

decomposed so rapidly as to make results meaningless. This is discussed further in section 4.6.4.

2.6 Regeneration of Adsorbent

2.6.1 General comments

According to Schweitzer (1979) it becomes economically viable for processes using over four hundred pounds of activated carbon per day to regenerate and re-use it. The publication is not recent, and the process economics have certainly changed. However, since there is generally a large volume of effluent to be processed, and the adsorbent usage rate will certainly be large, the question of regeneration is a relevant one.

In the same way as the forward process of adsorption exploits equilibrium, so too must regeneration. Thus it would clearly not be viable to wash the spent adsorbent with water at the same temperature as the feed-stream, since nothing would be achieved. What is required is a process or treatment which would reverse the adsorption process effectively without negating the financial and environmental progress achieved by the adsorption process.

2.6.2 Methods of regeneration

There are many possibilities for efficient regeneration, such as the use of water treated in some physical manner (example, heating) as a washing agent. This could take the form of steam-stripping.

Re-activation of spent adsorbent is what the term implies: spent adsorbent is activated, which results in the incineration of adsorbed chemicals. Since there is financial gain to be had by recovering the adsorbed chemicals, re-activation was not considered.

Another possibility is solvent-stripping, which involves

treatment of spent adsorbent with a solvent which adsorbs more strongly than the originally adsorbed species, thus displacing the originally adsorbed chemical. An obvious requirement of such a system is that the newly adsorbed solvent must itself be easily removable.

Finally, the adsorption equilibrium may be reversed by a chemical, as opposed to physical, treatment. An example of a chemical treatment would be using a solvent with a favourably adjusted pH.

A rigorous study of adsorbent regeneration would have to take into account the effects of interactions between adsorbed species on the kinetics and economics of the process. However, as stated in section 2.1 above, an extensive analysis of adsorbent regeneration and re-use is beyond the scope of this work. Regeneration studies in this research are elementary, and regeneration of only 'singly-adsorbed' activated carbon is considered - see experimental results below. Percentage regeneration, percentage adsorbate recovery, and percentage loss of adsorbent activity have been considered.

2.6.3 Acetic acid systems

As was mentioned in 2.2 above, the adsorption of acetic acid is greatly affected by the pH of the solution, and as shown in Fig. 2.2, adsorption decreases with increasing pH. This is the method of regeneration that was tested. Carbon pre-loaded with acetic acid was shaken in 0.1 M sodium hydroxide solution for approximately one hour. The results are summarised in Table 2.5 below.

Table 2.5
Acetic Acid Systems - Regeneration and Recovery

	CS-10	CS-15
θ_0	0.100	0.100
% recovery	80.0	70.0
% original activity	82.0	94.0

where θ_0 = initial loading of carbon before alkaline treatment

%recovery = % adsorbed acetate recovered in alkaline solution

%original activity = specific adsorbance of re-loaded, regenerated carbon as a percentage of θ_0 .

Details of experimental measurements may be found in APPENDIX II.

2.6.4 Furfural systems

As was mentioned in 2.2 above, adsorbates can be removed by the preferential adsorption of some other solvent, and this method is useful if the solvent can then be easily removed. If furfural-loaded carbon is treated with benzene, the benzene displaces the furfural and adsorbs in its place. The benzene may then be stripped off the adsorbent by steam at one atmosphere, since benzene's boiling point at that pressure is 80°C.

The displacement effect of the benzene on the furfural is enhanced by high temperature, so the benzene treatment was done at the boiling point of water at Johannesburg altitude, i.e. at approximately 82.5 kPa. The reason for this is that application of direct heat to benzene is hazardous. Thus the temperature of the benzene treatment was 91°C.

The results are summarised in Table 2.6 below.

Table 2.6		
Furfural Systems - Regeneration and Recovery		
	CS-10	CS-15
θ_0	0.155	0.100
% recovery	91.0	92.0
% original activity	86.0	92.0

Symbols as for Table 2.5.

Details of experimental measurements may be found in APPENDIX II.

2.6.5 Conclusions on adsorbent regeneration and solute recovery

As can be seen from Tables 2.5 and 2.6, solute recovery can be as high as 90%, though in practical applications it will not be as high since these are equilibrium values. The regeneration values will also not be quite as high as the tabulated values for the same reason, though these values give an idea of the maximum possible recoveries and regeneration efficiencies achievable. If it is assumed that an adsorbent particle retains only a particular percentage of its original activity after regeneration, as in Tables 2.5 and 2.6, the adsorbent make-up rate can easily be calculated, see section 7.5.5.

3 THEORY OF ADSORPTION AND DIFFUSION

3.1 Introduction

The modelling of a process is essential to the design of such process equipment. This section describes adsorption-diffusion models of various levels of sophistication, from a simplified situation soluble by analytical techniques, to a model accounting for various nonlinearities of a more realistic situation, which requires numerical solution.

All models considered in this work are for an adsorbent with a mono-disperse pore-structure. For details of models accounting for pore-size distributions, the reader is referred to Do (1983), Peel, Benedek and Crowe (1981) and Ruckenstein et al (1971). The full theoretical development of the most rigorous model discussed has been duplicated many times in the literature (Liapis and Rippin, 1977 for example), thus it is not duplicated here. All the simplified models may be derived from this basic model.

3.2 The Basic Diffusion-Adsorption Equation in Spherical Coordinates

3.2.1 Modes of Intraparticle Transfer

The following modes of transport inside adsorbent particles have been proposed (Liapis and Rippin, 1977):

- 1) Molecular diffusion in the fluid filling the adsorbent pores. This is modelled by Fick's law. The assumption is made here that the molecular diffusion coefficient of component i is independent of the concentrations of the rest of the components. This assumption has been shown by Liapis and Litchfield (1981) to be valid for a typical adsorption system. Liapis and Rippin (1977) give the full theoretical treatment for cases where this assumption is not true.

2) Diffusion of adsorbed components along the pore-surface is modelled in a manner analagous to 1) above, and is commonly referred to as 'surface diffusion'. The assumptions made with regard to the surface diffusivity are the same as are discussed in 1) above with regard to molecular diffusivity.

3) Diffusion of adsorbed species through the solid material of the adsorbent, referred to as 'solid diffusion', is modelled as in part 2) above, and since the form of the expressions for this and surface diffusion is identical, no distinction is made between them; they are lumped together into one contribution.

The most sophisticated model considered uses a Fick's law description of mass transfer, thus:

$$J_i = D_i \frac{\partial C_i}{\partial x} \quad \dots (3/1)$$

where J_i = flux of component i in the x direction [kg.m⁻².s⁻¹]

D_i = diffusivity of component i in dilute dilute aqueous solution. See 2). [m².s⁻¹]

C_i = concentration term. [kg.m⁻³]

This may be either a liquid or a surface concentration. Surface concentrations are dimensionless, and thus surface fluxes have to be multiplied by either adsorbent or liquid density for eqn.(3/1) to be meaningful.

It is usually assumed that attainment of local equilibrium between liquid and adsorbent is fast in comparison with the diffusion step (Liapis and Litchfield, 1981).

