1.2 Assumptions

Some assumptions have been made in order to build this liquid adsorption model. When the adsorbate is fast, meaning the residence time of the solution in bed is long enough for equilibrium to occur. In order to reach the equilibrium in short time, plug flow condition has to be apply which not considering velocity gradient and axial dispersion. Adsorption behavior is to be approximated by Freundlich adsorption isotherm. The model uses two components system with one component is adsorbed which is phenol.

Some other assumptions are as follow:

1. Constant of superficial velocity, bulk density and bed voidage.

2. Negligible of radial temperature, concentration and velocity gradients within the bed.
3. The effect of inert of carrier, mass and heat transfer resistance were neglected and local equilibrium was assumed at all points in the bed.
4. Neglect the effect of heterogeneity of surface.

3.1.3 Cooney Model for Differential Heat Balance

The prediction of temperature and concentration profiles requires simultaneous solution of the coupled differential heat and mass balance equations which describe the system. Most early non-isothermal adsorption column studies deal with binary adiabatic or near adiabatic systems with a small concentration of an adsorbable species in an inert carrier. Since the model proposed by Cooney well represents this class of system, it is thus used as the fundamental model in the modeling. The differential mass balance equation is

$$\frac{\partial c}{\partial t}+v\frac{\partial c}{\partial z}+\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial q}{\partial t}=0 \dots\dots\dots\dots\dots\dots\dots\dots\dots \text{(3.1)}$$

The differential heat balance equation is

$$\frac{\partial T_f}{\partial t}+v\frac{\partial T_f}{\partial z}+\frac{C_s}{C_f}\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial T_s}{\partial t}+\frac{\Delta H}{C_f}\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial q}{\partial t}=0 \dots\dots\dots \text{(3.2)}$$

Assume that $T_s = T_f = T$, equation (3.2) is therefore

$$\frac{\partial T}{\partial t}+v\frac{\partial T}{\partial z}+\frac{C_s}{C_f}\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial T}{\partial t}+\frac{\Delta H}{C_f}\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial q}{\partial t}=0 \dots\dots\dots\dots\dots \text{(3.3)}$$

3.1.4 Initial and Boundary Conditions for Adsorption Model

The Dirichlet type of initial and boundary conditions were used to define the response of an initial sorbate free column to a step change in the sorbate concentration. The initial and boundary conditions for the adsorption models are

At $\zeta > 0$ and $\tau = 0$,	At $\zeta = 0$ and $\tau \geq 0$,
$c_A = c_{A0}$	$c_A = c_{AI}$
$T = T_0$	$T = T_I$
$v^* = v^*_0$	$v^* = v^*_I$

where subscript 0 and I denote initial and boundary conditions.

Since the model studied is under constant velocity condition, v^* is assumed at 1m/s at all times. Data for initial and boundary conditions used in the simulation of phenol-activated carbon are selected arbitrarily and given in Table 3.1.

Table 3.1 Initial and Boundary Conditions for Adsorption Model

C_0	0 mol/L
C_I	0.01 mol/L
T_0	300 K
T_I	300 K

3.1.5 Equilibrium Data and Constants

The equilibrium data for adsorption of phenol on activated carbon extracted from a research done by Abdul Hameed REHAN, Pakistan Institute of Nuclear Science and Technology (1998). These values are applied accordingly into the Adiabatic-Constant-Velocity (ACV) adsorption model.

Table 3.2 Data for Adsorption of Phenol on Activated carbon

Model Parameters		Values
Voidage Fraction	ε	0.5
Solid Heat Capacity	C_s	1520 J/kg.K
Fluid Heat Capacity	C_f	197 J/mol.K
Adsorption Constant	K	27.68 (mg/g)(L/mg)
Adsorption Constant	1/n	0.288
Bulk Density	ρ_b	230 kg/m^3
Heat of Enthalpy	ΔH	-10902 J/kg

3.1.6 Method of Solution

In this case, ρ_b, ε and v are assumed constant. Rearrangement of equations (2.12) and replacement equation (2.13) by (3.3) give results,

$$\rho_b \frac{\partial q_A}{\partial t} + \varepsilon \frac{\partial C_A}{\partial t} + \varepsilon v \frac{\partial C_A}{\partial z} = 0 \quad \text{..........} \quad (3.4)$$

$$\frac{\partial T}{\partial t} + v \frac{\partial T}{\partial z} + \frac{C_s}{C_f}\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial T}{\partial t} + \frac{\Delta H}{C_f}\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial q}{\partial t} = 0 \quad \text{..........} \quad (3.5)$$

The following dimensionless variables were defined and introduced to the differential mass and heat balances

$$v^* = \frac{\varepsilon v}{\varepsilon_0 v_0} \quad \text{where } v^* \text{ is dimensionless velocity ....} \quad (3.6)$$

$$\tau = \frac{t \varepsilon_0 v_0}{l_b} \quad \text{where } \tau \text{ is dimensionless time ....} \quad (3.7)$$

$$\xi = \frac{z}{l_b} \quad \text{where } \xi \text{ is dimensionless length ....} \quad (3.8)$$

In this definition, τ is equal to the number of bed volume if the liquid that have passed through the column. Substituting the above expressions into equations (3.4) and (3.5) give

$$\rho_b \frac{\partial q_A}{\partial \tau} + \varepsilon \frac{\partial C_A}{\partial \tau} + v^* \frac{\partial C_A}{\partial \xi} = 0 \quad \text{..........} \quad (3.9)$$

$$\frac{\partial T}{\partial \tau} + v \frac{\partial T}{\partial \xi} + \frac{C_s}{C_f}\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial T}{\partial \tau} + \frac{\Delta H}{C_f}\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial q}{\partial \tau} = 0 \quad \text{..........} \quad (3.10)$$

The chain rule is applied to the τ dependent derivatives. In this case, q_A are functions of C_A and T. Therefore, by applying the chain rule to q_A gives

$$\frac{\partial q}{\partial \tau} = \frac{dq}{dC}\frac{\partial C}{\partial \tau} + \frac{dq}{dT}\frac{\partial T}{\partial \tau} \quad \text{..........} \quad (3.11)$$

Substitute equation (3.11) into equation (3.9) and equation (3.10) rearrange gives

$$\rho_b\left[\frac{dq}{dC}\frac{\partial C}{\partial\tau}+\frac{dq}{dT}\frac{\partial T}{\partial\tau}\right]+\varepsilon\frac{\partial C_A}{\partial\tau}+v*\frac{\partial C_A}{\partial\xi}=0 \ldots\ldots\ldots\ldots\ldots \text{(3.12a)}$$

$$\Rightarrow\left[\rho_b\frac{dq}{dC_A}+\varepsilon\right]\frac{\partial C_A}{\partial\tau}+\frac{dq}{dT}\frac{\partial T}{\partial\tau}+v*\frac{\partial C_A}{\partial\xi}=0 \ldots\ldots\ldots\ldots\ldots \text{(3.12b)}$$

$$\left[1+\frac{C_s}{C_f}\left(\frac{1-\varepsilon}{\varepsilon}\right)\right]\frac{\partial T}{\partial\tau}+\frac{\partial T}{\partial\xi}+\frac{\Delta H}{C_f}\left(\frac{1-\varepsilon}{\varepsilon}\right)\left(\frac{dq}{dc}\frac{\partial c}{\partial\tau}+\frac{dq}{dT}\frac{\partial T}{\partial\tau}\right)=0 \ldots\ldots\ldots \text{(3.13a)}$$

$$\Rightarrow\left[1+\frac{C_s}{C_f}\left(\frac{1-\varepsilon}{\varepsilon}\right)+\left(\frac{\Delta H}{C_f}\right)\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{dq}{dT}\right]\frac{\partial T}{\partial\tau}+\left[\frac{\Delta H}{C_f}\left(\frac{1-\varepsilon}{\varepsilon}\right)\left(\frac{dq}{dc}\right)\right]\frac{\partial c}{\partial\tau}+\frac{\partial T}{\partial\zeta}=0 \ldots\text{(3.13b)}$$

