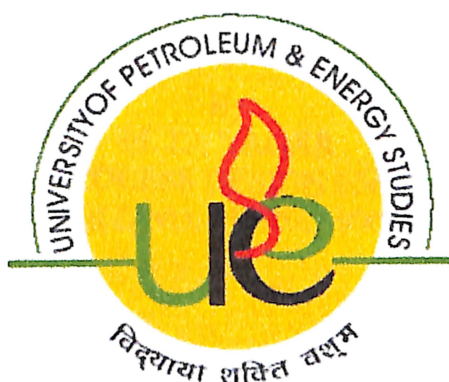# MODELING AND SIMULATION OF PRESSURE SWING ADSORPTION USING MATLAB

By
EKTA NAGAR
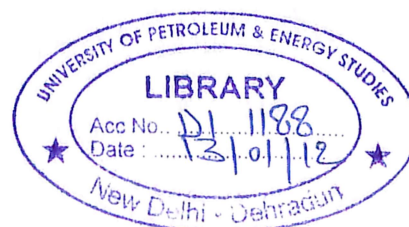
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University of Petroleum & Energy Studies
Dehradun
April, 2011

CERTIFICATE

This is to certify that the work contained in this thesis titled "**Modeling and Simulation of Pressure Swing Adsorption using Matlab**" has been carried out by Ekta Nagar (R670209006) under my supervision and has not been submitted elsewhere for a degree.

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ABSTRACT

Adsorptive separation is a widely used process in chemical industries. Pressure swing adsorption is one of the important methods used for separation and purification of gaseous mixtures. Pressure swing adsorption is an energy efficient and economical gas separation process compared to other separation process. The project involves developing a mathematical model and simulation studies on multi-component and multi bed pressure swing adsorption process to obtain optimum parameters to get maximum yield from the process. The product purity and recovery of the gas being separated by PSA process are significantly affected by process parameters and design parameters such as adsorption pressure, flow rate, cycle time, and pressurization and blow down steps time, bed length and porosity etc. in this work the binary component, dual bed pressure swing adsorption cycle under different conditions. A valve equation is incorporated into the simulation to consider dynamic change of the bed pressure during the pressurization and blow- down steps of a simple two bed air separation pressure swing adsorption (PSA) process.

ACKNOWLEDGEMENT

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Nomenclature

A   Cross-sectional area of the bed, m^2

b_i Langmuir isotherm constant for component i, atm

C_i Concentration of component i, $kmol/m^3$

D   Particle diameter, m

D_e Diffusivity, m^2/s

k_i LDF coefficient for component i, s^{-1}

L   Bed length, m

M_i Molecular weight of component i

P   Adsorption pressure, atm

p_i Partial pressure of component i, atm

q_i Adsorbed concentration of component i in solid phase, $kmol/m^3$

R   Gas constant, m^3 atm/Kmol-K

T   Temperature, K

t   Time, s

u   Interstitial velocity, m/s

V   Superficial velocity, m/s

y_i Mole fraction of component i

y_{feed} mole fraction in feed stream

y_{purge} mole fraction in purge stream

z   Bed length, m

Greek symbols

ε Bed porosity

μ Viscosity of gas

ρ density of gas

Superscript

*   Equilibrium

Subscript

i   Component

Chapter 1

Introduction

Adsorption is most often used as a purification process to remove small to medium amount of material from gas mixture. In the adsorption process one or more adsorbate from mixture, having high affinity to adsorbent adsorbs on solid surface. There are different adsorption processes used for separation of gas mixture with moderate to high concentration of adsorbates. Pressure Swing Adsorption (PSA) is one of the rapidly growing processes used to separate and purify gas in medium to large scale. It is applied extensively in various industrial applications due to its low energy requirements and cost advantages.

There are several methods used in chemical industries and petroleum refineries for separation of gaseous mixture at large scale such as cryogenic distillation, gas absorption and temperature and pressure swing adsorption etc. These separation methods can be classified as adsorptive and non-adsorptive separation processes. These methods are discussed here in brief.

1.1 Non-Adsorptive Gas Separation Processes

There are several non-adsorptive gas separation processes such as cryogenic distillation, gas absorption etc, to separate gaseous mixtures in chemical and other industries.

Cryogenic distillation process is widely used in air separation at large scale. This process is based on difference of boiling point of different components of the mixture. In this process gas mixture is cooled down to a very low temperature so that gas converts to liquid. In this process product stream is also obtained in liquid form. The main disadvantage of this process is consumption of high energy and capital cost. However at high capacities, this technique is still the most competitive.

In the gas absorption process gas mixture is separated by a liquid in which a soluble component absorbed in the liquid. This process is based on the solubility of the solvent used. The main disadvantage of this process is the regeneration of solvent and recovery of solute. The solute is recovered from the liquid by distillation or desorption process. Regeneration of solvent requires a large amount of energy.

1.2 Adsorptive Gas Separation Processes

Adsorptive gas separation processes are carried out in fixed-bed adsorbers which contain porous adsorbent particles. These are continuously increasing in chemical industries. There are many adsorptive gas separation processes used in chemical industries such as pressure swing adsorption, temperature swing adsorption process. These methods are categorized as follows.

1.2.1 Categorizations of adsorptive separation processes

Based on method of adsorbent regeneration

The adsorbent can be regenerated by a number of methods. In the temperature swing adsorption (TSA) process, the adsorbent is regenerated by heating provided by preheating a purge gas. In the pressure swing adsorption process, the adsorbent is regenerated by decreasing the pressure in the bed followed by purging a fraction of product stream at low pressure. In the inert purge process, the adsorbent is regenerated by passing a non-adsorbing gas through the bed.

Based on feed composition

The separation processes may be divided into bulk separation and purification. The bulk separation involves adsorption of a fraction, more than 10% by weight from a gas stream. And purification involves adsorption of less than 10% by weight of a gas stream (Keller, G.E., 1983)

Based on mechanism of separation

The adsorptive separation is achieved by one of the three mechanisms: (1) steric, (2) kinetic, and (3) equilibrium. Steric mechanism is related to the molecular sieving property of adsorbents. In this mode of separation only small and properly shaped molecules can diffuse into the adsorbent. Kinetic separation is achieved by the difference in diffusion rates of different molecules. Equilibrium separation processes is based on the equilibrium of different component of the mixture.

1.2.2 Different adsorptive separation methods

For gas separation and purification a number of adsorptive processes are used in chemical industries. Some of them are listed below:

Temperature-swing adsorption: Temperature swing adsorption process is mainly used for purification purpose. In this process, the bed is regenerated by passing a preheated purge gas. The limitation of this process is that regeneration takes long time.

Pressure-swing adsorption: This is the widely used process for gas separation. In this process the bed is regenerated by lowering the pressure and passing a purge stream through the bed.
Inert purge: In this process, an inert gas or weakly adsorbed gas is used to regenerate the bed.
Gas chromatography: Gas chromatography is used in laboratory for analysis of gases. It is also used in many commercial processes for large scale separation.

Moving bed processes: Moving bed process is a steady state process in which flow rate and composition of all stream entering and leaving the bed are constant. In these processes the gas mixture and solid sorbent are contacted in a countercurrent movement.

Out of the adsorption separation processes mentioned, Pressure swing adsorption is the most widely used process. This report deals with this unique method of separation technology.

1.3 Pressure Swing Adsorption (PSA) Process

The above few process discussed here, suffer from high capital cost and large amounts of energy used for operating process. For the separation of medium and small volumes of gas, adsorption-based processes may improve the overall economics due to lower operating costs. Pressure swing Adsorption (PSA) is one of the most significant processes for the separation of gases. In some fields, PSA technology has entirely replaced the conventional process; in other fields it has become more and more competitive at larger and larger scales.

1.3.1 Process description

PSA is a cyclic process where adsorption is carried out at higher pressure and regeneration of adsorbents is achieved by lowering the bed pressure followed by purging. This process is based on the differences in adsorption thermodynamics and kinetics between adsorbent and different gas components present in the gas mixture. Adsorbents used in the process are selected on the basis of composition of gas and the objective of separation. Some commonly used adsorbents are zeolites, carbon molecular sieves, silica gel and activated carbons. Generally PSA are operated either on the basis of equilibrium or kinetic based separation, depending on the adsorbent-adsorbate system. In the equilibrium based operation, the strongly adsorbed component adsorbs comparatively in large amounton the adsorbent surface. The raffinate contains the less strongly adsorbed species. In case of kinetic based separations, the separation obtained is due to a difference in the diffusion rate of the components. Separation of Nitrogen from air is an important example of this class. A typical PSA system contains two or more beds. Each bed goes through the same steps. For a two bed PSA process, the basic steps involved are pressurization, high pressure adsorption, counter current blow down and purge. In the pressurization step, bed is pressurized by high pressure feed in short time. In the adsorption step, high pressure feed passes through the bed and strongly adsorbing component adsorbs in large amount comparatively to the less adsorbing component. Separation takes place in this step. In the blow down step, bed is depressurized up to atmospheric pressure. In the purge step after blow-down, a fraction of the purge stream from one bed passed through another bed counter current to the direction of feed. After the purge the bed is again ready for next cycle. Though these are the basic steps, different cycles may be constituted by incorporating different steps such as pressure equalization, inert

purge etc. based on the system and the desired purity and recovery of the product. The performance of the separation process is measured by three parameters: (1)product purity (2) product recovery (3)adsorbent productivity.

1.3.1 Industrial applications

PSA is relatively inexpensive, capable of producing products of desired purity and is suitable for handling relatively small to medium throughputs of gas streams.

Some key industrial applications include oxygen, nitrogen, hydrogen purification, gas drying, solvent vapor recovery, fractionation of air, separation between linear and branched hydrocarbons and recovery of aromatic hydrocarbons (Ruthven, D.M., 1984).

1.4 Objective of the project

The work involves a model based studies of Pressure Swing Adsorption process and verification of the model. It involves developing of a mathematical model, its validation and studies of the effect of different parameters.

The main objectives of this work are as follows.

1. To compare the dual bed four steps PSA cycle with the traditional Skarstrom two bed, four-step cycle (Hassan et al., 1986)

2. To study the effect of process parameters like bed pressure, adsorption pressure, height of the bed and valve coefficients on the product purity, recovery and productivity.