3.2.2 The fundamental diffusion-adsorption model

Under the above assumptions, the equation describing unsteady diffusion in a spherical adsorbent particle immersed in a

multicomponent liquid solution may be written as follows:

$$\epsilon_s \frac{\partial C_{p,i}}{\partial t} + \rho_s \frac{\partial \theta_i}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left\{ r^2 \left[\epsilon_s D_{p,i} \frac{\partial C_{p,i}}{\partial r} + \rho_s D_{s,i} \frac{\partial \theta_i}{\partial r} \right] \right\} \quad \dots (3/2)$$

Where ϵ_s = fractional pore volume in adsorbent [-]
 $C_{p,i}$ = concentration of component i in the fluid in the pores of the adsorbent [kg.m⁻³]
 t = time [s]
 ρ_s = average density of adsorbent particle [kg.m⁻³]
 θ_i = specific adsorbance of component i [-]
 This is calculated using an 'adsorption isotherm', see section 2.1
 r = radial coordinate [m]
 r_o = particle radius [m]
 $D_{p,i}$ = molecular diffusivity of component i in the pore fluid [m².s⁻¹]
 $D_{s,i}$ = diffusivity of component i on the surface of the pore [m².s⁻¹]

Notes

- Terms involving $C_{p,i}$ refer to pore-diffusion as in 1) above.
- Terms involving θ refer to surface and solid diffusion as in section 3.2. above, parts 2) and 3). $D_{p,i}$, $D_{s,i}$ may depend on $C_{p,i}$ respectively. Dependence on the concentrations and specific adsorbances of other components is discussed in section 3.2.1 above.

The derivation of eqn.(3/2) consists of simple application of mass balances and mass transfer relations such as described in section 3.2.1 above. Liapis and Rippin (1977) give the derivation of the equation, as well as the full attendant initial and boundary conditions, which are as follows:

$$C_{p,i}(r,t=0) = C_{p,i}^0(r) \quad 0 \leq r < r_o \quad \dots(3/3)$$

$$\theta_i(r,t=0) = \theta_i\left[C_{p,i}(r)\right] \quad 0 \leq r < r_o \quad \dots(3/4)$$

$$\epsilon_s D_{p,i} \frac{\partial C_{p,i}}{\partial r} \bigg|_{r=r_o} + \rho_s D_{s,i} \frac{\partial \theta_i}{\partial r} \bigg|_{r=r_o} = K_{L,i} \left[C_{bulk,i} - C_{p,i}(r_o,t) \right] \quad t \geq 0 \quad \dots(3/5)$$

$$\frac{\partial C_{p,i}}{\partial r} \bigg|_{r=0} = \frac{\partial \theta_i}{\partial r} \bigg|_{r=0} = 0 \quad t \geq 0 \quad \dots(3/6)$$

Where $C_{p,i}^0(r)$ = initial pore-fluid concentration profile of component i [kg.m⁻³]
 $\theta_i(C_{p,i}^0(r))$ = specific adsorption of component i evaluated at $C_{p,i}^0(r)$ [-]
 $K_{L,i}$ = liquid-phase mass-transfer coefficient of component i at the particle exterior [m.s⁻¹]
 $C_{bulk,i}$ = liquid-phase bulk concentration of component i in the body of liquid [kg.m⁻³]

Notes

- $C_{bulk,i}$ may be time-dependent, as it would be in the case of a finite mass of adsorbent added to a finite volume of solution in a batch system, see section 3.4.2 below.
- In order to solve eqn.(3/2), the equation and boundary conditions must be expressed in terms of either $C_{p,i}$ or θ_i which are linked by the adsorption isotherm.

The rigorous simulation of multicomponent adsorption involves the solution of a system of N equations of the form (3/2), where N is the number of components in the solution. Although

the equations (3/2) appear to be independent, note that the θ_i , $i=1,N$ are all functions of all the concentrations $C_{p,j}(r,t)$, $j=1,N$, and so the system of equations is in fact linked.

3.3 Model Simplifications

Although the equations have already been simplified by assuming no inter-species effects on diffusion coefficients, more simplifications may be made, some of them without too seriously compromising the applicability of the results. This section describes possible simplifications and the corresponding model solutions, in order of decreasing applicability to real situations.

3.3.1 Disregarding the pore-diffusion effects.

In a publication by Neretnieks (1976 b), it was shown that the contribution by pore-liquid diffusion relative to that by surface/solid diffusion was negligible for all the solutes tested but one. Of course the type of activated carbon used in this work is different; however, this shows that discarding the pore diffusion contribution is probably realistic. Hand, Crittenden and Thacker (1983) give a practically oriented treatment of adsorption and diffusion, where it is shown that results calculated using this assumption adequately describe many data. The equation and boundary conditions for a single component system may be written as follows:

$$\frac{\partial \theta}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_s \frac{\partial \theta}{\partial r} \right) \quad \dots (3/7)$$

$$\theta(r, t=0) = \theta^0(r) \quad 0 \leq r < r_0 \quad \dots (3/8)$$

$$\rho_s D_s \left. \frac{\partial \theta}{\partial r} \right|_{r=r_o} = K_L \left[C_{\text{bulk}} - C_p(r_o, t) \right] \quad \dots(3/9)$$

$t \geq 0$

$$\left. \frac{\partial \theta}{\partial r} \right|_{r=0} = 0 \quad t \geq 0 \quad \dots(3/10)$$

Symbols as in section 3.2.2

Note that in this case eqn.(3/7) is in terms of θ only. The term $C_p(r_o)$ in boundary condition (3/9), however is the pore-fluid concentration at the particle surface. If the system is still to be solved in terms of θ , however, the pore-concentration term must be evaluated from the specific adsorbance at the particle exterior. Thus the term is written as follows:

$$C_p(r_o) = C_p(\theta(r_o)) \quad \dots(3/11)$$

The calculation of $C_p(r_o)$ for a particular value of $\theta(r_o)$ involves 'inversion' of the adsorption isotherm, since isotherm evaluation normally produces θ from a given liquid-phase concentration. Finally, the instantaneous rate of adsorption may be calculated as follows:

$$r_a(\hat{t}) = \rho_s D_s \left. \frac{\partial \theta(r, t)}{\partial r} \right|_{r=r_o} = K_L \left[C_{\text{bulk}}(t) - C_p(r_o, \hat{t}) \right]$$

$\hat{t} > 0$

$\dots(3/12)$

Where r_a = rate of adsorption into particle [kg.m⁻².s⁻¹]

$\hat{t}$ = 'age' of adsorbent particle [s]

The complexity of the model has been greatly reduced by a simple and realistic assumption. However, due to the general nonlinearity of adsorption isotherms and the possible dependence of D_s on θ , the solution of (3/7) still requires numerical techniques.

3.3.2 Disregarding the external mass transfer resistance

It has been shown for many solute-adsorbent systems that models which disregard external mass-transfer resistance describe adsorption adequately - see for example Suzuki and Kawazoe (1975), Hashimoto, Miura and Nagata (1975), and Fritz, Merk and Schlünder (1981). Since this assumption would greatly reduce computational effort, its validity was investigated.