The spatial derivatives with respect to dimensionless length (in this case) are approximated by using backward finite difference method. Thus, the partial differential equations of (3.12b) and (3.13b) are then reduced to a set of ordinary differential equations as given below,

$$\left[\rho_b\frac{dq}{dC_A}+\varepsilon\right]\frac{\partial C_A}{\partial\tau}+\frac{dq}{dT}\frac{\partial T}{\partial\tau}=-v*\frac{C_A|_i-C_A|_{i-1}}{\Delta\xi} \ldots\ldots\ldots\ldots\ldots \text{(3.14)}$$

$$\left[1+\frac{C_s}{C_f}\left(\frac{1-\varepsilon}{\varepsilon}\right)+\left(\frac{\Delta H}{C_f}\right)\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{dq}{dT}\right]\frac{dT}{d\tau}+\left[\frac{\Delta H}{C_f}\left(\frac{1-\varepsilon}{\varepsilon}\right)\left(\frac{dq}{dc}\right)\right]\frac{dc}{d\tau}=-\frac{T_i-T_{i-1}}{\Delta\xi} \ldots\ldots\text{(3.15)}$$

The above equations are arranged in matrix form,

$$\begin{bmatrix}\left[\rho_b\frac{dq}{dC_A}+\varepsilon\right] & \frac{dq}{dT}\\ \left[\frac{\Delta H}{C_f}\left(\frac{1-\varepsilon}{\varepsilon}\right)\left(\frac{dq}{dc}\right)\right] & \left[1+\frac{C_s}{C_f}\left(\frac{1-\varepsilon}{\varepsilon}\right)+\left(\frac{\Delta H}{C_f}\right)\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{dq}{dT}\right]\end{bmatrix}\begin{bmatrix}\frac{\partial C_A}{\partial\tau}\\ \frac{\partial T}{\partial\tau}\end{bmatrix}=\begin{bmatrix}-v*\frac{C_A|_i-C_A|_{i-1}}{\Delta\xi}\\ -\frac{T_i-T_{i-1}}{\Delta\xi}\end{bmatrix}$$

(3.17)

The matrix represents the set of equations for 1 stage. In this adsorption model, the column is divided into n equal stages. The actual equations to be solved in the numerical simulation for one time step were n times the set of equations in (3.17).

3.1.7 Computational Algorithm

The procedure used to solve the mathematical equations is summarized here. The constants for adsorption isotherm, physical properties and model parameters are supplied to the dynamic model. Initial and boundary conditions as well as $\Delta\xi$ are also specified. The τ-derivatives coefficients are evaluated based on the values from a time step backwards and then integrated using DSOLVE to get the c and T of the same time step. The procedure is iterated until at the time step specified by the user. DSOLVE is a function of Symbolic Math Toolbox, which provides a link between MATLAB and symbolic algebraic program known as Maple. In dealing with differential equation, the Symbolic Math Toolbox leads to explicit formulas for the solutions. The algorithm is given in the flowchart of Figure 3.1.

3.2 TOOL(S) REQUIRED

3.2.1 Software

In developing this model, *MATLAB version 6.1* is a selected tool to solve the mathematical models and to generate the curves required. Matlab script is used to store the relevant adsorption model data and calculate breakthrough curves. This script allows the manipulation of parameters and exploration of the dynamic model.

A complete program code will be written in MATLAB language to model the adsorption process. Basically, program codes will be written in MATLAB language to model the adsorption process and then the codes will be solve iteratively by the software to plot the concentration and temperature profile so that comparison and analysis could be carried out accordingly.

The code is divided into 3 main parts. The first part requires the user to input the number of stages of which the column is to be divided into and maximum run time of the process. At the same time, equilibrium data, initial and boundary conditions are initialized. In the second part, the differential equations are solved. Lastly, in the final part, the data generated are plotted into concentration and temperature profiles. The source codes are as of Appendix A.

Microsoft Excel 2004 is another tool used to modify the graph obtained from MATLAB. It is an application that helps the in visualizing the obtained results from the mathematical and statistical analysis conducted through MATLAB programming. In this project, Microsoft Excel is used to tabulate the results including the estimated parameters and residuals and presents the data from many graphs to be combined in one graph.

3.2.2 Hardware

The projects has been simulated and run by using the computer of NEC Intel® Pentium®M computer. The specification of the computer used is shown in Table 3.3 below:

Table 3.3: Computer Specifications

Computer Model	*NEC Versa E680*
Processor	*1.4 GHz (Intel Centrino)*
Ram	*256 MB*
Display Card	*Intel Graphic*
Sound Card	*ACS 97*