Chapter 2
Literature Review

Pressure swing adsorption (PSA) is a cyclic process used for the separation of gas mixtures. PSA processes have been developed for a variety of application, including oxygen enrichment from air, hydrogen purification and air drying. Now a day this process is used at large scale separation of gases. Generally a pressure swing adsorption systems consist two or more beds of sorbents. Skarstrome (1960) and Guerin de Montgareuil (1964) proposed two different PSA process for separation of air and air drying. In the Skarstrom cycle the saturated bed is regenerated by purging at a low pressure by a fraction of the product stream, and in the Guuerin-Domine cycle, desorption is carried out vacuum. These PSA cycle gave modest separation of oxygen and nitrogen. However, Skarstrome cycle was very efficient in air drying process (Skarstrome, 1960). Without major modification, the Skarstrom PSA cycle was immediately accepted for commercial use in air drying as well as other purification processes. The Skarstrom cycle uses two bed apparatus. Feed is introduced to the first bed to pressurize the bed and after pressurization; adsorption step starts in which a fraction of the feed adsorbed on the bed. After the adsorption step, the first bed is depressurized to atmospheric pressure. At the same time the compressed feed mixture is passed through the second bed to pressurize it. After pressurization, adsorption step starts in the second bed. A fraction of the purified puoduct from the second bed is passed through the first bed, countercurrent to the feed direction, to purge the bed at atmospheric pressure. After the purge, the first bed is again ready for the next cycle. Thus each bed undergoes two half-cycles, the times of which are equal.

Guerin-Domine cycle (Guerin de Montgareuil and D. Domine, 1964) consist three step. Depending on the nature of the mixture to be separated, this cycle can vary in the number of beds. In the pressurization step only feed end opens to pressurize the bed. Blow down in the first bed is achieved by the second bed in the co current direction of feed. Last step is evacuation from the midpoint of the bed when weak adsorptive is withdrawn. Using 5A zeolite in the Guerin-Domine cycle, excellent results were obtained on air separation.

For modeling and simulation purpose of a PSA cycle different researchers used different assumptions. Carter and Wyszynski (1983) assumed the bulk gas is in instantaneous equilibrium with the adsorbent during all four steps in the cycle. Few others researchers also studied the equilibrium-based PSA units for oxygen production from air (Fernandez and Kenney, 1983, Ruthven, 1984, Hill and Knaebel, 1985, Hayashi, et al, 1985, Kayser and Knaebel, 1986 and Sircar 2002). Linear driving force (LDF) approximation was suggested by Glueckauf and Coates (1947). Shendalman and Mitchell (1972) were the first to use linear driving force approximation in pressure swing adsorption modeling. The simulation of Mitchell and Shendalman (1972), Carter and Wyszynski (1983), Chihara and Suzuki (1983), Raghavan et al., 1985, Farooq et al., 1989, Raghavan and Ruthven (1985), and Hassan and Ruthven, (1986) all use frozen solid approximation. In this approximation it was assumed that pressure changes instantly in the pressurization and blow-down step to the predetermined value and mass transfer between gas and solid phase during these two steps is neglected. Chou et al., 1992 and Cheng-Tung Chou and Wen-Chun Hung (1993) incorporated a valve equation into the simulation of a pressure swing adsorption process and showed that valve equation approach gives the pressure history of the whole process and also obtain good agreement with the experimental data for the separation of air

over 5A zeolite and carbon molecular sieve (CMS). Few researchers have studied the effect of process parameters on product purity and recovery for air separation and also suggested the optimized process conditions (Mendes et al., 2000 and Jain et al.. 2003).

PSA process is more efficient than the TSA process for drying of air and industrial gases (Skarstrom, 1972). Unlike air drying, some processes such as hydrogen purification. air separation and the removal of longer chain hydrocarbons from natural gas also use PSA technology at large scale. Purities and recoveries are changed by using different steps such as co-current depressurization, pressure equalization (Doshi et al., 1971), pretreatment beds and purge by strong adsorptive component (Tamura, 1974) in this basic Skarstrom cycle.

Chapter 3

Process Modeling

When a PSA cycle is started, each bed undergoes a series of steps in the order in which the cycle is constituted. As each bed passes through each step of the cycle, it is enough to make and solve a model for a single bed. The model equations for each step of the cycle are same but initial and boundary conditions are different for each step. The final conditions in the bed during a step are used as the initial conditions for the next step.

3.1 Assumptions in Making Model Equations

While doing the model formulation, the following assumptions have been made.

- Gaseous mixture is considered to be ideal.

- The fluid is assumed to be in an axial plug flow manner.

- Axial dispersion as well as radial distribution is neglected.

- The system is assumed to operate at isothermal conditions.

- The equilibrium relationships for both the adsorbate components are represented by binary Langmuir isotherms.

- Mass transfer between fluid and the solid particle is described by linear driving force (LDF) approximation.

- Pressure drop across the adsorbed bed is described by Ergun's Law.

3.2 Mass Balance

Component Mass Balances:

Component balance across an element of width ΔZ is:

Input = Output +Accumulation within the bulk phase + Amount adsorbed on to the Adsorbent

$$C_i A V_{in} - C_i A V_{out} = \varepsilon A(\Delta Z) \frac{\partial C_i}{\partial t} + (1-\varepsilon) A(\Delta Z) \frac{\partial q_i}{\partial t} \qquad 3.1$$

This gives

$$\frac{\partial(VC_i)}{\partial Z} + \varepsilon \frac{\partial C_i}{\partial t} + (1-\varepsilon) \frac{\partial q_i}{\partial t} \qquad 3.2$$

Ideal Gas Law

$$P \quad \sum_{i=1}^{n} C_i RT \qquad 3.3$$

Adsorption kinetics

The following linear driving force (LDF) model expresses the adsorption rate equation for

diffusion control process.

$$\frac{\partial q_i}{\partial t} = \frac{\Omega D_e}{r^2} (q_i^* - q_i) \qquad 3.4$$

The adsorption equilibrium between the gas and adsorbed phase is expressed by Langmuir

model. For n components the isotherms are expressed by the extended Langmuir model.

$$q_i^* = \frac{q_{s,i} \, b_i p_i}{1 + \sum_{j=1}^{n}(b_j p_j)} \qquad 3.5$$

Pressure Gradient Equation

If the gas flows at high velocity through a packed bed then the steady state momentum balance of

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gas flow is expressed by Ergun's law.

$$-\frac{\partial P}{\partial z} = 150\frac{\mu(1-\epsilon)^2}{\epsilon^2 d_p^2}u + 1.75\frac{\rho(1-\epsilon)}{\epsilon d_p}u^2 \qquad 3.5$$

Where

$$\frac{V}{\epsilon} \qquad 3.6$$

Valve Equation

Valves play an important role in any PSA process. Generally, valve equations are used for the calculation of flow rates at the ends of a bed in terms of the pressure gradient available across the valves. The entire performance of a PSA depends on pressure levels. Valve equation relates the flow through valve to pressures on its upstream and down stream sides. The pressures in the feed, raffinate (desired product) and extract (exhaust) tanks are assumed to be constant with time. The following equations used in the present work.

$$V(z=0,t) = C_{v1}\left(\frac{P_f-P(z=0,t)}{\frac{P(z=0,t)}{RT}\sum_{j=1}^n(M_iy_i(z=0,t))}\right)^{\frac{1}{2}} \qquad 3.7$$

$$V(z=L,t) = C_{v2}\left(\frac{P(z=L,t)-P_{ref}}{\frac{P(z=L,t)}{RT}\sum_{j=1}^n(M_iy_i(z=L,t))}\right)^{\frac{1}{2}} \qquad 3.8$$

3.3 Governing Equations

The model equations for a general n-component system can be written as follows.

From overall material balance

$$\frac{\partial P}{\partial t} = -u\frac{\partial P}{\partial z} - P\frac{\partial u}{\partial z} - \frac{(1-\epsilon)}{\epsilon}RT\sum_{j=1}^m\frac{\partial q_i}{\partial t} \qquad 3.9$$

From Component balance

$$\frac{\partial y_i}{\partial t} = -u\frac{\partial y_i}{\partial z} - \frac{(1-\epsilon)}{\epsilon}\frac{RT}{P}\frac{\partial q_i}{\partial t} - \frac{(1-\epsilon)}{\epsilon}\frac{RT}{P}y_i\sum_{j=1}^m\frac{\partial q_i}{\partial t} \qquad 3.10$$

The LDF expression for adsorption rate

$$\frac{\partial q_i}{\partial t} = \frac{\Omega D_c}{r^2}\left(\frac{q_{s,i}b_i Py_i}{1+\sum_{i=1}^{n}(b_j Py_i)} - q_i\right)$$ 3.11

Momentum balance of gas flow

$$-\frac{\partial P}{\partial z} = 150\frac{\mu(1-\epsilon)^2}{\epsilon^2 d_p^2}u + 1.75\frac{\rho(1-\epsilon)}{\epsilon d_p}u^2$$ 3.12

Boundary Conditions

The following boundary conditions are used to solve the above set of differential and algebraic

equations.

For Pressurization

At $z = 0$, $y_i(z=0, t) = y$, $¥$ $t \in (0,t)$, $i=1,2,\ldots\ldots n$ 3.13

$z=L$, $\frac{\partial P}{\partial z} = 0$ 3.14

$z=L$, $u(z=L, t) = 0$; $¥ t \in (0,t)$ 3.15

The inlet velocity (at $z = 0$) is obtained from the valve equation, and the flow rate at the closed

end ($z = L$) is always zero.

For production

At $z = 0$, $y_i(z=0,t) = y_{feed}$; $¥ t \in (0,t)$, $i=1,2,\ldots\ldots n$ 3.16

At $z=L$, $\frac{\partial yi}{\partial z} = 0$; $i=1,2,\ldots\ldots n$ 3.17

The velocity at $z=0$ is the preset feed velocity, and the velocity at $z=L$ is calculated from valve

equation.

For Blowdown

At $z=L$, $\frac{\partial yi}{\partial z} = 0$; $i=1,2,\ldots\ldots n$ 3.18

$u(z=L, t)=0;$ $\quad\quad\quad\quad\quad\quad$ ¥ t ∈ (0,t) $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ 3.19

The outlet velocity at (z=0) comes from the valve equation, and the flow rate at the closed end

(z=L) is zero.

For Purge

At z=0, $\dfrac{\partial yi}{\partial z} = 0;$ $\quad\quad\quad\quad\quad\quad$ i=1,2,........n $\quad\quad\quad\quad\quad\quad\quad$ 3.20

At z = L, $y_i(z=L, t) = y$ $\quad\quad\quad$ ¥ t ∈ (0,t), i=1,2,......n $\quad\quad\quad\quad$ 3.21

The velocity at z=L is the preset purge velocity, and the velocity at z=0 is calculated from yhe

valve equation.

Initial Conditions

The following initial conditions for the start up of the cyclic operation with a clean bed are used to

solve the set of differential and algebraic equations for first cycle.