The only change this assumption makes to the model discussed in section 3.3.1 above is in the boundary condition, eqn.(3/9), at the particle exterior. The amended boundary condition is as follows:

$$\theta(r_o, t) = \theta \left[C_{bulk}(t) \right] \quad t \geq 0 \quad \dots(3/13)$$

Symbols as in 3.3.1 above. The right-hand side of eqn.(3/13) is evaluated using the adsorption isotherm. Again, the instantaneous rate of adsorption may be calculated as follows:

$$r_a(\hat{t}) = \rho_s D_s \left. \frac{\partial \theta(r, \hat{t})}{\partial r} \right|_{r=r_o} \quad \hat{t} > 0 \quad \dots(3/14)$$

Again due to the general nonlinearity of adsorption isotherms and the possible dependence of D_s on θ , the solution of the so-called 'homogeneous surface-diffusion model' (HSDM) equation requires numerical techniques, which are discussed in section 6.2

3.3.3 Partial linearisation of the HSDM equations

For relatively dilute solutions, the variation of specific adsorbance with solute concentration can be approximated by a linear form. To appreciate this, examine the plots of the adsorption isotherms in section 2.4, in the low concentration range. Such an approximation could be most useful in the design of a low-concentration pollutant removal system.

In this case, the isotherm expression is simply as follows:

$$\theta = q C$$

where q = average slope of the adsorption isotherm
over a low concentration range $[m^3.kg^{-1}]$

Note that $\theta(0)=0$ is essential, since this is a fundamental characteristic of adsorption isotherms.

Although there is no satisfactory explanation as to why surface diffusion displays such a high dependence on the local extent of adsorption, many workers as referenced by Neretnieks (1976 a) have reported this effect. However, over a small range of specific adsorbance, an assumption of constant surface diffusivity would be useful. The equation resulting from this assumption and that of a linear adsorption isotherm is as follows:

$$\frac{\partial \theta}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \theta}{\partial r} \right) \quad \dots(3/15)$$

$$\theta(r, t=0) = \theta^0(r) \quad 0 \leq r < r_0 \quad \dots(3/16)$$

$$\theta(r_o, t) = \theta \left[C_{\text{bulk}}(t) \right] = q C_{\text{bulk}}(t) \quad \dots (3/17)$$

$$t \geq 0$$

$$\left. \frac{\partial \theta}{\partial r} \right|_{r=0} = 0 \quad t \geq 0 \quad \dots (3/18)$$

This equation has an analytical solution for the cases where the adsorbent is immersed in well-stirred finite and infinite baths - see section 3.4 below.

3.4 The external boundary condition for cases of particular interest.

There are two cases of practical interest, namely adsorption in an infinite bath, and adsorption in a finite bath. The interest in these cases arises from design of a continuous fluidised bed, and estimation of parameters, respectively. For a discussion of the need for models of these two situations, see section 4.1.

Any of the models described in sections 3.3.1 to 3.3.3 could be used in modelling either of these two situations; it is the boundary condition at the particle surface that requires modification to meet the needs of the situation. For the sake of brevity, the external boundary condition is illustrated for the simpler forms of the model as described in 3.3.2 or 3.3.3. Analytical solutions to the simplest model - see section 3.3.3 - are presented for these two cases of interest; the more rigorous models require numerical solution.

3.4.1 Adsorption in an infinite bath

This is the simpler of the two cases, since it is clear that for adsorption by a finite mass of adsorbent in an infinite volume of liquid, the liquid-phase concentration remains constant. Thus:

$$\theta(r_o, t) = \theta \left[C_{\text{bulk}}(t) \right] = \theta \left[C_{\text{bulk}}^o \right] \quad t \geq 0 \quad \dots(3/19)$$

Where C_{bulk}^o = initial liquid-phase concentration of the solute [kg.m⁻³]

In the case of a linear adsorption isotherm, eqn.(3/19) simplifies to give $\theta(r_o, t) = q C_{\text{bulk}}^o$.

In this case, and with no initial loading, see eqn.(3/8), the solution to eqn.(3/15) is as follows (see APPENDIX II for the method of solution):

$$\theta(\xi, \tau) = 1 + \frac{1}{\xi} \sum_{k=1}^{\infty} \frac{(-1)^k e^{-k^2 \pi^2 \tau}}{k \pi} \sin(k \pi \xi) \quad \dots(3/20)$$

The following dimensionless quantities have been used in the solution above:

$$\begin{aligned} \theta &= \theta(C)/\theta(C^*) = \theta(C)/\theta^* & [\cdot] \\ \xi &= r/r_o & [-] \\ \tau &= t D_s / r_o^2 & [-] \\ C^* &\text{ is some reference concentration} & [\text{kg.m}^{-3}] \end{aligned}$$

Eqn.(3/20) may be used to calculate the instantaneous rate of adsorption for the corresponding simplified situation by differentiation, thus:

$$\hat{r}_a(t) = \rho_s D_s \left. \frac{\partial \theta(r, t)}{\partial r} \right|_{r=r_o} = \rho_s D_s \frac{\theta^*}{r_o} \left. \frac{\partial \theta(\xi, \tau)}{\partial \xi} \right|_{\xi=1} \quad \dots(3/21) \quad t > 0$$

Where $\hat{r}_a$ = rate of adsorption into particle [kg.m⁻².s⁻¹]
 $\hat{t}$ = 'age' of adsorbent particle [s]

$\hat{\tau}$ = dimensionless time corresponding to $\hat{t}$ [-]

Eqn.(3/20) is differentiated, and substituted into eqn. (3/21) to complete the rate expression. Thus the instantaneous rate of adsorption depends on the 'age' of the particle, or, how long it has been exposed to the solution. The rate of adsorption calculated in eqn.(3/20) would be most useful in situations in which the adsorption isotherm was roughly linear, and in which the surface diffusivity could be considered constant, such as in the treatment of dilute wastes.

3.4.2 Adsorption in a finite bath.

In the case of adsorption in a finite bath, the liquid-phase concentration varies with time.

A mass balance on the solute, and transformation to dimensionless variables gives the following expression for the time-dependent bulk liquid-phase concentration. See APPENDIX II for the derivation.

$$\zeta_{\text{bulk}}(\tau) = \zeta_{\text{bulk}}(0) - \frac{3}{B} \int_0^1 x^2 \theta(x, \tau) dx \quad \dots(3/22)$$

An equivalent form of the mass-balance statement in eqn.(3/22), one which is used in the analytical solution of the linearised problem solved below, is as follows:

$$\frac{\partial \zeta_{\text{bulk}}(\tau)}{\partial \tau} = -\frac{3}{B} \frac{\partial \theta}{\partial \xi} \Big|_{\xi=1} \quad \dots(3/23)$$

Where $\zeta = C/C^*$ [-]

B, the dimensionless parameter, is as follows:

$$B = \frac{V_1 C^*}{W_s \theta^*} \quad \dots (3/24)$$

$$V_1 = \text{liquid volume} \quad [\text{m}^3]$$

B may be simplified for the case of the linear adsorption isotherm to give $B = V/(W_s q)$. Eqn.(3/23) is derived by Suzuki and Kawazoe (1975).

Either eqn.(3/22) or eqn.(3/23) may be used in the external boundary condition of one's choice for the solution of any of the models discussed in sections 3.2.2 and 3.3.3 above.