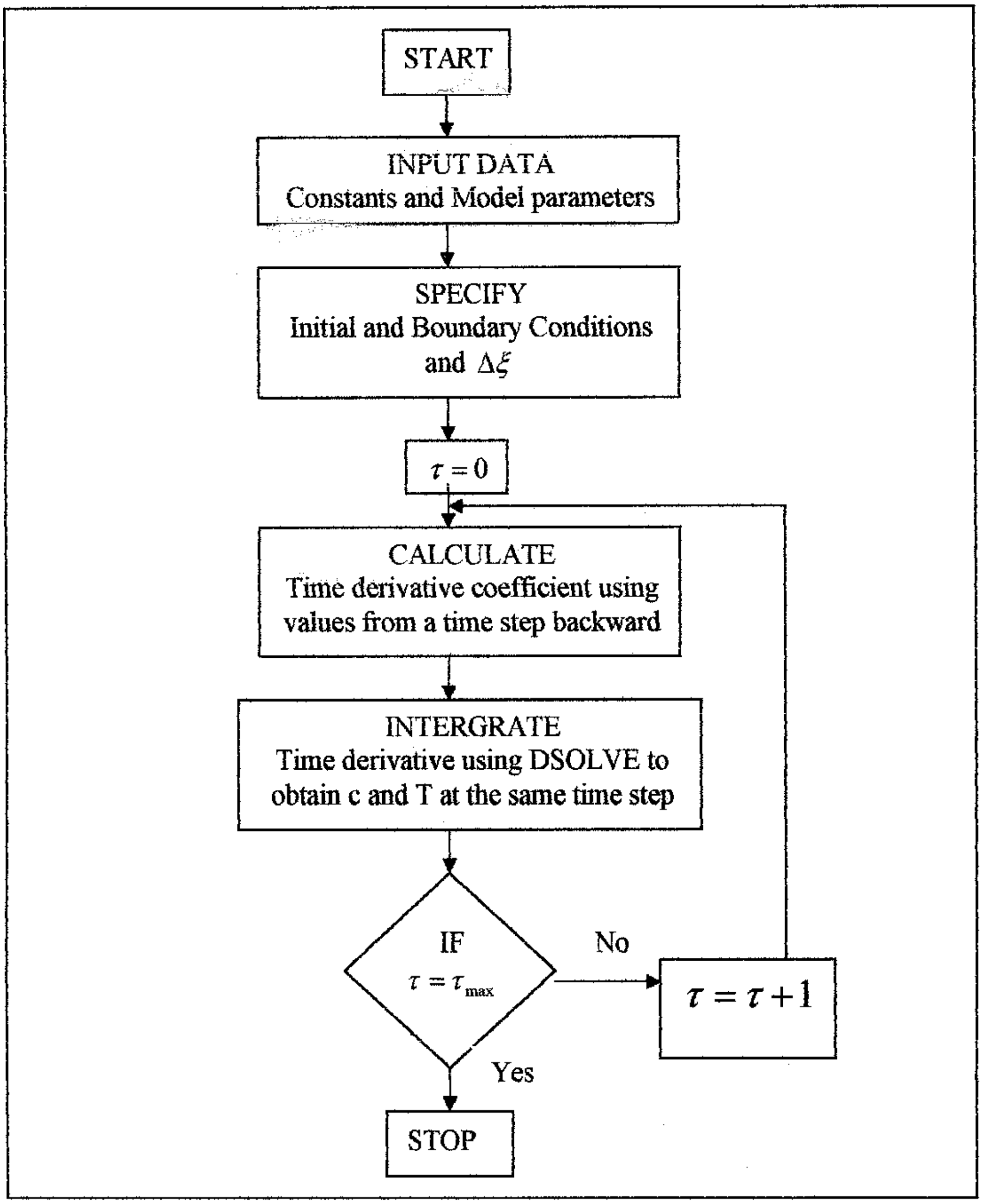


Figure 3.1 Computational Algorithm for ACV Models

CHAPTER 4

RESULTS AND DISCUSSION

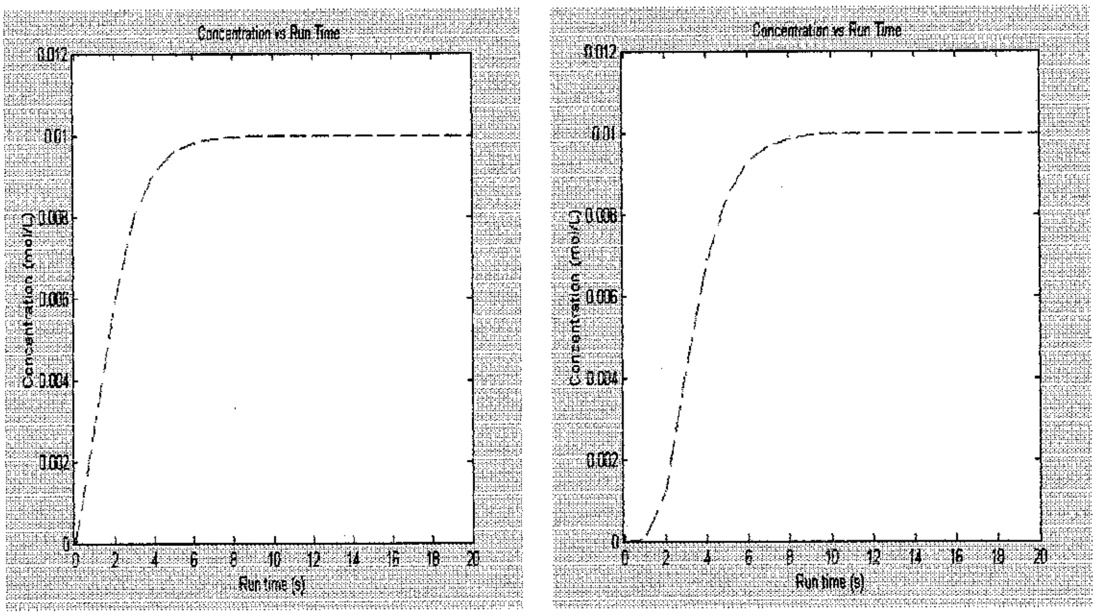
4.1 Simulation of Adiabatic Constant Velocity (ACV) Adsorption Model

The dynamic model for phenol-activated carbon by using Freundlich isotherm was simulated using MATLAB by discretizing the column into 30 equal stages for an operating time of 20 seconds and solved by means of NUMOL. The column length was specified at 1m and the fluid velocity at 1m/s. The adiabatic adsorber is sorbate free and preheated to a specific temperature, i.e. 300K prior to the initiation of adsorption process. The fluid with trace concentration of phenol (i.e. 0.01 mol/L) was injected continuously into the adsorber at a temperature of 300K. Concentration and temperature profiles of the process were plotted and as shown in Figure 4.1 and Figure 4.2.

From Figure 4.1, the dynamic model has predicted an increase in temperature from the initial 300 K to 328 K and 338 K for bed length at 0.2m and 0.8m. The temperature changed is because of adsorption process is an exothermic reaction. The temperature is increasing as the adsorption took place along the certain bed length at start to decrease whenever the adsorption is completed. At 0.2m of the bed, the fluid passes the region is phenol free, i.e. bed remains clean, for approximately 2s after the start of the process. The phenol concentration is then gradually built up to the maximum at 5s-8s and thereafter phenol concentration is at its maximum indicating the bed has turned saturated. On the other hand, the region at 0.8m of the bed remains clean for 5s before any adsorption takes place there.

In terms of temperature, the temperature at 0.2m started to increase at time less than 5s, which is approximately 15s before adsorption actually occurs at that region. The earlier temperature build up is due to thermal wave propagation from earlier regions where adsorption has taken place. However, as soon as the adsorption rate decreases, the temperature decreases to the initial preheated temperature at a fast rate and remains at 300K when no adsorption occurs.

(a) Concentration Vs Run Time at ξ=0.2 m (b) Concentration Vs Run Time at ξ =0.8m