$y_i(z, t=0) = 0; P(z, t=0) = 1$ atm $\quad\quad\quad$ i=1,2,......n $\quad\quad\quad\quad\quad\quad\quad$ 3.22

$q_i(z, t=0) = 0;$ $\quad\quad\quad\quad\quad\quad\quad\quad$ i=1,2,......n $\quad\quad\quad\quad\quad\quad\quad\quad$ 3.23

For subsequent cycles, the condition of the bed at the end of the previous cycle is taken as the

initial condition of the bed for the new cycle.

$y_i^{k+1}(z, t=0) = y_i^k(z, t=t_c); P^{k+1}(z, t=0) = P^k(z, t=t_c);$

$q_i^{k+1}(z, t=0) = q_i^k(z, t=t_c);$ $\quad$ ¥ z ∈ (0,L), i=1,2,.....n; k=1,2,.....m $\quad\quad\quad$ 3.24

3.4 Performance Measures for the PSA Process

The separation performance of a PSA process is measured on the basis of product purity and

product recovery once the cyclic steady state is reached. (Nilchan and Pantelides, 1998)

1. Product purity in terms of the desired component is expressed as the ratio between the amount

of desired component collected in the product over a cycle and the total amount of the product.

$$\text{Purity} = \frac{\int_0^{tc} u(L,t)*y(L,t)dt}{\int_0^{tc} u(L,t)dt} \qquad\qquad 3.25$$

2. The Recovery of desired component is defined as the ratio of amount of desired component collected in the product stream over a cycle and the amount of desired component fed to the bed over the same cycle.

$$\text{Recovery} = \frac{\int_0^{tc} u(L,t)*y(L,t)dt}{\int_0^{\frac{tc}{2}} u(o,t)*y(0,t)dt} \qquad\qquad 3.26$$

3.5 Numerical method

The mathematical model of the PSA process is represented by a system of partial, differential and algebraic equations (PDAEs). This set of non-linear PDAEs (Partial Differential and Algebraic Equations) was reduced to non-linear simultaneous algebraic equations by discretizing the equations in both time and spatial direction. Here a first order finite backward difference method is used for spatial direction discretization to convert partial differential equation in ordinary differential equation and implicit euiler technique for converting set ODE into algebraic equations. These resultant discretized equations are solved by using Newton-raphson method. A MATLAB code is developed to solve the model equations.

Chapter 4

Simulation studies of breakthrough curve

In this work for the study of breakthrough curve a code is programmed in MATLAB for simulation purpose. Here an air-CMC (carbon molecular sieves) system is used to obtain breakthrough curve. It was assumed that the feed air contains only oxygen and nitrogen and other components of air like argon, carbon dioxide and water vapor are already removed from the feed.

4.1 Breakthrough curve

The breakthrough curve gives the response of initially cleaned bed, to constant or time invariant composition of feed. Breakthrough curve provides us the information on how the effluent concentration varies with respect to time. Break through curve for a gas is obtained by the solution of the mass balance equation for both the bed and sorbent particle, along with the equilibrium isotherm. The equation developed here gives the concentration at each and every point inside the column. The concentration profile of strongly adsorbed component at the outlet with respect to time gives the breakthrough curve shown in figure 4.1. Here to simulate breakthrough curve for single component, data used is tabulated in Appendix I (Hassan et al., 1986).

The shape or the width of the breakthrough curve is crucially important in the design of adsorbers and cyclic separation processes. A sharp concentration front is desirable for efficient separation (Yang R.T., 1987). When the concentration reaches some limiting permissible value, or break point, the flow is stopped or diverted to a fresh adsorbent bed. The break point is often taken as a relative concentration of 0.05. The point on the given curve at a time of 60 seconds is known as the break point. For the given process condition the adsorption time should be less than or equal to the break point. The nature of the breakthrough curve largely depends on the adsorbent and the

adsorbate properties, such as diffusivity, porosity, bed length etc. Thus for a different adsorbate-asorbent system the curve would be different from the one shown.
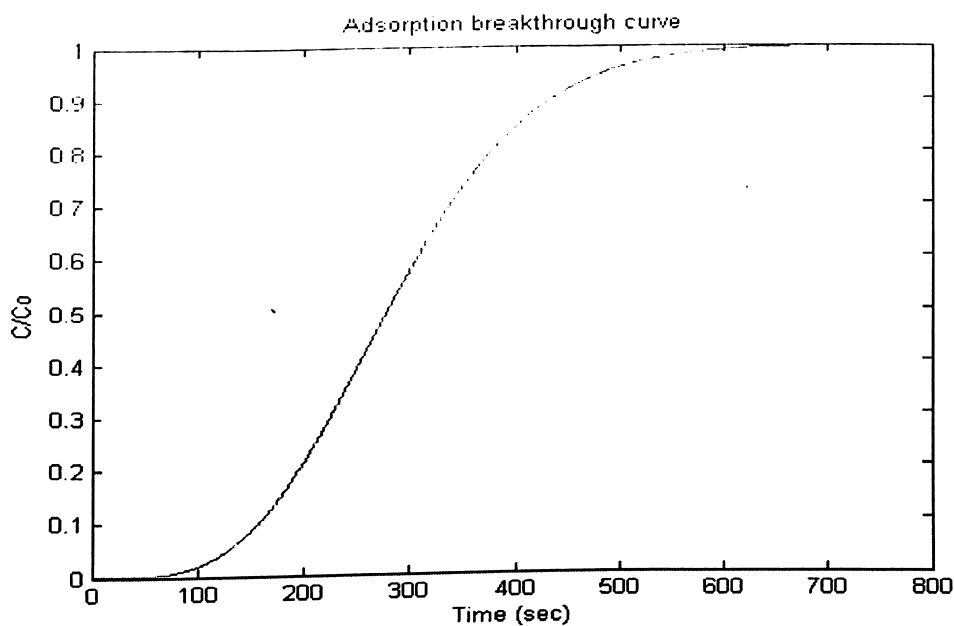
Adsorption breakthrough curve

Figure 4.1 Adsorption breakthrough curve for oxygen on CMS with flow rate of 2.0 SLPM

4.2 Bed concentration Profile

In fixed-bed adsorption, the concentrations in the fluid phase and the solid phase change with time as well as with position in the bed. At first, most of the mass transfer takes place near the inlet of the bed, where the fluid first contacts the adsorbent. To know the nature and amount of variation of the concentration inside the bed, figure 4.2 shows the concentration profile of strongly adsorbing component along the length of the column at different time. As the adsorption progresses further the concentration profile becomes horizontal, thus indicating saturation of the adsorbent. To obtain the concentration profile parameter was used from Appendix I.
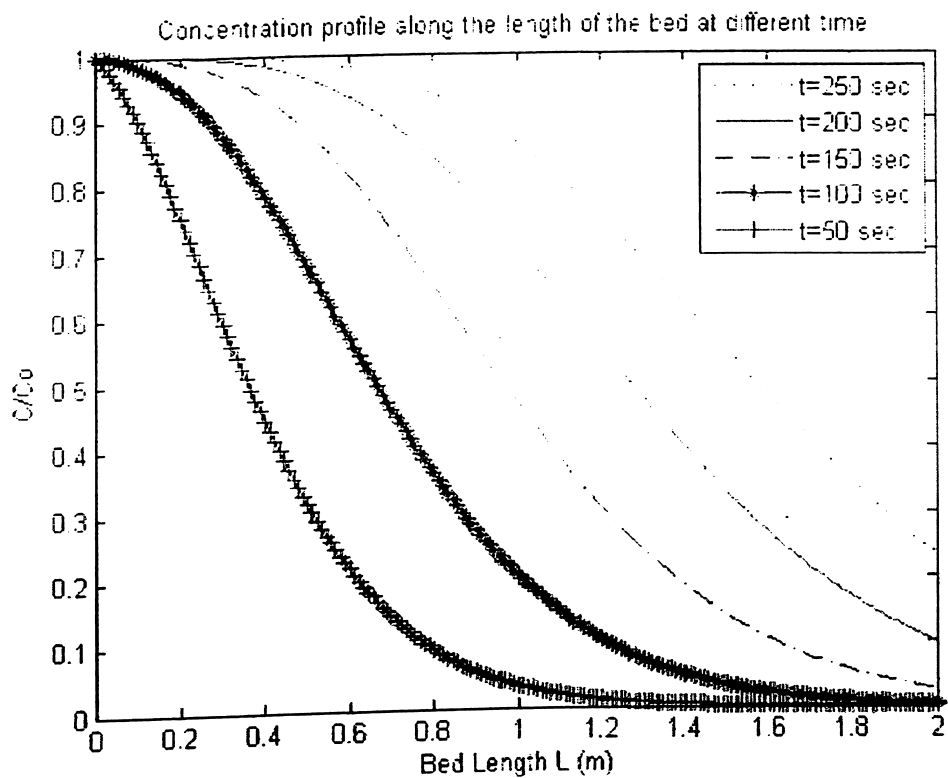
Figure 4.2 Concentration profile of oxygen along the length of the bed at different time with flow rate 2.0 SLPM

4.3 Effect of various parameters

Operating and design variable highly affects the adsorption process. Breakthrough curve and amount adsorbed gets changed with change in these parameters. The break point and the slope of the breakthrough curve would change with the change in various parameters of the system. The variations in the breakthrough curve are discussed below:

4.3.1 Effect of change in column length

By increasing the length of the column there would be more amount of adsorbent available for adsorption of the adsorbate. Thus it will take more time for the break point to be achieved and thus, the breakthrough curve will shift to the right. Long adsorption column require more energy

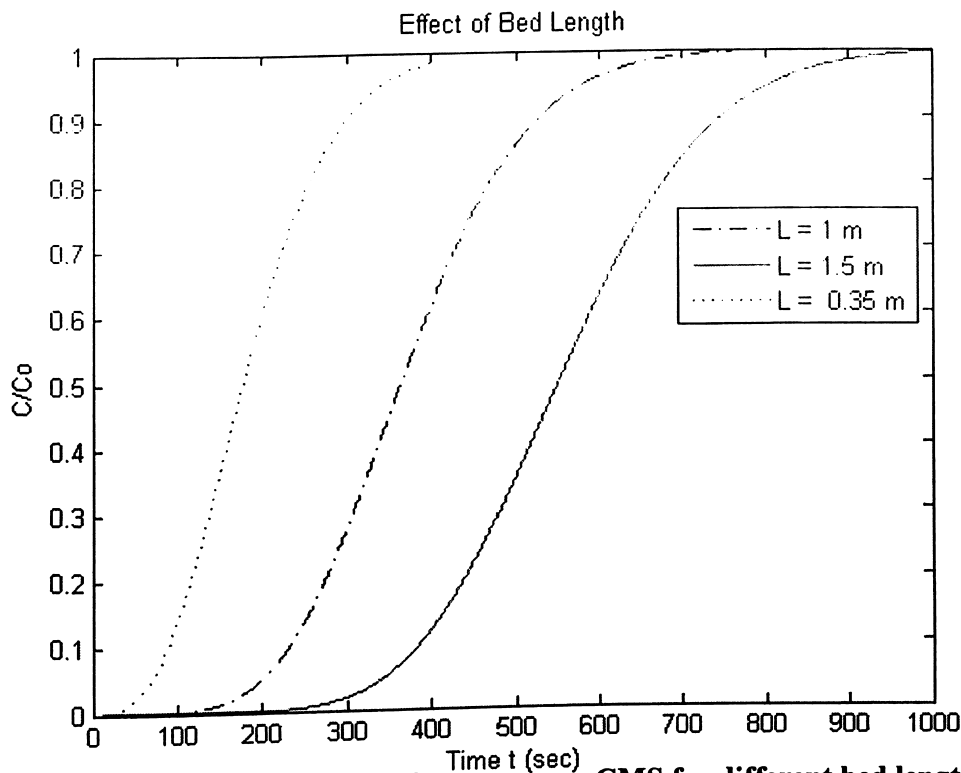because due to high pressure drop. The variation is shown in figure 4.3 keeping other parameters constant.