In the case of the simplified model discussed in section 3.3.3, an analytical solution of the model equations is possible. In fact when eqn.(3/15) and the initial and boundary conditions eqn. (3/16) and eqn.(3/18) respectively are written in dimensionless form as follows, the model equations have the same form as those describing the cooling of a sphere in a well-stirred liquid.

$$\frac{\partial \theta}{\partial \tau} = \frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left(\xi^2 \frac{\partial \theta}{\partial \xi} \right) \quad \dots (3/15')$$

$$\theta(\xi, \tau=0) = \theta^0(\tau) \quad 0 < \xi \leq 1 \quad \dots (3/16')$$

$$\theta(1, \tau) = \theta \left(\xi_{\text{bulk}}(\tau) \right) = \xi_{\text{bulk}}(\tau) \quad \tau \geq 0 \quad \dots (3/17')$$

$$\left. \frac{\partial \theta}{\partial \xi} \right|_{\xi=0} = 0 \quad \tau \geq 0 \quad \dots (3/18')$$

The model equations describing the cooling of a sphere in a well-stirred finite bath of liquid of constant thermal transport properties have been solved in detail in the literature (Bird,

Stewart and Lightfoot, 1963), and the equation expressing the variation of the liquid-phase concentration, analagous to the liquid temperature in the cooling-sphere model is merely quoted here:

$$\zeta_{\text{bulk}}(r) = \frac{B}{1+B} + 6B \sum_{k=1}^{\infty} \frac{\exp(-b_k^2 \tau)}{B^2 b_k^2 + 9(1+B)} \quad \dots (3/25)$$

The b_k are defined as the roots of the following equation:

$$\tan(b_k) = \frac{3b_k}{3 + Bb_k^2} \quad \dots (3/26)$$

Note that eqn.(3/25) has infinitely many roots, and that these roots are characteristic of the amount of liquid, the amount of adsorbent, and the adsorption capacity of the particular adsorbent. At $\tau \rightarrow \infty$, it is easy to see that $\zeta = B/(1+B)$, which may easily be verified by a mass balance.

In the case of finite-bath adsorption, the rate of adsorption is of little interest or use, and it is not considered here.

3.5 Conclusions

The model of adsorption-diffusion in a particle of adsorbent may be simplified in various ways to facilitate solution. The nature and extent of the simplifications depends on the situation; various major simplifications have been vindicated in the literature as referenced above, and these simplifications greatly reduce the complexity of the model.

The practical application of the model solutions is discussed in sections 4.1 and 7; it is clear however that the actual specific adsorption profile in the particle is of little use in itself. The main use of the models is in calculating the rate

of adsorption or the amount of solute adsorbed, as discussed above. See section 6.2 for a discussion of the method of solution of the HSDM equations.

4 MASS TRANSFER PARAMETER ESTIMATION

4.1 Introduction

There are two possible approaches to the design of a steady-state continuous fluidised-bed adsorber. The most rigorous approach would account for the fact that a particle is exposed to varying concentrations in its travels up and down the bed. This model would have to include the effects of the 'diffusivity' of particles within the bed and the liquid-phase concentration profile up the bed, with the result that the design procedure would be iterative and thus lengthy. A model of this sort is more realistic than that described below, since the concentration profile is sure to have a significant effect on the overall rate of adsorption. The other approach assumes the adsorbent particles to be perfectly mixed, and exposed to some average concentration.

In both of the above cases, the solid (adsorbent) phase may be modelled as being in a Continuously Stirred Tank Reactor (CSTR). Thus the distribution of loadings (and hence rates of adsorption) among the particles may be calculated from the 'segregated' model. Both cases require the instantaneous rate of adsorption, which is difficult to measure accurately, under various conditions.

The instantaneous rates of adsorption may be evaluated using a model of the adsorption process, such as the HSDM. For such a model to be of any use, certain parameters characteristic of the adsorbent and adsorbate are required. The form of the model and its parameters is discussed in section 4.2. The estimation of parameters for adsorber design has been extensively researched, and a vast volume of published literature on the subject is available: Fritz, Merk and Schlunder (1981), Hashimoto and Miura (1975), Liu and Weber (1981) to name but a few.

This chapter deals with the experimental measurements and procedures used for the estimation of the mass-transfer

parameters.

4.2 Experimental Procedure

Estimation of parameters requires measurement of process variables which are included either explicitly or implicitly in a model of the process. The more simple the model dependence on the variable, the easier the estimation will be. The model response is then calculated for various values of the desired parameters, and the parameters which cause the model to most closely represent the system behaviour are those used in predictive modelling.

It would clearly be difficult to actually measure the variation of the adsorption profile with time in a particle of adsorbent. Thus the experimental determinations would have to be made on a property which is easily measured. The most obvious choice is the measurement of the time-dependent liquid-phase concentration in some suitable experimental apparatus.

Two main types of apparatus have been proposed for this purpose. Liu and Weber (1981) proposed a micro-column experiment in which the variation with time of effluent concentration at the exit is measured. The main advantage claimed for this method is that the effect of the external film-coefficient of mass transfer can be separated from that of internal diffusion by the early breakthrough which is characteristic of such micro-column experiments. However, this method requires the solution of a system of two unsteady-state partial differential equations, one in terms of particle radius and time, the other in terms of bed-length and time. It was decided that this procedure was too involved and required too much computational effort and experimental sophistication to justify the results.

The other type of apparatus is the finite volume, stirred-tank batch adsorber. The experimental procedure consists of stirring a suspension of adsorbent in a solution of known initial concentration, and measuring the liquid-phase

concentration as time progresses, otherwise known as the liquid-phase concentration history. The major advantage of this method is that the model of the system is simple, and consists of only one unsteady-state partial differential equation with boundary conditions for each component in the solution. Further, as is discussed in section 3.2.1, it is commonly assumed that for each component the surface- and molecular-diffusivities are independent of the concentration of the other components. Thus experiments are usually performed on single component solutions, and only a single equation needs to be solved to estimate the parameters. However, recall section 2.2, where the presence of sulphur dioxide in all of the experimental solutions is discussed.

The latter method was selected for its simplicity and modest degree of numerical and experimental sophistication required. It remained to select the particular form of the model. On the personal recommendation of Dr. van Vliet of the National Institute for Water Research (NIWR) of the Council for Scientific and Industrial Research, (CSIR) the homogeneous surface-diffusion model, hereafter referred to as the HSDM, without pore-diffusion effects was selected; for details of the model, see section 3.3.1.

4.3 Experimental Results

Measurement of the variation of liquid-phase concentration in a stirred suspension of adsorbent was required. These measurements were made on systems with two different adsorbent-solution ratios, each with different initial concentrations. This was done to ensure independence of the parameters estimated. Sufficient adsorbent was used in each experiment so that the equilibrium liquid-phase concentration was less than half the initial value. This was done since it is clear from graphs presented by Hashimoto, Miura and Nagata (1975) that model sensitivity to the parameters increases as final liquid-phase concentration decreases.

Details of quantities such as mass of adsorbent, initial concentrations, and liquid volumes, as well as experimental measurements and raw data may be found in APPENDIX IV.

4.3.1 Experimental results for carbon type CS-10

Experimental results for the batch adsorption of acetic acid and furfural are plotted in Figs.4.1 and 4.2 respectively. Experimental conditions and quantities are summarised in APPENDIX IV.