(c) Temperature Vs Run Time at ξ=0.2 m (d) Temperature Vs Run Time at ξ =0.8m

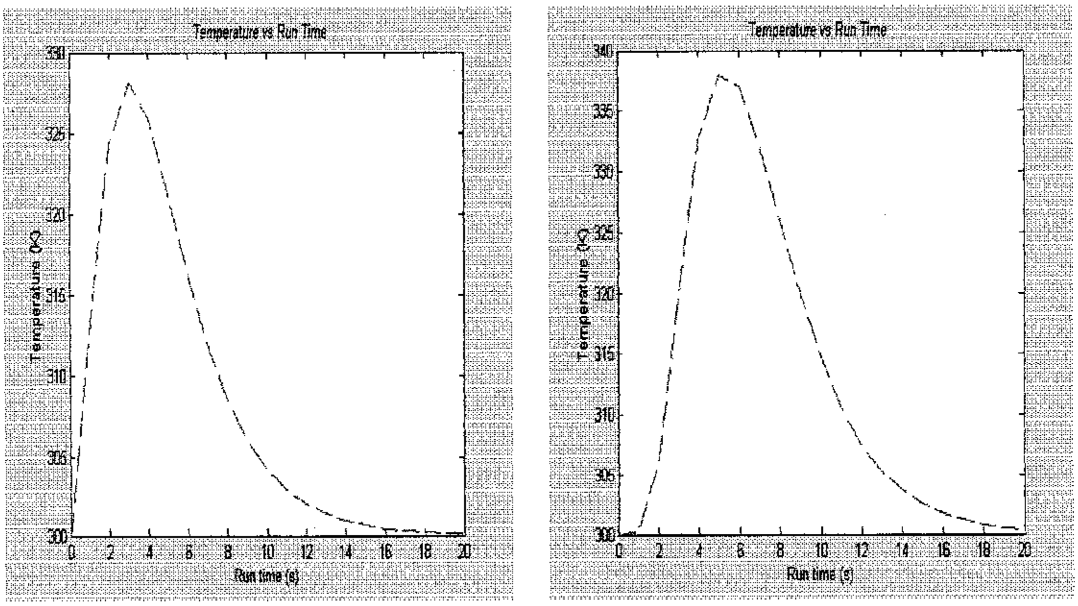
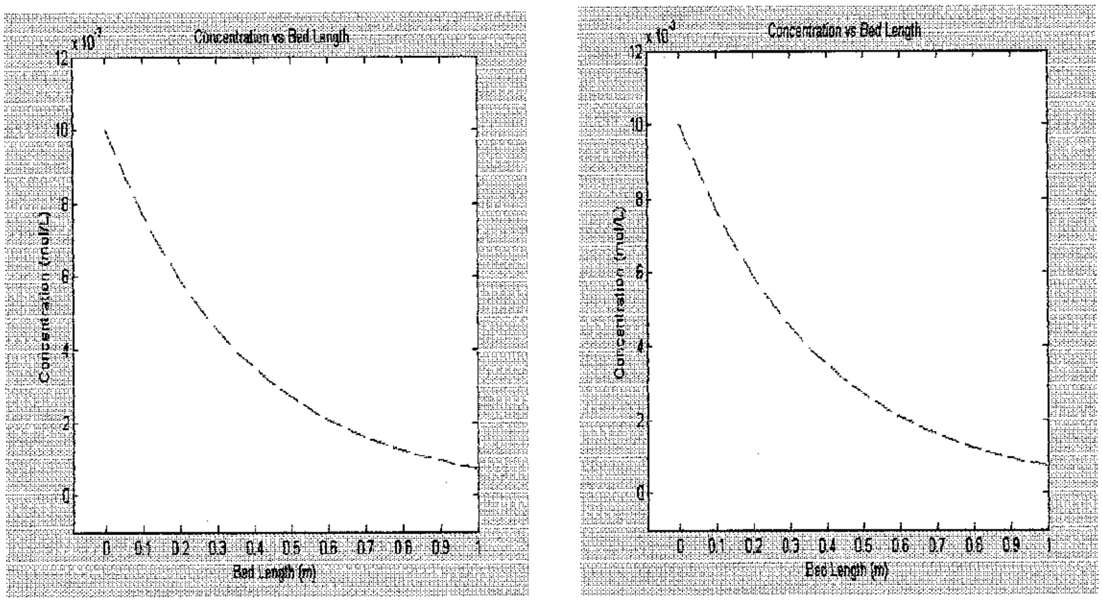


Figure 4.1: Breakthrough curves and bed profiles predicted by Freundlich isotherm with respect to length

(a) Concentration Vs Bed Length at t = 10s (b) Concentration Vs Bed Length at t = 15s



(c) Temperature Vs Bed Length at t = 10s (d) Temperature Vs Bed Length at t = 15s

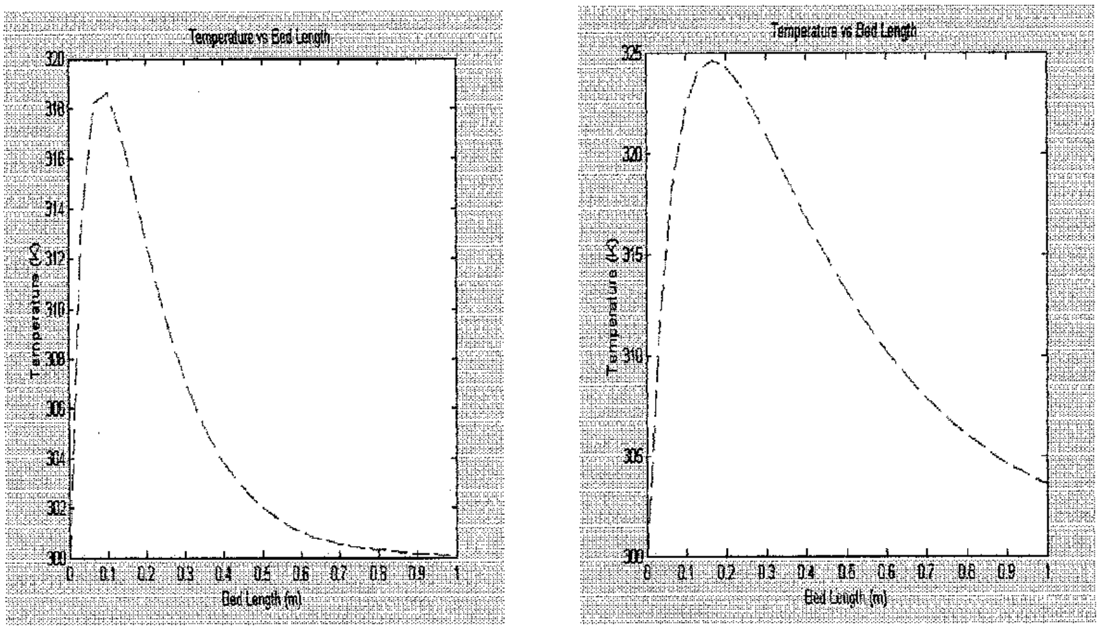


Figure 4.2: Breakthrough curves and bed profiles predicted by Freundlich isotherm with respect to time

From another perspective, as shown in Figure 4.2, the temperature profile is observed that the temperature remains at preheated temperature for saturated region and begins to rise at MTZ. Beyond MTZ, temperature starts to decrease but at a very slow rate until the exit of the column. This is because the system is assumed to be in adiabatic and thus heat liberated is contained. From the concentration profile, the trend of graph is not so accurate since the adsorption took place at 0.1 m at 5 s. It goes the same for the breakthrough curve at 10 s. It is not so logical and considered to have some error occur on this model. Some study has been made in order to identify the possible uncertainty in this model that could lead of this error. The errors could influence by the constants used in Freundlich isotherm, the inlet temperature, or the parameters used in this model.

In any adsorption process, when the fluid first contacted the bed, most mass transfer and adsorption will take place at the inlet. As the fluid passes through the bed, the concentration in the fluid drops very rapidly with distance in the bed to zero before the end of the bed is reached. When the bed at near the inlet will be saturated and mass transfer and adsorption will takes place at a point further from the inlet. The fixed bed located nearer to the inlet will get saturated first. Slightly downstream of the saturated region is known as the mass transfer zone (MTZ). MTZ is where concentration gradient exists and adsorption takes place.