Effect of Bed Length

Figure 4.3 Breakthrough curve for oxygen on CMS for different bed length with flow rate of 2.0 SLPM

4.3.2 Effect of change in Bed Porosity

Bed porosity is the ratio of void volume of the bed to the total volume of the bed. The porosity can be changed by selecting adsorbent particle size and shape. Bed porosity significantly affects the product purity and recovery. It is observed that decrease in bed porosity i.e., increase of adsorbent in the bed of given size which results in higher adsorption capacity. If the adsorption capacity of the bed is more, the highly adsorbing component of mixture gets adsorbing considerably more than less adsorbed component and enhances percentage of less adsorbing component in the exit stream. The effect of bed porosity on breakthrough curve is shown in figure 4.4
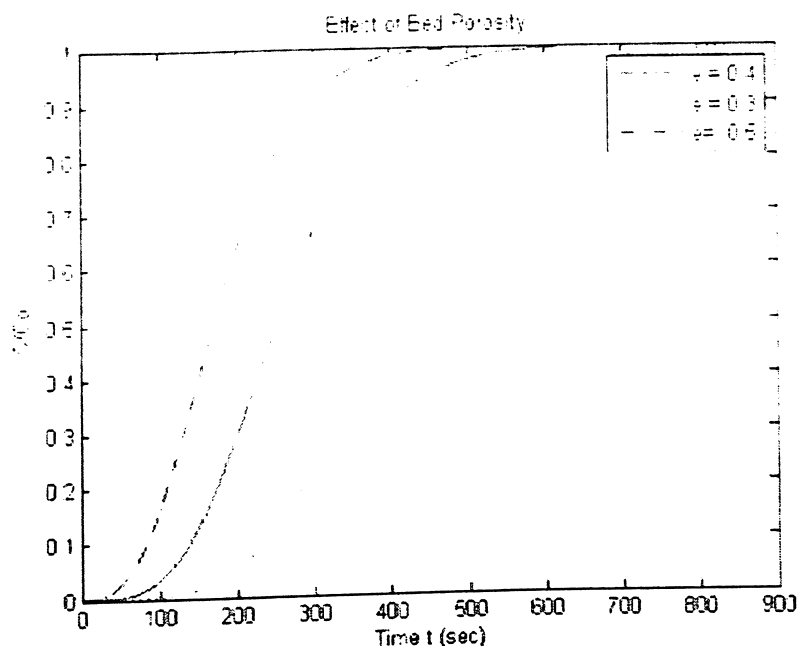
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Figure 4.4 Breakthrough curve for oxygen on CMS at different porosity of the bed with flow rate of 2.0 SLPM

4.3.3 Effect of change in adsorption pressure

Pressure has a pronounced effect on the adsorption of any compound. According to the isotherms used, the amount of the gas that gets adsorbed on to the adsorbent during adsorption steps is dependent on its partial pressure in bulk phase. This amount increases with increase of its partial pressure. So with increase of adsorption pressure, the amount of relatively highly adsorbed component that gets adsorbed also increases. Increasing the pressure increases the rate of adsorption for both oxygen and nitrogen. Thus, the break point is achieved much earlier and thereby the breakthrough curve shifts to the left. The variation in outlet concentration of oxygen with pressure is shown in figure 4.5. Same parameters used to calculate pressure effect.
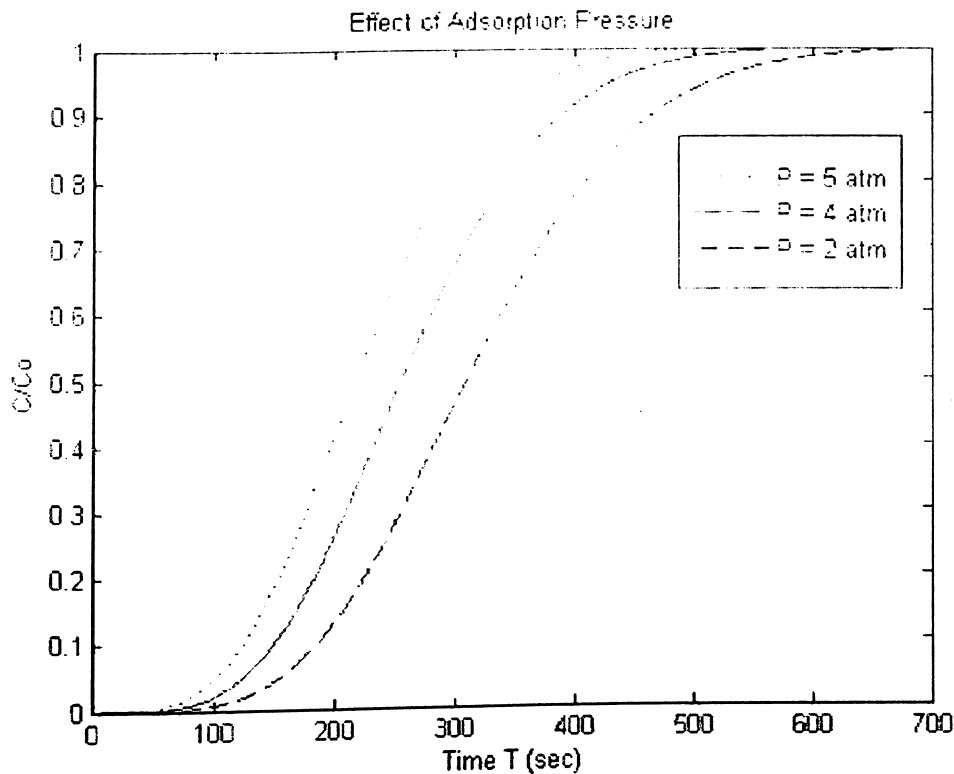
Figure 4.5 Breakthrough curve for oxygen on CMS at different adsorption pressure with flow rate of 2.0 SLPM

4.3.4 Effect of change in flow rate

Increasing the flow rate of the feed decreases the residence time of the adsorbate to get adsorbed on the surface of the adsorbent. With high flow rates most of the component passes out in the product without getting adsorbed and thus separation is affected. The effect of this can be noticed by the change in the breakthrough curve given in figure 4.6. The parameters used to calculate the effect of flow rate are given in Appendix I.
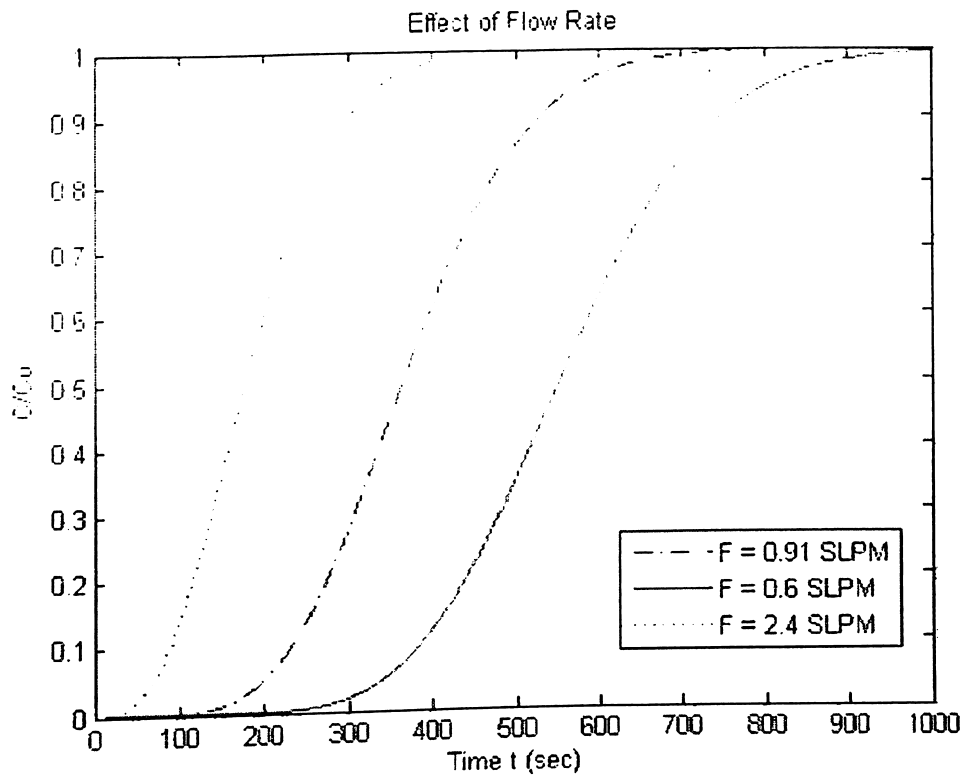
Figure 4.6 Breakthrough curve for oxygen on CMS at different flow rate.