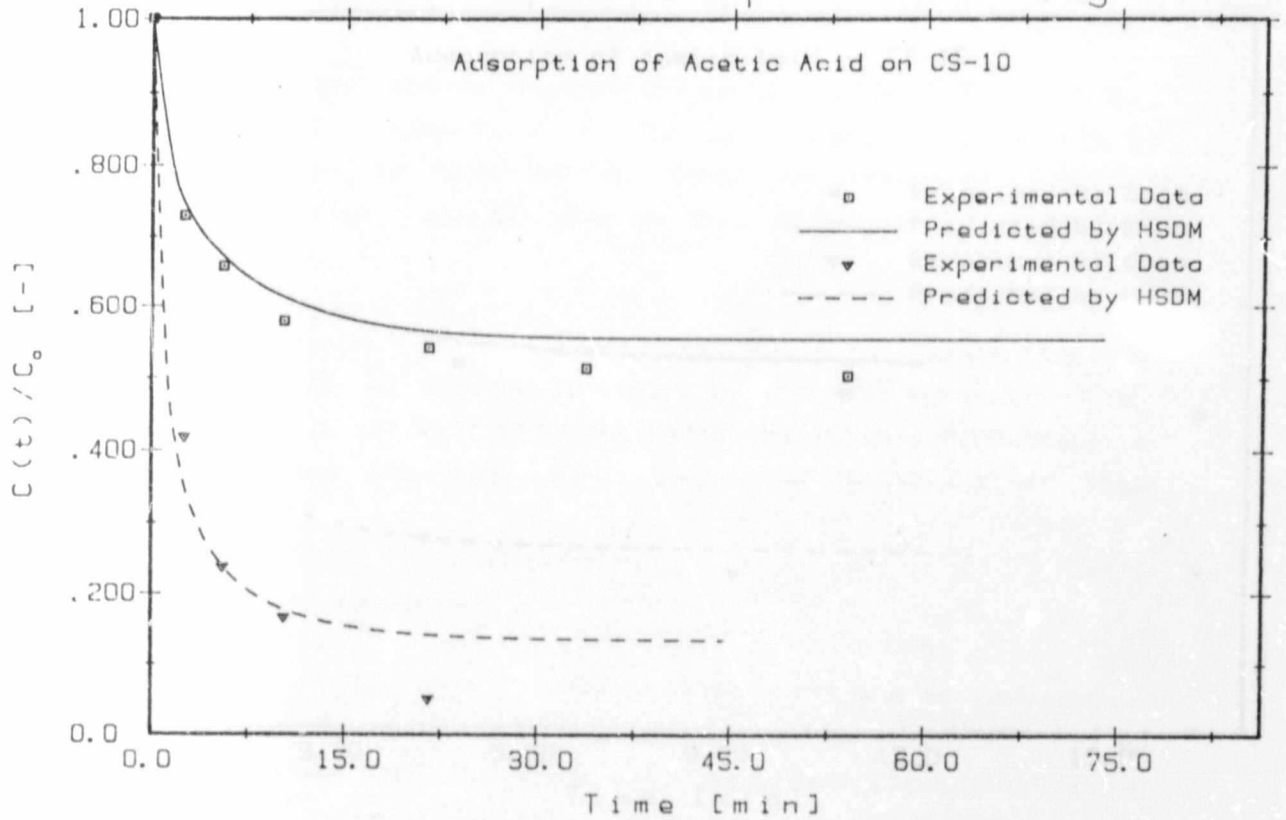
By comparison to the computational results of Liapis and Rippin (1977), the adsorption behaviour of the acetic acid/CS-10 system is seen to be very close to that of an ideal mono-disperse pore-structure adsorbent. For this reason, as will be seen below, it was possible to find parameters which very closely described the behaviour of this system.

As regards the adsorption of furfural on CS-10, especially at high initial concentration, the behaviour of this system is characteristic of an adsorbent with a bi-disperse pore structure, as can be seen by comparison to the computational results presented by Peel, Benedek and Crowe (1981). The sharp decline in concentration followed by a relatively slow decline at a later stage is characteristic of the bi-disperse pore-structure adsorbents. Thus it will be seen below that the best parameters for the model based on a mono-disperse pore-structure can only approximate the behaviour of this system.

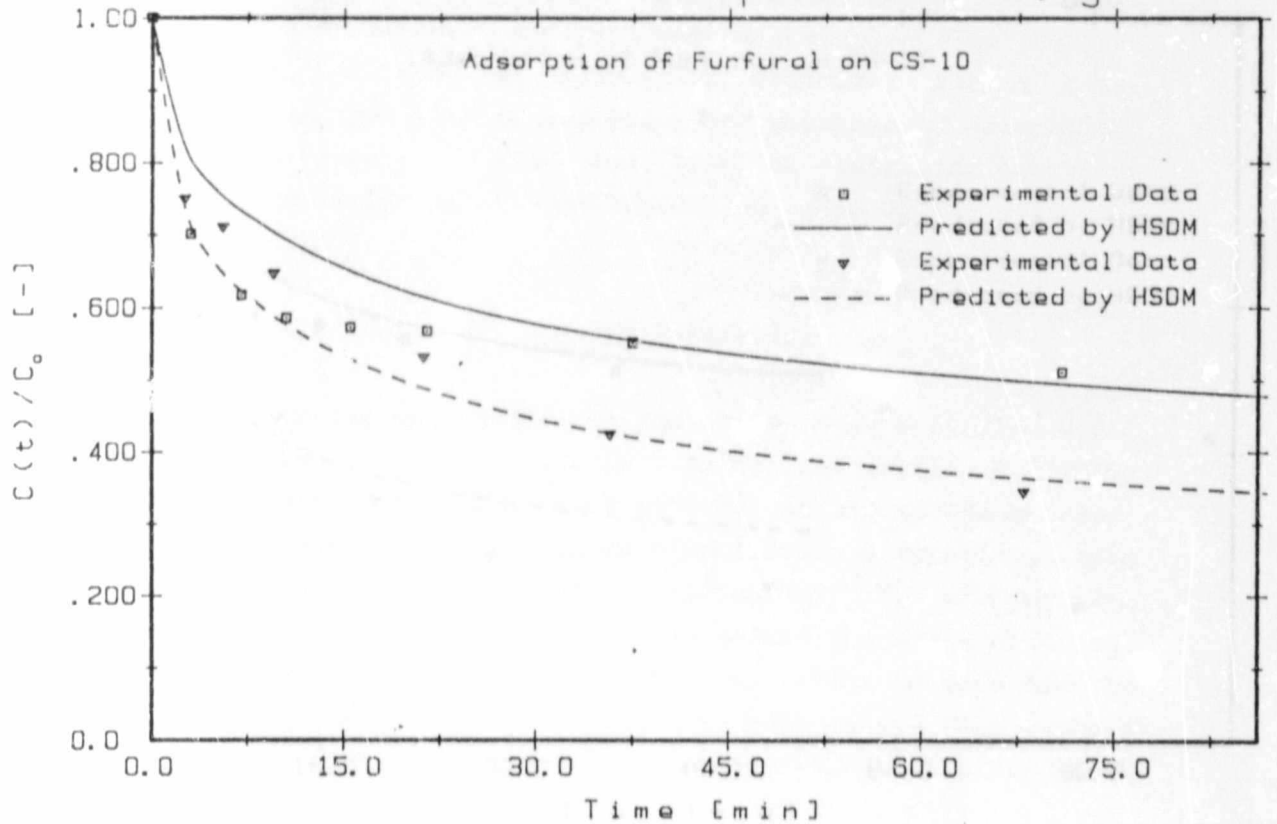
4.3.2 Experimental results for carbon type CS-15