Other possibility that could lead to the error is that the temperature used. For the three model parameter isotherm, the literature said that it is best to conduct at 298 K which closes to the testing temperature in this model. But, for Freundlich isotherm, it can work better at the initial temperature 328 K.

4.2 Simulation of ACV using Different Number of Stages

In stage method, the accuracy of prediction is highly dependent on the number of stages the column of a certain length is divided into. Intuitively, the more number of stages, the more accurate the prediction is. This is because, when the number of stages increases, the bed length division gets smaller and thus the concentration and temperature which are assumed to be constant within the division will be able to approximate more closely to the actual values at that particular position. The system can even be assumed as continuous if the number of stages is large enough.

To compare results using different number of stages, the ACV model is simulated for 20s at 1m column length for 30 and 60 stages. The predicted results for concentration and temperature at certain region of the bed are tabulated as follows:

Table 4.1: Comparison Results for ACV Model at 20s for 30 and 60 Stages

Bed Length	30 Stages (Δz = 3.33cm)		60 stages (Δz = 1.67cm)		Percentage Difference (%)	
	Conc.	Temp	Conc.	Temp	Conc.	Temp
0.00	0.010000	300.00	0.010000	300.00	0.0000	0.0000
0.02	0.009988	300.12	0.010000	300.00	0.0012	0.0004
0.04	0.009975	300.24	0.009999	300.01	0.0024	0.0012
0.06	0.009963	300.36	0.009999	300.01	0.0006	0.0012
0.08	0.009950	300.48	0.009999	300.01	0.0050	0.0012
0.10	0.009937	300.61	0.009998	300.02	0.0061	0.0020
0.12	0.008920	300.76	0.009998	300.02	0.1080	0.0025
0.14	0.007593	302.55	0.008998	300.02	0.1561	0.0084
0.16	0.003237	312.36	0.004595	301.88	0.2956	0.0347
0.18	0.000901	328.88	0.000709	315.42	0.2708	0.0428
0.20	0.000533	330.72	0.000461	319.77	2.3110	0.1497

From Table 4.1, it is noticed that the percentage difference of concentration increases gradually as we move deeper into the adsorber bed whereas the percentage difference of temperature remains almost the same. Therefore, it can be concluded that concentration is more sensitive towards the number of stages than temperature. This is because MTZ which was neglected when model was simulated at 30 stages is not taken into account at 60 stages simulation. Insensitivity of temperature to the number of stage is mainly due to the heat liberated gets propagated and distributed to other regions of the bed causing it to be rather uniform.

4.3 Simulation of ACV at Various Operating Temperature

Adsorption is a separation process which is highly dependent on temperature. At low temperature, adsorption is favored whereas at high temperature, desorption is favored. MATLAB is used to simulate the effects on concentration and temperature profiles at various operating temperatures i.e. 300K, 350K and 400K, of a 1m adsorber bed using 30 stages. The profiles are as shown in Figure 4.3.

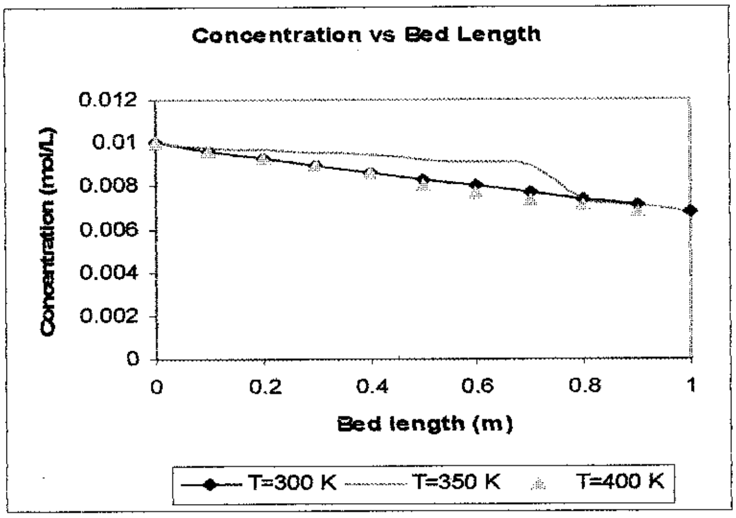


Figure 4.3: Concentration Profile at Various Operating Temperatures at t =10s

From Figure 4.3, it is observed that 0.1m of the bed is saturated at an operating temperature of 300K but near 0.2m of the bed is already saturated at an operating temperature of 350K after 10s of process time. This is because Van der Waal energy, which is a crucial element in for physical adsorption, is less at operating temperature 300K as compared to 350K. Therefore, it takes a longer time for adsorbate to accumulate enough energy to get adsorbed to the adsorbent surface for 300K operating temperature. On the other hand, at operating temperature of 350K, not all phenol is adsorbed onto the activated carbon at earlier region even though the bed is not saturated. Similarly, for 400K operating temperature, only half of the initial concentration of phenol is adsorbed to activated carbon after passing through the whole adsorber bed. This is mainly because, at higher operating temperature, the adsorbed particles have energy higher then the Van der Waal forces causing the particles to break the bond.

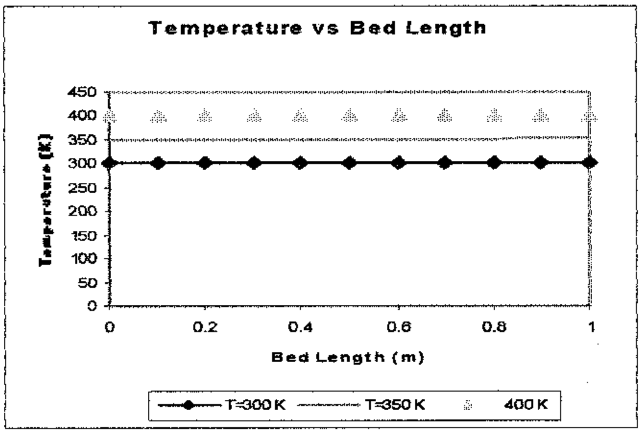


Figure 4.4: Temperature Profile at Various Operating Temperature at t =10s

From Figure 4.4, the temperature profile is directly related to the behavior of the adsorption process. Since MTZ exists at earlier region at 10s process time for operating temperature of 300K then 350K, the temperature started rising at earlier zones. Since the reaction is the same, temperature rise due to exothermic reaction is the same for both operating temperature, i.e. 20K. As for 380K operating temperature, since mass transfer occurs from the inlet until 0.3m to fully adsorbed phenol in the fluid, the temperature rises from 380K and eventually stabilizes at 400K when all phenol is adsorbed. On the other hand, adsorption seems to occur from inlet to outlet of the column for 450K operating temperature, therefore, its temperature profile shows an increasing trend through the bed.

4.4 Simulation of ACV at Various Fluid Velocity

In a fixed bed adsorption process, the fluid to be treated is usually passed down through the bed at a constant flow rate. ACV model is simulated using MATLAB at 30 stages for 10s at various fluid velocities to investigate their effects of on concentration and temperature profiles on a 1m long adsorber bed. 3 velocities arbitrarily selected are 0.1, 1 and 1.5 m/s. The large difference among the velocity values gives clearer view of effects sensitivity. The profiles obtained are as illustrated in Figure 4.5 and 4.6.