4.3.5 Effect of constant velocity

In the adsorption process velocity within the bed varies due to loss of material in adsorption and due to pressure drop along the bed. Due to adsorption velocity within the bed decreases. Constant velocity throughout the bed gives the earlier breakthrough compared to variable velocity. This comparison is shown in figure 4.7 keeping other parameters fixed as tabulated in Appendix I.
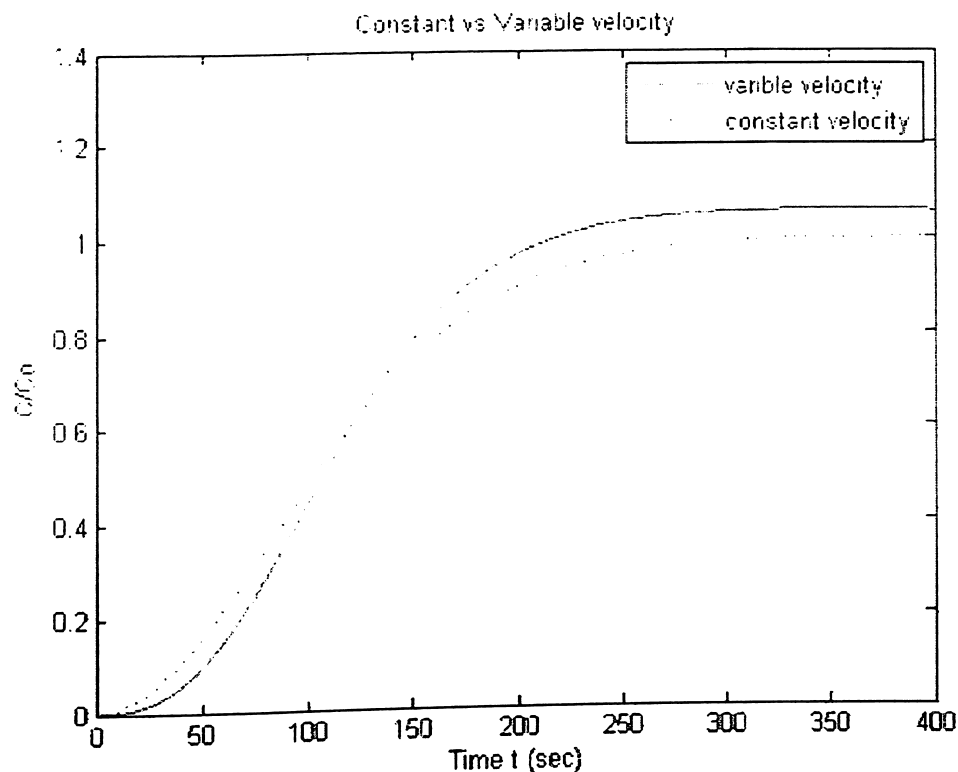
Figure 4.7 Breakthrough curve for oxygen on CMS with constant and variable velocity.

4.4 Desorption breakthrough curve

Desorption breakthrough curve gives the response of a bed saturated with adsorbate. The adsorbent gets saturated with the adsorbate after the adsorption step. To regenerate the adsorbent, it is required to free it from the adsorbate material. To know the response of the saturated bed to desorption, the desorption breakthrough curve for the system is generated by using the same parametric values that were used to generate the adsorption breakthrough curve and also assuming bed is fully saturated. For this desorption of the bed is performed using a purge gas. The purge gas is usually a fraction of the cleaned product from the adsorber, any nonadsorbing inexpensive gas, or heated feed. The desorption breakthrough curve is shown in figure 4.8. Like the adsorption breakthrough curve the nature of desorption breakthrough curve too largely depends on the adsorbent and the adsorbate properties, such as diffusivity, porosity etc.
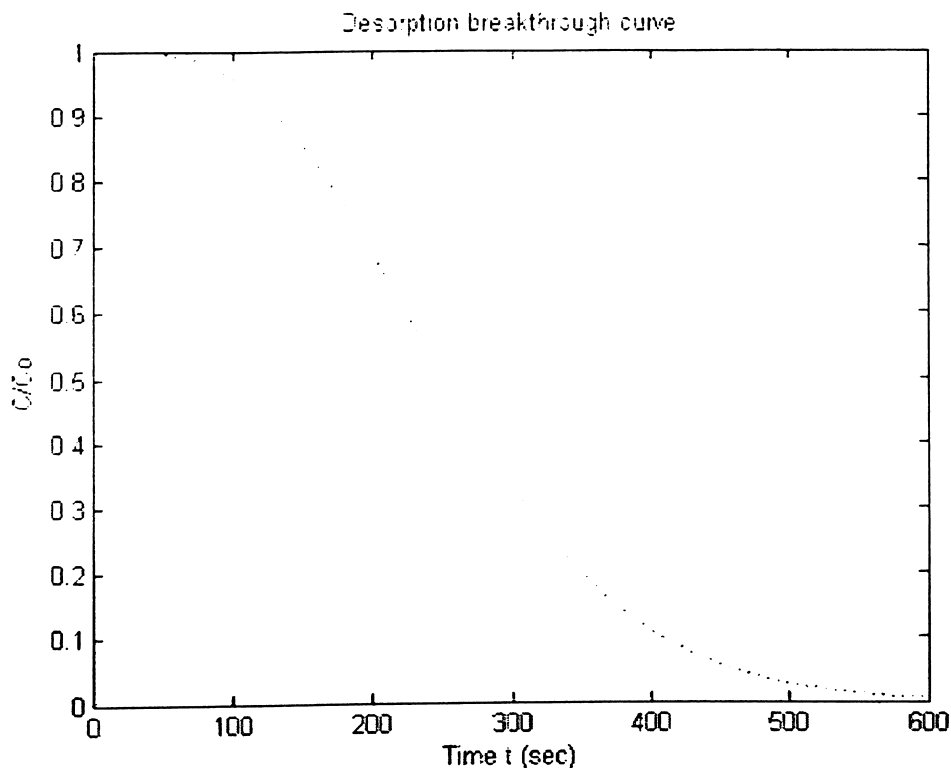
Figure 4.8 Desorption breakthrough curve for oxygen on CMS with flow rate of 1.2 SLPM

4.5 Breakthrough curve for multi-component system

When the gas or fluid mixture contains more than one absorbable species, the concentration of various species shifts relative to one another as the fluid flows through the bed. The presence of other component highly affects the breakthrough curve of the component. A common phenomenon often occurs in multi-component system, when outlet concentration exceeds the inlet concentration. This phenomenon is called as roll-up or roll-over. This is occurred due to the displacement of weaker adsorbate by stronger adsorbate. Figure 4.9 shows the binary-component breakthrough curve for oxygen and nitrogen on carbon molecular sieves. In this system, weaker nitrogen is displaced by stronger oxygen. The parameters used to obtain the curve are given in Appendix I (Hassan et al., 1986).
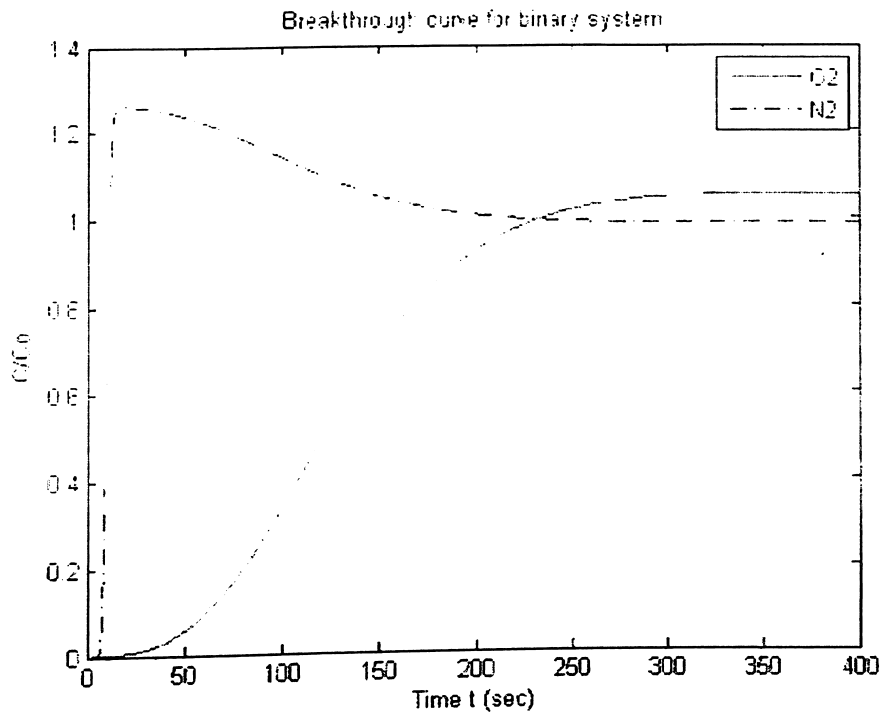
Figure 4.9 Breakthrough curve for oxygen and nitrogen on CMS with flow rate of 1.2 SLPM.

Chapter 5

Simulation Studies of PSA Processes

In this work Skarstrom cycle is used to study pressure swing adsorption process. The Skarstrom cycle is relatively simple and required two bed apparatus. Skarstrom cycle is effective in separating air, air drying and many others process. Skarstrom cycle produces either purified nitrogen or purified oxygen depending on the adsorbent in the bed.

5.1 Nitrogen Pressure swing adsorption cycle

In this work Nitrogen PSA process based on Skarstrom cycle (Skarstrom, 1960) is studied. This cycle employs two beds packed with Carbon Molecular Sieves (CMS) and consists of four steps functioning in the order in which they are shown in figure.
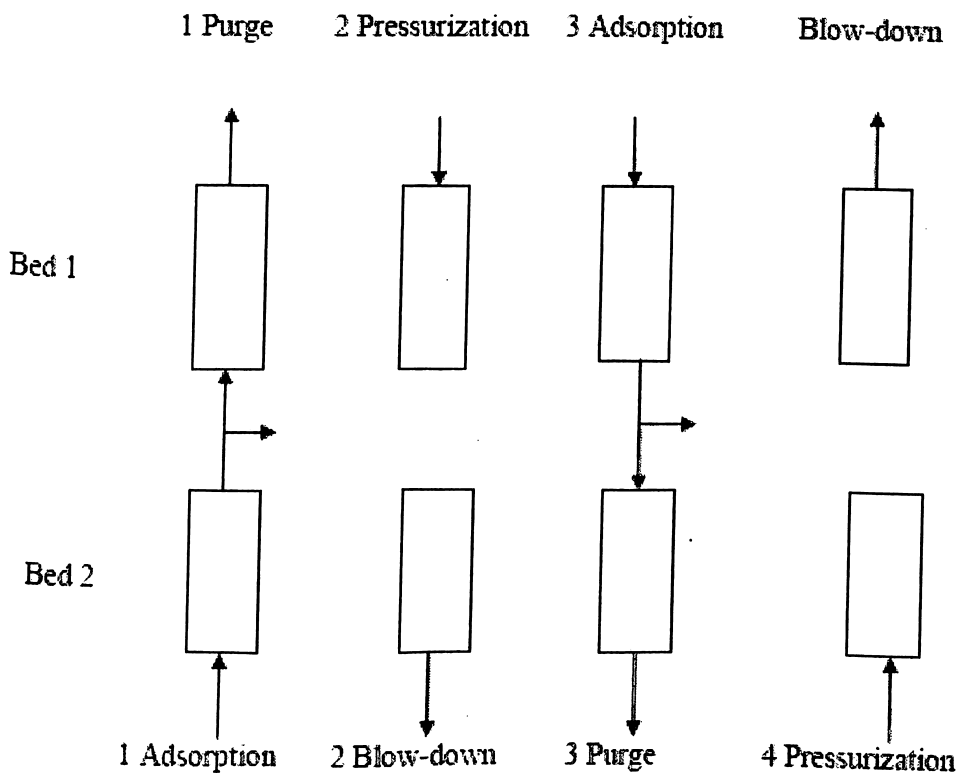
Figure 5.1 Schematic diagram of Skarstrom cycle

Figure 5.1 Schematic diagram of Skarstrom cycle

Pressurization step: During this step, the bed is pressurized to adsorption pressure by using feed. So, this step is called feed pressurization step.