Experimental results for the batch adsorption of acetic acid and furfural are plotted in Figs.4.3 and 4.4 respectively. Experimental conditions and quantities are summarised in APPENDIX IV

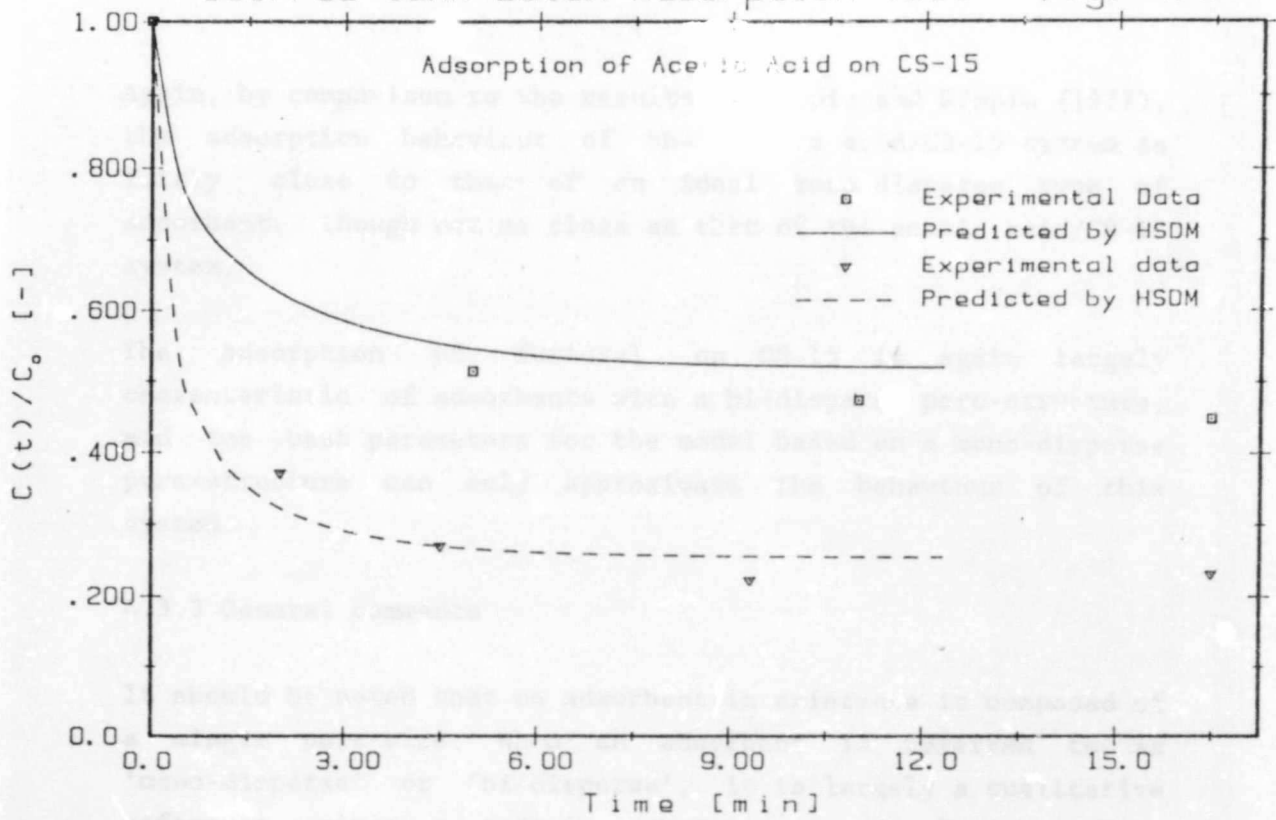
Stirred-tank Batch Adsorption Test Fig. 4.1



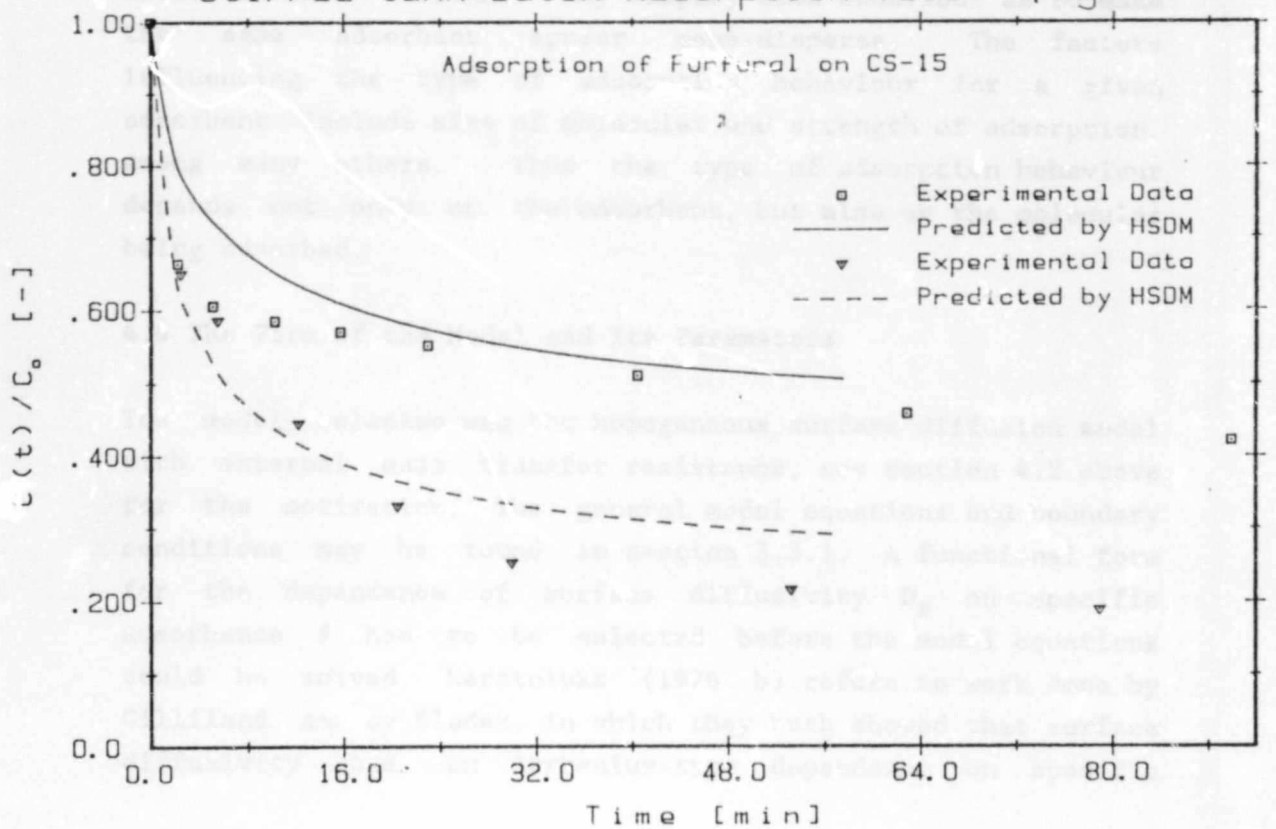
Stirred-tank Batch Adsorption Test Fig. 4.2



Stirred-tank Batch Adsorption Test Fig. 4.3



Stirred-tank Batch Adsorption Test Fig. 4.4



Again, by comparison to the results of Liapis and Rippin (1977), the adsorption behaviour of the acetic acid/CS-15 system is fairly close to that of an ideal mono-disperse type of adsorbent, though not as close as that of the acetic acid/CS-10 system.