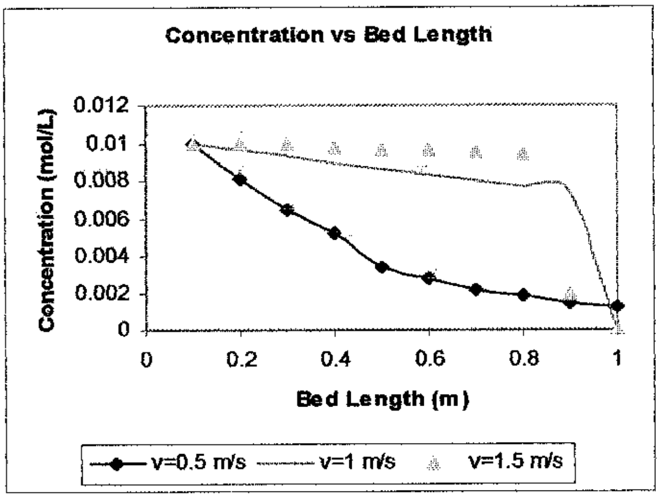


Figure 4.5: Concentration Profile at Various Fluid Velocities

From Figure 4.5, it is noticed that at 10s, almost half of the bed is saturated when the fluid velocity is at 1.5 m/s. On the other hand, less than 0.05m bed is saturated fluid flows at 1 m/s and no part of the bed is saturated at a fluid velocity of 0.1 m/s after 10s of operating time. In general, at higher fluid velocity, the faster the adsorber gets saturated. This is because the column cross sectional area is assumed constant for all 3 velocities and thus the fluid velocity is directly proportional to the volume of fluid injected continuously into the column at a time. In other words, the higher the fluid velocity, the larger amount of adsorbate is carries into the bed and thus the uptake rate increases. When the adsorption rate increases, the faster will the MTZ moves deeper into the system.

From the perspective of temperature, as observed from Figure 4.6, the temperature is only indirectly related to fluid velocity and very much related to mass transfer (i.e. adsorption process). For 1.5 m/s fluid velocity, the temperature profile is as explained earlier; the increase of temperature from initial 300K to 302K is due to exothermic reaction of adsorption process. As for 0.5 m/s, since adsorption takes place at region in the middle of the bed length, the heat liberated is not large enough to bring and sustain the temperature at regions deeper into the column at 302K, thus temperature drops gradually to 301 K until the outlet. At the outlet, some degree of temperature change due to the heat of exothermic reaction is still "sensed". On the other hand, for 1 m/s fluid velocity, the temperature increased from 300K to 302.5K.

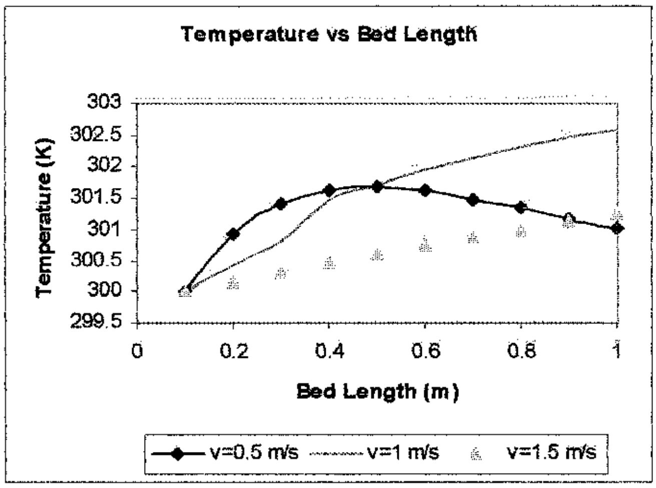


Figure 4.6: Temperature Profile at Various Fluid Velocities

With reference to Figure 4.5 and 4.6, the concentration and temperature profiles all 3 fluid velocities are rather close to each other. However, at the same dimensionless time step, the profiles of the 3 fluid velocities are expected to be the same. The slight deviation is due to the mathematical model. Recall equation (3.8), the model developed is only "semi-dimensionless" because the constants are kept with dimension, which then leads to oversimplification of the dimensionless variable.

4.5 Simulation of ACV at Various Concentration

The simulation is run at various concentrations and the result of concentration and temperature profile is shown at Figure 4.7 and 4.8 below. The graph shows that there is not much difference between the bed lengths for the concentration at 0.001 mol/L. When compared to the 0.1 mol/L, the concentration is decreasing until it exits the column. This shows that there is an adsorption occurs when the concentration is at high quantity. Small value of concentration results no effect of adsorption is happened. It had a trend to increase capacity as concentration increased.

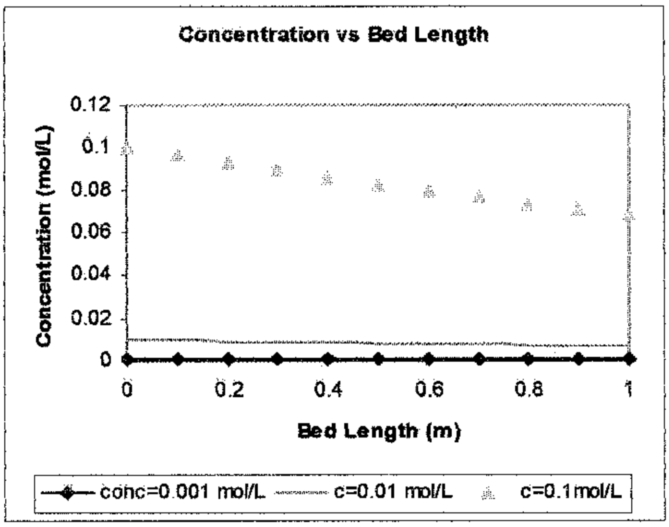


Figure 4.7: Concentration Profile at Various Concentrations

In terms of temperature, from Figure 4.8, the concentration at 0.001 mol/L resulted small difference concentration between the stages. For concentration at 0.01 mol/L, it has a little change of temperature between stages since the adsorption is an exothermic process. Compared to the concentration at 0.1 mol/L, the temperature start to increase from 300 K to 318 K. The big difference of temperature through stages because of the higher amount mass goes through the column; the more heat is released during the adsorption.