Adsorption step: In this step, feed containing nitrogen and oxygen is admitted in the direction co-current to pressurization in to the bed. During adsorption step considerable amount of oxygen gets adsorbed. Oxygen free nitrogen comes out as raffinate.

Blow down: In this step, the bed is depressurized to atmospheric pressure in the direction counter-current to pressurization to let oxygen and nitrogen adsorbed on to the bed gets desorbed.

Purge: During this step, a part of the product, nitrogen, at atmospheric pressure is admitted in to the bed in the direction counter-current to pressurization to make traces of oxygen being in the bed get desorbed.

Here a nitrogen pressure swing adsorption cycle based upon Skarstrom (1960) to purify nitrogen is simulated by using data tabulated in Appendix I (Hassan et al., 1986). Since oxygen is preferentially adsorbed over nitrogen on CMS, it is termed relatively strongly adsorbed component, whereas nitrogen is termed as weakly adsorbed component. Nitrogen is obtained in raffinate as a product.

5.2 Comparison with Experimental data

The comparison between the experimental data (Hassan et al., 1986) of air –CMS and the theoretically calculated in this work is shown in table 1. The used model approximately represents the experimental data for oxygen and nitrogen concentration in product stream. The hump in the earlier cycles due to competitive adsorption of O_2 and N_2 as verified experimentally by Hassan et al, (1986) is correctly predicted by the used model.

Table 5.1 Comparison of calculated data with experimental data of Hassan et al. (1986)

N0.	Feed rate (SLPM)	Purge rate (SLPM)	Time for step 1 and 3	Time for step 2 and 4	Ω for O_2	Ω for N_2	Product conc. % at steady state Expt	Product conc. % at steady state Theory	Product conc. % at steady state, Present steady	Percentage error %
1[a]	1.21	0.644	60	15	12	65	97.45	97.09	96.410	1.060
2[b]	1.20	0.405	60	15	12	65	95.80	95.51	94.392	1.467
3[c]	0.96	0.320	60	15	12	65	97.05	97.30	97.291	0.24

a –run 5; b –run 6; c- run 7 (Hassan et al., 1986)

5.3 Pressure profiles

In the PSA cycle, pressure gradually increases in the pressurization step due to high flow rate and pressure remains constant throughout production step and purge step but in the blow-down step pressure decrease rapidly. In this cycle, pressurization step time is 15 s; adsorption step time is 60 s; blow down step time is 15 s; purge step time is 60 s. This pressure variation in the bed over the entire cycle is shown in figure 5.2.
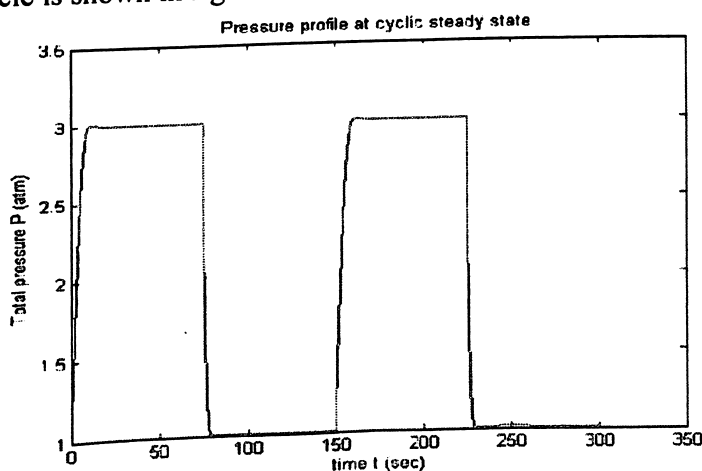

Figure 5.2 Pressure profile in the bed at z=L in two consecutive cycle.

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5.4 Velocity profile

Velocity varies in the PSA process mainly in pressurization and blowdown steps. In the starting of pressurization step velocity is very high and then goes to zero value, same phenomenon occurs in blow-down step. Figure 5.3 shows the velocity profiles at the bed inlet $z = 0$ during the pressurization step.
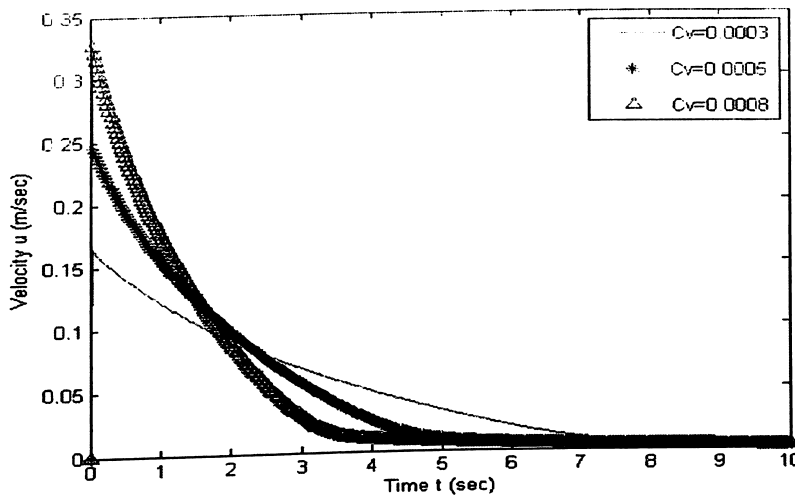

Figure 5.3 velocity profile at z=0 during pressurization step.

5.4 Mole fraction profile of Oxygen

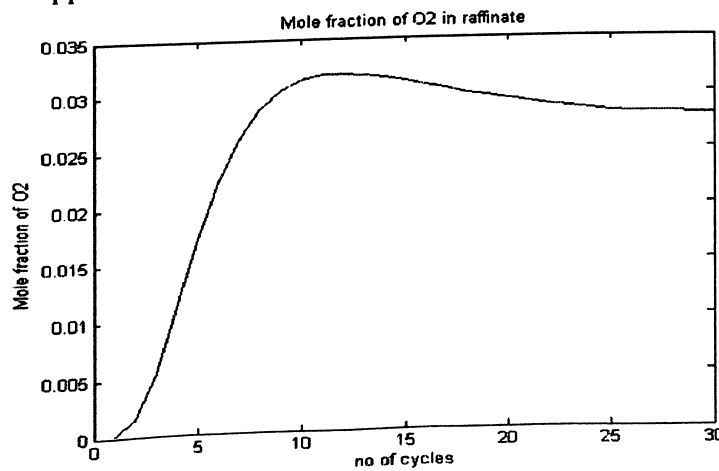Figure 5.4 shows the approach of residual oxygen concentration in the product stream to cyclic steady state.

Figure 5.4 Mole fraction of oxygen in product.

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5.5 Effects of different parameters on purity and recovery

5.5.1 Effect of Adsorption Pressure

Adsorption pressure plays a vital role in the performance of PSA process. Higher adsorption pressure increases the product purity and production rate. According to the isotherms used, the amount of the gas that gets adsorbed on to the adsorbent during pressurization and adsorption steps is dependent on its partial pressure in bulk phase. This amount increases with increase of its partial pressure. So with increase of adsorption pressure, the amount of relatively highly adsorbed component oxygen that gets adsorbed also increases and enhances product purity. Figure 5.5 shows product purity increase with increase of adsorption pressure. Recovery decreases at higher adsorption pressure because higher amount of product is required for removal of highly adsorbed component from bulk phase during purging step. The another reason is that at higher adsorption pressure less adsorbing component gets adsorbed in higher amount in comparison to low pressure adsorption. Variation of nitrogen concentration and recovery with adsorption pressure has been plotted in figure 5.6.
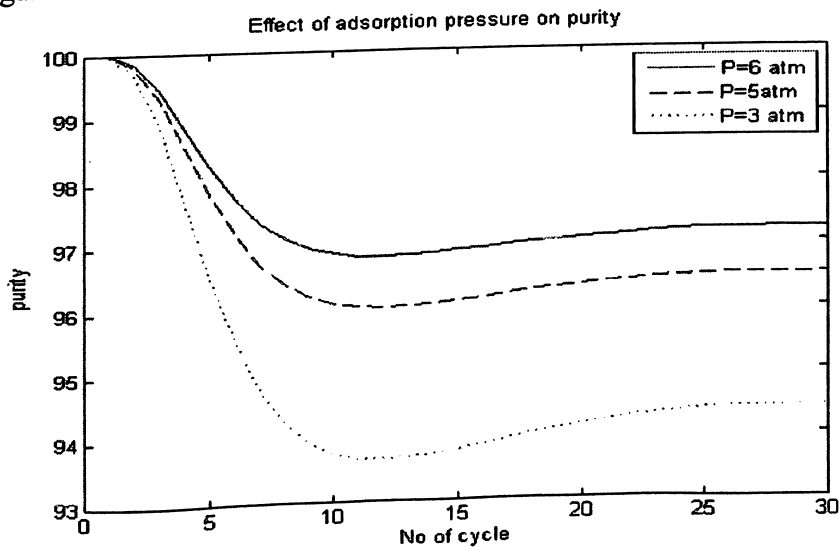