The adsorption of furfural on CS-15 is again largely characteristic of adsorbents with a bi-disperse pore-structure, and the best parameters for the model based on a mono-disperse pore-structure can only approximate the behaviour of this system.

4.3.3 General comments

It should be noted that no adsorbent in existence is composed of a single pore-size. When an adsorbent is referred to as 'mono-disperse' or 'bi-disperse', it is largely a qualitative reference, since a certain substance may display adsorption behaviour which makes the adsorbent appear to be bi-disperse, while another substance may display such behaviour as to make the same adsorbent appear mono-disperse. The factors influencing the type of adsorption behaviour for a given adsorbent include size of molecules and strength of adsorption, among many others. Thus the type of adsorption behaviour depends not only on the adsorbent, but also on the molecules being adsorbed.

4.4 The Form of the Model and Its Parameters

The model selected was the homogeneous surface diffusion model with external mass transfer resistance, see section 4.2 above for the motivation. The general model equations and boundary conditions may be found in section 3.3.1. A functional form for the dependence of surface diffusivity D_s on specific adsorbance θ had to be selected before the model equations could be solved. Neretnieks (1976 b) refers to work done by Gilliland and by Sladek, in which they both showed that surface diffusivity has an Arrhenius-type dependence on specific

adsorbance. This results in a functional form as follows:

$$D_s = D_s^* e^{\beta\theta} \quad \dots(4/1)$$

Where D_s^* = surface diffusivity at $\theta=0$ [m².s⁻¹]
 β = a fitted parameter [-]

The full model may be stated as follows, in dimensionless form:

$$\frac{\partial\theta}{\partial\tau} = \frac{1}{\xi^2} \frac{\partial}{\partial\xi} \left(e^{\beta\theta} \xi^2 \frac{\partial\theta}{\partial\xi} \right) \quad \dots(4/2)$$

$$\theta(\xi, \tau=0) = \theta^0(\xi) \quad 0 < \xi < 1 \quad \dots(4/3)$$

$$\left. \frac{\partial\theta}{\partial\xi} \right|_{\xi=1} = \frac{Bi \ A2}{e^{\beta\theta(1,\tau)}} \left(\zeta_{bulk}(\tau) - \zeta_p(1,\tau) \right) \quad \dots(4/4)$$

OR

$$\theta(1,\tau) = \theta \left(\zeta_{bulk}(\tau) \right) \quad \dots(4/5)$$

the symmetry boundary condition,

$$\left. \frac{\partial\theta}{\partial\xi} \right|_{\xi=0} = 0 \quad \dots(4/6)$$

and the mass-balance equation.

$$\zeta_{bulk}(\tau) = \zeta_{bulk}(0) - A1 \int_0^1 x^2 \theta(x,\tau) dx \quad \dots(4/7)$$

where $A1 = 3W_s \theta^* / (VC^*)$ [-]

$$\begin{aligned}
 A2 &= C^*/(\rho_s \theta^*) & [-] \\
 B1 &= \text{Biot number} = K_L r_o / D_s^* & [-] \\
 D_s^* &= \text{surface diffusivity at } \theta=0 & [m^2.s^{-1}] \\
 &\text{Other symbols as defined before.}
 \end{aligned}$$

The model parameters are thus:

$$\beta \quad B1 \quad \sigma \quad D_s^* \quad A1 \quad A2$$

Only the first three are fitted parameters. The fourth parameter is deduced using the first three parameters, and the last two are combinations of measurements and calculations using physical properties of the adsorbent (as estimated in section 5.4), and the adsorption isotherms. See section 4.5 below for the significance of σ , the time-scale parameter.

Eqn.(4/2) may be solved for any choices of β and $B1$ up to any desired dimensionless time τ . The procedure for the solution of the equation is described in section 6.5.

4.5 The Procedure for Estimation of Parameters

The estimation of parameters consists of finding values for $B1$ and β which give the best fit of the model results to the experimental results. One way of doing this would be the classical minimisation of errors approach, the least-squares best-fit.

Many cases reported in the literature have been shown to be adequately modelled by neglecting the external mass-transfer resistance, see Hashimoto, Miura and Nagata (1975), and Muraki, Iwashima and Hayakawa (1982) for example. Thus it was decided to test the hypothesis that external mass transfer could be neglected. The method used to find the parameters for this simplified situation is described below:

1) Neglecting external mass transfer, the value of β was found which gave shapes of computed concentration histories acceptably

close to those of the measured results for the particular single component system under consideration. The value of β was found by inspection since in the dimensionless time domain, the main effect of β is on the shape of the concentration history curve. A larger value of β gives a sharper curve - Fig. 4.5 demonstrates this effect.

2) The time-scaling factor σ was found which best superimposed the computed concentration histories on the experimental results. Thus σ is the value by which the dimensionless times τ were multiplied to best superimpose the computed results on the experimental results. Note that σ is equal to the ratio of the real time to the dimensionless time:

$$\sigma = t/\tau \quad \dots(4/7)$$

From section 3.4.2, the definition of τ may be rearranged to give:

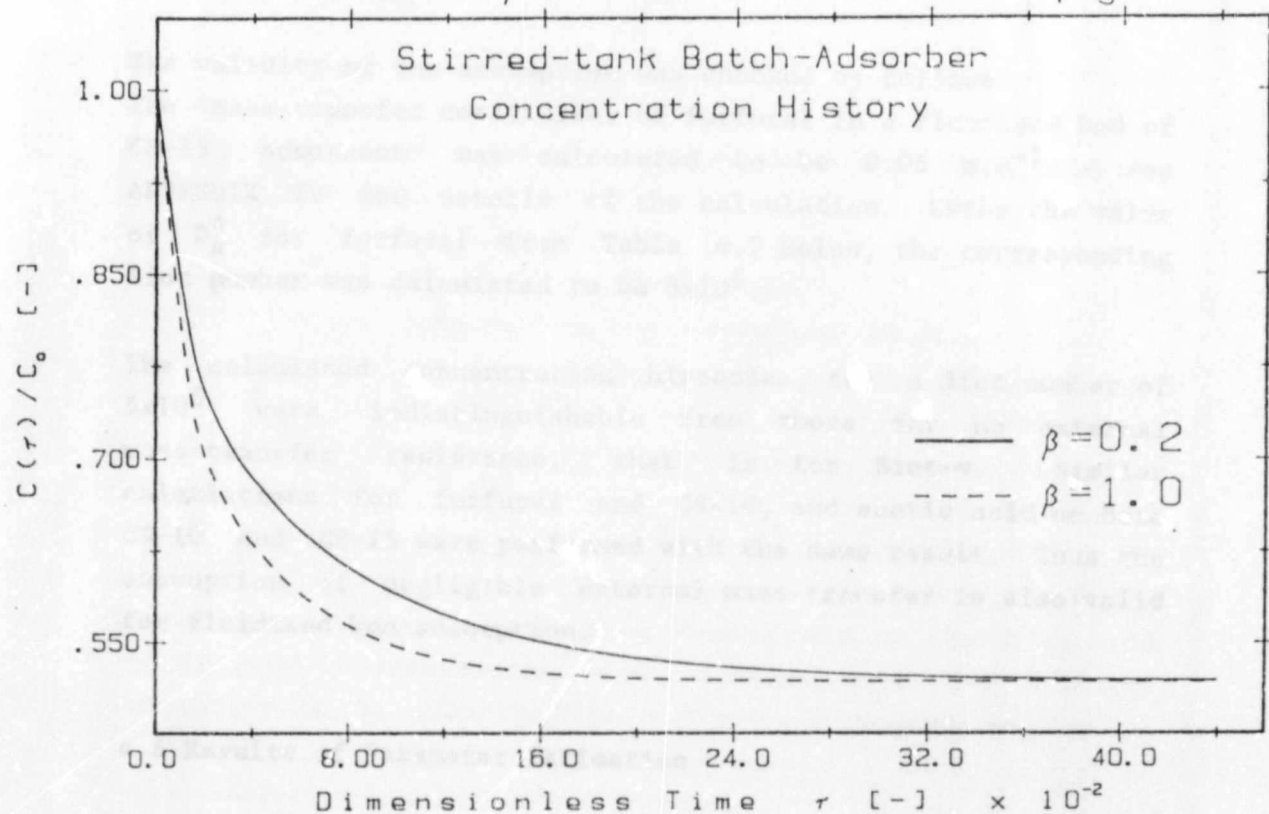
$$D_s^* = \tau r_0^2/t = r_0^2/\sigma \quad \dots(4/8)$$