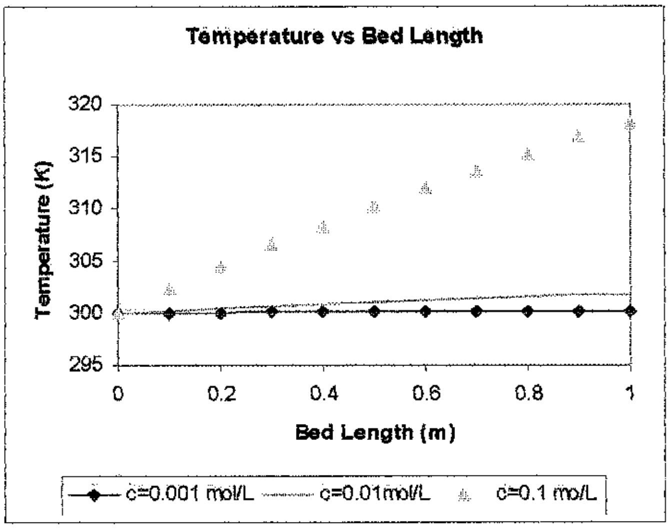


Figure 4.8: Temperature Profile at Various Concentrations

4.6 Simulation of ACV at Various Void Faction

The dynamic model at various bed void fraction is run at 10 stages with maximum running time at 10 s with 1m of adsorber length. Void fraction also would give an effect to the adsorption model since it consumes the percentage of volume to be adsorbed. From Figure 4.9, there is no difference of concentration between these three voidage. Compared to the theory, bed void fraction is measured minimizely to increase the breakthrough time of the column. At the large bed voidage, the concentration should get fast saturated. But, in this figure below, the three bed voidage are consumed at the same concentration and the time is too fast.

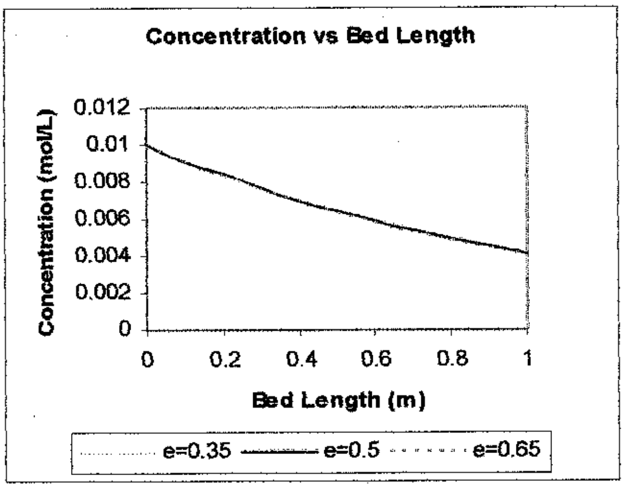


Figure 4.9: Concentration Profile at Various Voidage

In terms of temperature, when the voidage is 0.65, the temperature increase from 300 K to 301 K. As the voidage is bigger i.e 0.5, the temperature is more increase from 300 K to 302 K. This is followed by temperature increment to 303 K whenever voidage at 0.35 is used. Bed void fraction be measured more accurately and minimized to increase the breakthrough time of the column. A more accurate estimate of the bed void fraction would greatly enhance the accuracy of the model. The small increment between the temperatures is because of in liquid adsorption, the effect of temperature changes in not the major issue compared to the gas adsorption.

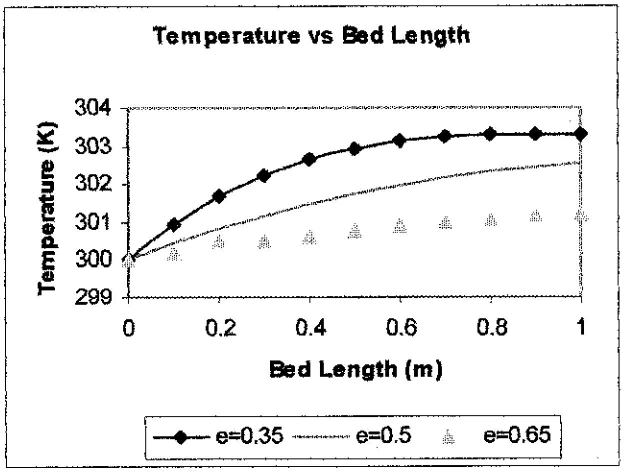


Figure 4.10: Temperature Profile at Various Voidage

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

Most researchers preferred to study the liquid adsorption by using pilot tests. This requires huge investment, provides limited knowledge on the adsorption behavior and exposes the personnel-in-charge to the hazardous environment during tests. Hence, prediction using adsorption modeling is a better option.

The dynamic model for fixed-bed adsorber was developed using the stage method. The adsorber was divided into 30 equal stages and the spatial derivatives at each stage were approximated using the backward finite difference method. The time derivatives were integrated using DSOLVE, which is a function in symbolic mathematics. The model took into account of the effects of velocity and heat, i.e. adiabatic and constant velocity conditions, and ideal Freundlich isotherm was assumed. The parameters and equilibrium data were obtained from Abdul Hameed REHAN, Pakistan Institute of Nuclear Science and Technology (1998) to simulate the ACV behavior of phenol-activated carbon adsorption system. The mathematical model was modified accordingly to differential heat balances only for adiabatic adsorption column proposed by Cooney (1974).

The transient analysis of phenol-activated carbon adsorption system using the dynamic model developed by using the Freundlich was reasonably not very well. The temperature and concentration profiles generated has comply with the theoretical predictions of a general adsorption system but not so accurate. When compared with the predicted breakthrough curves and experimental data for adsorption of phenol by activated carbon in fixed bed adsorber (Frank L.Slejko, 1985), the concentration and temperature profiles generated give reasonably not very precise predictions. Since this model has not been justified experimentally of its validity, it could not be used for quantitative prediction of the dynamic behavior of the phenol in activated carbon bed yet. However, it could be useful in the preliminary understanding of dynamic adsorption behavior due to its simplicity and less complicated computational procedure.

Knowing that temperature is an important factor in adsorption process, few initial operating temperatures were simulated. From the results, it is concluded that at high temperature, the adsorbed loading tends to be lowered and mass transfer is impeded. At smaller stages and less time running, the increment of temperature is not much give a big difference compared to the larger stages at more time running. On top of that, profiles were simulated using various fluid velocities and came to a conclusion that velocity is directly related to the adsorption rate; the higher the flow rate, the faster the bed gets saturated. Since stage method prediction accuracy depends on the mesh size, it is found that the prediction of concentration is more sensitive to mesh size than temperature.

Liquid phase isotherms are useful screening tools for determining the following:

1. The equilibrium capacity or approximate capacity at breakthrough, so a preliminary estimate of carbon usage can be made.
2. Changes in equilibrium adsorption capacity relative to the concentration of contaminants in the waste stream, and the effects of changes in waste stream concentration.
3. The maximum amount of contaminant that can be adsorbed by GAC at a given concentration.
4. The relative efficiencies of different types of carbons to identify which should be used for dynamic testing.

5.2 RECOMMENDATION

Experimental verification of the model developed is necessary to confirm the validity the model and quantify the deviation between experimental and simulation results. With this, strong confidence will be gained to apply the model as a design toll and aid particularly for phenol-activated carbon system.

Since the main purpose of model development is to determine the effects of velocity and heat of an adsorption process, other adsorption models, such as non-adiabatic-constant-velocity, adiabatic-variable-velocity and non-adiabatic-variable-velocity models to better represent real adsorption process.

Advanced adsorption modeling with inclusion of mass and heat transfer resistance and the axial dispersion term and other considerations are necessary for better quantitative prediction of the concentration and temperature profiles. A finer mesh size, i.e. more number of stages, could be applied to the bed for better prediction and higher accuracy of concentration and temperature profiles. Parametric studies should be carried out using the model developed for better understanding of the adsorption dynamic.