Figure 5.5 Product purity at different adsorption pressure with flow rate 1.2 SLPM
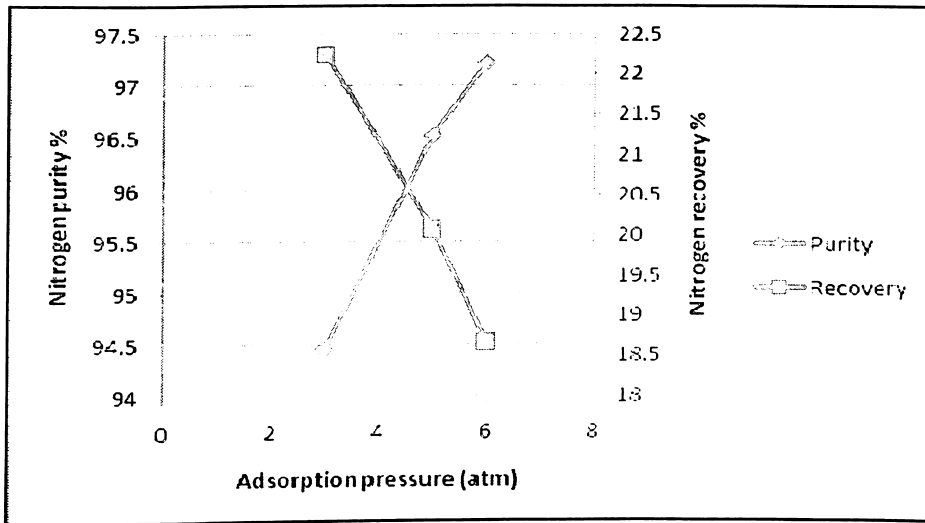
Figure 5.6 Effect of adsorption pressure on nitrogen purity and recovery

5.5.2 Effect of Valve Coefficients

Valves are used in PSA system to control flow rates and adjusting pressure in different steps. Valve coefficient plays an important role in product purity and product recovery. Valve coefficients in pressurization and blow down highly affect the PSA performance. Fig 5.7 and 5.8 show the effect of different valve coefficients on the pressure profile in pressurization and blow down step respectively.
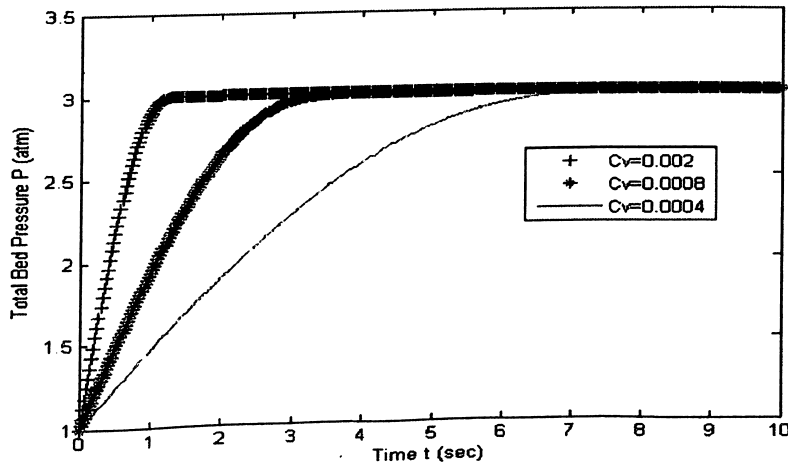

Figure 5.7 Effect of feed valve coefficient on pressure in pressurization step.
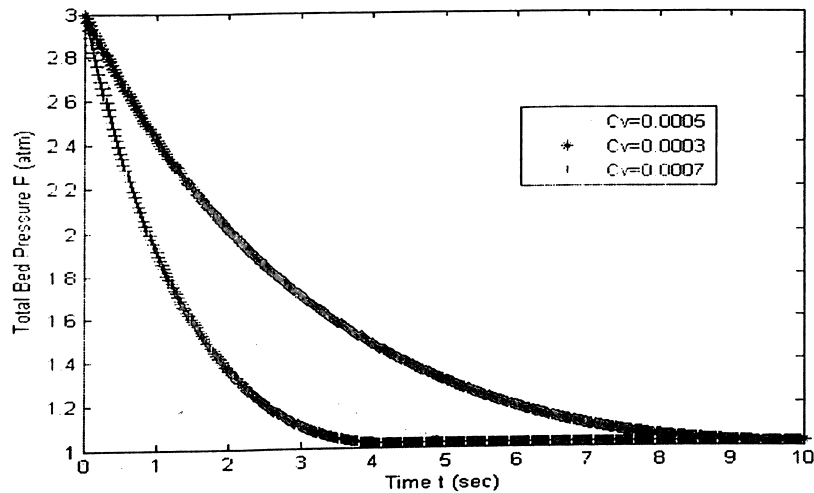
Figure 5.8 Effect of blow-down valve coefficient on pressure in depressurization step

With increase of valve coefficient for pressurization step keeping all others valve coefficient constant, as the velocity of gas into the bed increases the required time to pressurize the bed decrease and also amount adsorbed decrease if step time is short. If pressurization step time is not short then the lower pressurization rate gives the higher concentration of nitrogen for air-CMS system. This is shown in figure 5.9. This is because air – CMS is a kinetic separation. At low pressurization rates O_2 diffuses faster and is adsorbed more rapidly then N_2, but at higher pressurization rates the bed pressure reaches the adsorption pressure rapidly so that N_2 in the feed has sufficient time to diffuse into the CMS and is adsorbed in competition with O_2. Figure 5.10 shows the effect of valve coefficient for pressurization step on nitrogen purity and recovery.
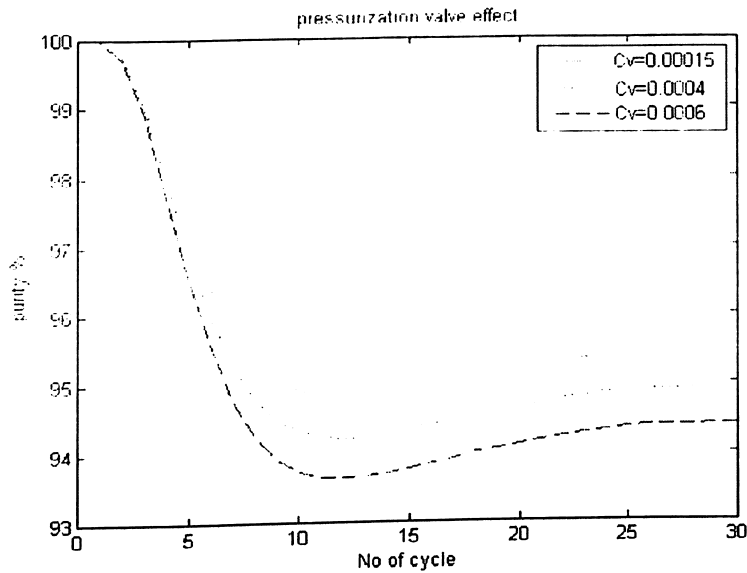
Figure 5.9 Effect of feed valve coefficient on product purity
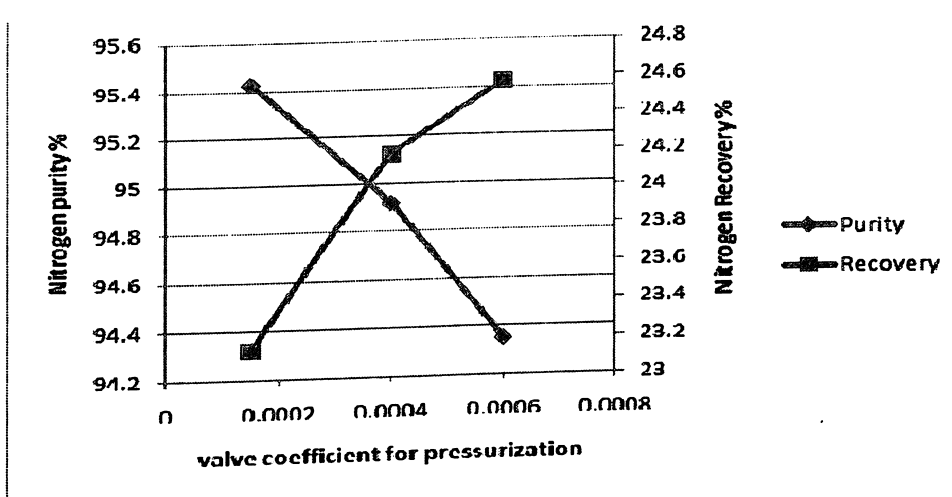
Figure 5.10 Effect of valve coefficient for pressurization step on nitrogen purity and recovery

With increase of valve coefficient for blow down step keeping valve coefficient for other step constant, it is observed that product concentration slightly increases whereas product recovery decreases. The effect of blow-down valve coefficient on product purity is shown in figure 5.11. The decrease in product recovery is due to the requirement of more product stream in purging

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because higher blow down coefficient increases the rate of depressurization and bed take less time to gain minimum bed pressure so that more amount of highly adsorbed component desorbed. Figure 5.12 shows the effect of blow-down valve coefficient on product purity and recovery.

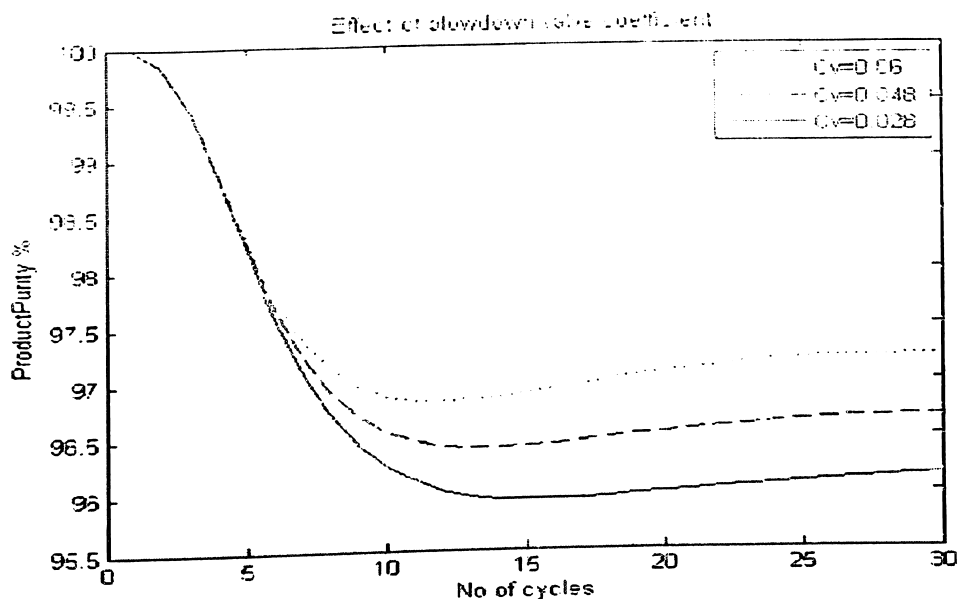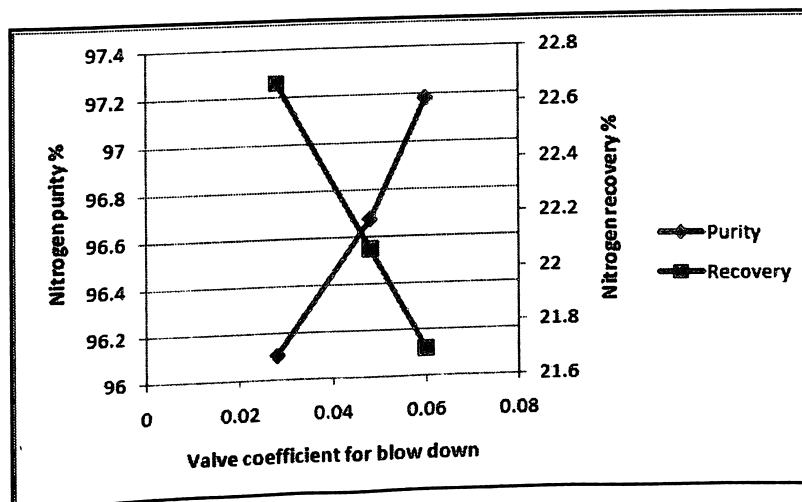**Figure 5.11 Effect of blow-down valve coefficient on product purity.**