The MATLAB programming should allow more interaction with the user so that the program is more versatile and less rigid. In addition, GUI (graphical user interface) should be implemented for more user friendly interaction. Optimization on the program should be carried to reduce the workstation virtual memory usage. Software that can be used to run the same model is Fortran, SAS or C++. The time constraint for this project could be effectively managed by using high speed computer for give a fast result and more study can be made on the results.

Since the ACV adsorption model involves both time and spatial terms, NUMOL is by far the most recommended approach to solve the system numerically.

Some investigation is performed through this dynamics adsorption model. This research showed that the adsorption model is very sensitive to a few parameters. The bed length, bed void fraction and are three of the more sensitive parameters. Bed length and velocity are fixed by design, so it is recommended that the bed void fraction be measured more accurately and minimized to increase the breakthrough time of the column. A more accurate estimate of the bed void fraction would greatly enhance the accuracy of the model.

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APPENDIX A

COMPUTER PROGRAMS

Appendix A.1 : MATLAB Source Code: Main Program

```
%                    LIQUID ADSORPTION MODEL OF PHENOL VIA ACTIVATED CARBON
%                                          BY
%                                NURSAAIDAH BINTI HASSIM
%                          DEPARTMENT OF CHEMICAL ENGINEERING
%                             UNIVERSITI TEKNOLOGI PETRONAS

% This program is used to simulate dynamic ACV adsorption of Phenol on Activated Carbon



clear;
clc
disp (' Welcome to Dynamic Modeling of Phenol-Activated Carbon on Fixed Bed Adsoprtion System');

disp (' ');
disp ('    General Description of The Adsorption System:');
disp ('    The adsorption of phenol from wastewater on activated carbon adsorbent (charcoal)');
disp ('    Assuming the feed behaves as liquid, the phenol concentration in feed is approximately 0.01 mol/L');
disp ('    On top of that, the feed is fed at 300K and the bed is preheated to 300K at initial state.');

disp (' ')
disp ('    Please specify the following:');
h = input ('        Height of column [m]:');
a = input ('        Number of division in z-direction:');
tmax = input ('     Maximum run time [s]:');

%Initial and boundary conditions
disp (' ');
disp ('    Initial and boundary conditions specified for the system are as follows:')
disp ('    Phenol concentration in column at t = 0 [mol/L]: 0.00');
disp ('    Feed temperature at t = 0 [K]:300');
disp ('    Phenol concentration on in column at z = 0 when running [mol/L]:0.01 mol/L');
disp ('    Feed temperature at z = 0 when running [K]:300');

n = a +1 ; % number of equations to be solved
tn = tmax+1; % number of time nodes
dZ = h/a; % length of each division
ca = zeros (tn,n); % preallocation of memory for ca
T = zeros (tn,n); % preallocation of memory for T

%-----------------------------------------------------------------------------------------
% Method of Solution: Numerical Method of Lines
for i = 1:tn % time nodes
  for j = 1:n % spatial nodes
    if i==1 % initial condition
      ca(i,j) = 0;
      T (i,j) = 300;
      else if i>1 & j ==1 %boundary condition
```

```
        ca(i,j)= 0.01;
        T (i,j)= 300;
       else if i>1 & j>1
          cct = ca ((i-1),j);
          Tot = T ((i-1),j);
          cc = ca(i,(j-1));
          To = T(i,(j-1));
          X = adsorp_funcT(cc,To,dZ,cct,Tot);
          Dcp = X (1,1);
          DTc = X (2,1);
          f = strcat('Dcp = ', char(Dcp));
          g = strcat('DTc = ', char(DTc));
          S = dsolve (f,g, 'cp(0)=0', 'Tc(0)=300');
          syms t;
          p = subs (S.cp, {t}, {i});
          r = subs (S.Tc, {t}, {i});
          if p < 0
            p = 0;
          end
          ca(i,j)= p
          T (i,j)= r
        end
      end
    end
  end
end

%-----------------------------------------------------------------------------------------------------------
%Data Viewing and Profiles Plotting
met = 1;
while met
  disp (' ')
  disp (' How do u want to view the data?');
  method = input (' [1] Raw Data or Profiles with respect to [2] bed length or [3] run time:');
  switch method
    case 1 % raw data
        Conc_Data = ca
        Temp_Data = T
    case 2  % wrt bed length
        b = input (' Please specify bed length at which you would like to view the profiles [s]:');
          if b > h
            disp ('Error: Bed length of interest is out of the range.');
          continue;
          else
            x = 0:tmax; % run time
            stg = (b/dZ)+1;
            plot (x,ca(:,stg)) % concentration profile
            title ('Concentration Profile')
            xlabel ('Run time (s)')
            ylabel ('Concentration (mol/L)')
```

```
          pause
          plot (x, T(:,stg)) % Temperature profile
          title ('Temperature Profile')
          xlabel ('Run time (s)')
          ylabel ('Temperature (K)')
        end
  case 3 % wrt time
      tv = input (' Please specify time at which you would like to view the profiles [s]:');
        if tv > tmax
          disp ('Error: Time of interest is out of the range.');
        continue ;
        else
          x = 0:dZ:h; % bed length
          tau = tv+1;
          plot (x,ca(tau,:)) % concentration profile
          title ('Concentration Profile')
          xlabel ('Bed Length (m)')
          ylabel ('Concentration (mol/L)')
          pause
          plot (x, T(tau,:)) % Temperature profile
          title ('Temperature Profile')
          xlabel ('Bed Length (m)')
          ylabel ('Temperature (K)')
        end
 end
 met = input (' Do you want to continue? [0/1]:');
end
%-------------------------------------------------------------------------------
```

Appendix A.2: MATLAB Source Code: Adsorption Functions

```
%                    LIQUID ADSORPTION MODEL OF PHENOL VIA ACTIVATED CARBON
%                                            BY
%                                 NURSAAIDAH BINTI HASSIM
%                              DEPARTMENT OF CHEMICAL ENGINEERING
%                                 UNIVERSITI TEKNOLOGI PETRONAS

% This program contains mathemtical model for dynamic ACV adsorption model of Phenol on Activated Carbon

function X = adsorp_funcT(cc,To,dZ,cct,Tot)

% equilibrium data and other constants
k0 = 27.68; % constant of phenol,(mg/g)(L/mg)
n = 3.472; % constant of phenol(dimensionless)
pb = 230; % bulk density of absorbent,kg/m3
delH = -10902; %J/mol
Cs = 1520; %heat capacity of adsorbent bed, J/kg.K
Cf = 197; % heat capacity of fluid, J/mol.K
v = 1; %m/s
e =0.5; %voidage fraction; dimensionless

% Define symbolic object
syms QA;
syms Told;
syms C;
syms cp;
syms delZeta;
syms Tc;
syms Cz;
syms Toldz;

% basic equations
QA = k0*(C*exp(1/n));

% Diffentiation terms in model
dqadca = diff (QA, C);
dqadT = diff (QA, Told);

% substitute numerical values into Material Balances
A = e+(pb*dqadca);
B = dqadT;
D = (delH/Cf)*((1-e)/e)*(dqadca);
E = 1+((1-e)/e)*(Cs/Cf)+((1-e)/e)*(delH/Cf)*(dqadT);

F = [A B; D E];
G = [-v*((cp-Cz)/delZeta) ; -v*((Tc-Toldz)/delZeta)];
```