Figure 5.12 Effect of valve coefficient for blow-down step on nitrogen purity and recovery

5.5.3 Effect of Bed Porosity

Bed porosity is the ratio of void volume of the bed to the total volume of the bed. The porosity can be changed by selecting adsorbent particle size and shape. Bed porosity significantly affects the product purity and recovery. It is observed that decrease in bed porosity i.e., increase of adsorbent in the bed of given size which results in higher adsorption capacity. If the adsorption capacity of the bed is more, the highly adsorbed component of mixture gets adsorbed considerably more than less adsorbed component and enhances percentage of less adsorbing component in the exit stream. Consequently, product purity increases with decrease of bed porosity. Effect of bed porosity on product purity is shown in figure 5.13.

The variation of nitrogen concentration and recovery with changes in bed porosity are shown in figure 5.14. Figure shows on decreasing bed porosity product purity and also recovery increases. This is due to the reason that when bed porosity is low then amount of highly adsorbed component in the void space after blow down will be small and it require less amount of product stream in purging. Hence it increases product recovery.
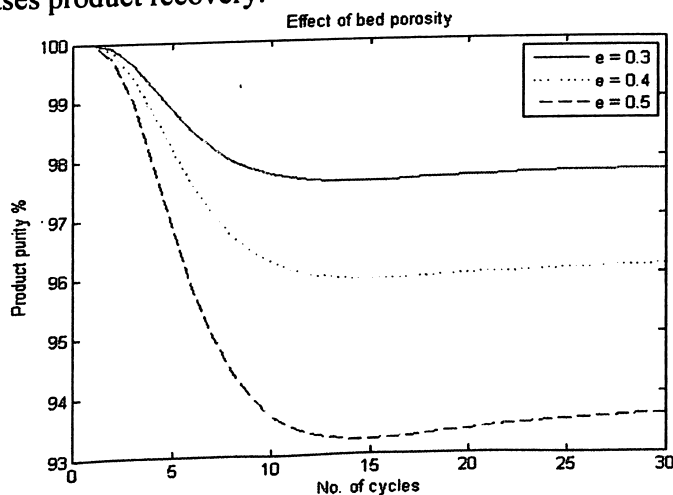

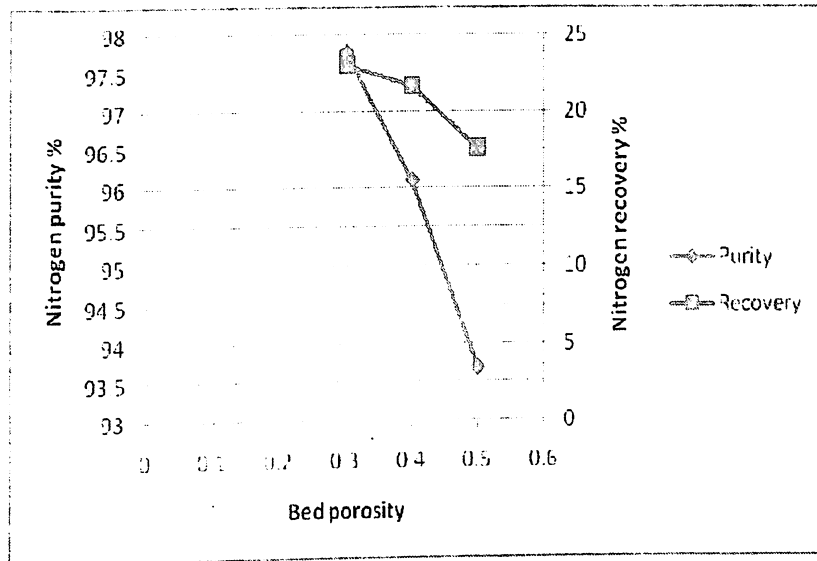**Figure 5.13 Effect of bed porosity on product purity**

Figure 5.14 Effect of bed porosity on nitrogen purity and recovery

Chapter 6

Conclusion and future work

In the present work, a detailed study of pressure swing adsorption process as well as breakthrough curve is carried out. A dual bed binary component pressure swing adsorption model is formulated and programmed a code to simulate the PSA cycle as well as to simulate breakthrough profile. The model used in this work approximately predicts the experimental data (Hassan et al., 1986). Effect of various parameters on breakthrough curve and PSA cycle are also studied in this work.

The effects of various parameters on product purity and recovery are given below

Adsorption pressure: On increasing adsorption pressure product purity increases but product

recovery decreases.

Valve coefficients

Pressurization valve coefficient: Product purity decreases and product recovery increases on increasing pressurization valve coefficient.

Blow-down valve coefficient: On increasing blow-down valve coefficient product purity increases whereas small decrease in recovery occurs.

Bed porosity: It is observed that the product purity as well as product recovery decreases on increasing bed porosity.

The future work will focus on extending the present model for more complex system. Present work is carried out with binary component and dual bed system. The future work will involve

developing different strategies for purification and separation of valuable component fromn industrial tail gases.

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Appendix I

Simulation Parameters for Breakthrough curve and PSA cycle

Table A I.1: Design Parameters (Hassan et al., 1986).

Parameter	Value
Adsorbent	Carbon molecular sieve (Bergbau Forschung)
Composition of oxygen in feed	21%
Composition of nitrogen in feed	79%
Feed pressure	3 atm
Purge pressure	1 atm
Column length	35 cm
Cross-sectional area	9.62 cm^2
Bed voidage	0.40
Temperature	298 K
Particle size	0. 16 cm
Particle density	0.9877 gm/cm^3
Equilibrium constant for oxygen	9.25
Equilibrium constant for oxygen	8.90
Saturation constant for oxygen	2.64 X 10^{-3} $mole/cm^3$
Saturation constant for nitrogen	2.64 X 10^{-3} $mole/cm^3$
Diffusional time constant for oxygen	3.73 X 10^{-3} s^{-1}
Diffusional time constant for nitrogen	1.17 X 10^{-4} s^{-1}
Pressurization step time (blow-down step time)	15 sec
Adsorption step time (purge step time)	60 sec

Appendix II

Mat Lab Codes used in Simulation–

For adsorption breakthrough curve with calling file-

M-file

```
function [c,x,t] = adsorption(u,de,rp,k1,e,xf,T,itc0,bx0,itq0,M,N)
dx = xf/M; x = [0:M]*dx;
dt = T/N; t = [0:N]*dt;
for i = 1:M+1
    c(i,1)=itc0(i);
    q(i,1)=itq0(i);
end
for n = 1:N + 1
    c(1,n)=bx0(n);
end
for k = 1:N
for i = 2:M+1
c(i,k+1)=c(i,k)-(u*dt*(c(i,k)-c(i-1,k)))/(dx)-(((1-e)/(e))*15*de*dt*(k1*c(i,k)-
q(i,k)))/(rp*rp);
q(i,k+1)=q(i,k)+((dt*((15*de)/(rp*rp))*(k1*c(i,k)-q(i,k))));
end
end
plot(t,c(M+1,:)/5,'r')
xlabel('Time in sec')
ylabel('C/C0')
title('adsorption break through curve')
hold on
```

Calling file-

```
clc;
clear all
k1=2.64;
u=2.0*10^-2;
e=0.3;
rp=1.6*10^-3;
de=1.0*10^-13;
rho=970;
xf=1.5;
T=100;
M=150;
N=3000;
for i = 1:M+1
itc0(i)= 0;
itq0(i)= 0;
end
for n = 1:N+1
bx0(n)= 5;
end
adsorption(u,de,rp,k1,e,xf,T,itc0,bx0,itq0,M,N)
```

M-file

```
% constant velocity in bed for single component and langmuir isotherm
function [p,x,t] =   langsingpressure(u,de,rp,a,e,xf,Qs1,T,itc0,bx0,itq0,M,N)
dx = xf/M; x = [0:M]*dx;
dt = T/N; t = [0:N]*dt;
for i = 1:M+1
    p(i,1)=itc0(i);
    q(i,1)=itq0(i);
end
for n = 1:N + 1
    p(1,n)=bx0(n);
end
for k = 1:N
for i = 2:M+1
p(i,k+1)=p(i,k)-(u*dt*(p(i,k)-p(i-1,k)))/(dx)-(((1-
e)/(e))*15*de*dt*24.45*((Qs1*a*p(i,k)/(1+a*p(i,k)))-q(i,k))/(rp*rp));
q(i,k+1)=q(i,k)+((dt*((15*de)/(rp*rp))*((Qs1*a*p(i,k)/(1+(a*p(i,k))))-
q(i,k))));
end
end
plot(t,p(M+1,:)/0.21,':')
hold on
```

Calling file

```
clc;
clear all
a =.149;

Qs1=2.64;

u=0.02;
e=0.4;
rp=1.61*10^-3;
de =9.12*10^-9;

xf=0.35;
T=600;
M=35;
N=18000;
for i = 1:M+1
itc0(i)= 0.21;
itq0(i)= 0.080091;
 end
for n = 1:N+1
bx0(n)=0;
end
        langsingpressure(u,de,rp,a,e,xf,Qs1,T,itc0,bx0,itq0,M,N)
```