Thus since r_0 is known - see section 5.4.1 for the actual values, D_s^* may be calculated. This value is only valid for infinite Biot numbers, or equivalently, no external mass-transfer resistance.

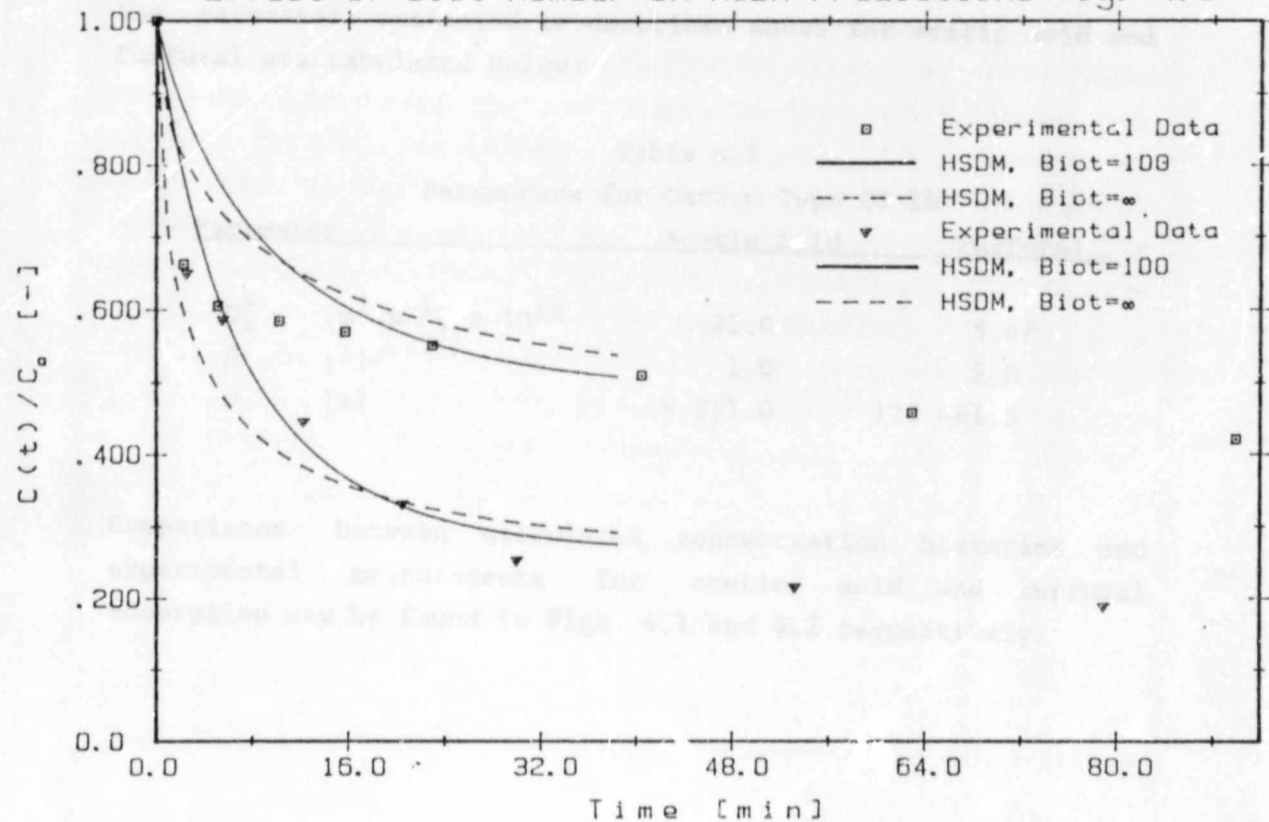
It was found that very small Biot numbers, for example Biot=100, made little improvement to the quality of the fits obtained with Biot= ∞ . See Fig.4.6 for a comparison of the fits obtained for these two Biot numbers, calculated for a value of $\beta=0$. Thus it was decided to use the simplification of neglecting external mass-transfer effects in the estimation of the parameters β and σ . Of course this would not necessarily be valid for cases where the suspension was not as well-stirred as in the tank used for these experiments. Before this approach could be used for the calculation of adsorption rates in a fluidised-bed, its applicability to fluidised-bed operation had to be verified.

The Effect of β on HSDM Predictions

Fig. 4.5



Effect of Biot Number on HSDM Predictions Fig. 4.6



The validity of the assumption was checked as follows:

The mass-transfer coefficient of furfural in a fluidised bed of CS-15 adsorbent was calculated to be 0.06 m.s^{-1} - see APPENDIX IV for details of the calculation. Using the value of D_s^* for furfural from Table 4.2 below, the corresponding Biot number was calculated to be 5×10^6 .

The calculated concentration histories for a Biot number of 5×10^6 were indistinguishable from those for no external mass-transfer resistance, that is for $\text{Biot} = \infty$. Similar calculations for furfural and CS-10, and acetic acid on both CS-10 and CS-15 were performed with the same result. Thus the assumption of negligible external mass-transfer is also valid for fluidised-bed adsorption.

4.6 Results of Parameter Estimation

4.6.1 Parameters for adsorption onto CS-10

The parameters estimated as described above for acetic acid and furfural are tabulated below:

Table 4.1
Parameters for Carbon Type CS-10

Parameter		Acetic Acid	Furfural
D_s^*	$[\text{m}^2.\text{s}^{-1}] \times 10^{12}$	82.0	5.47
β	[-]	1.0	2.0
σ	[s]	9 231.0	138 461.5

Comparisons between calculated concentration histories and experimental measurements for acetic acid and furfural adsorption may be found in Figs. 4.1 and 4.2 respectively.

4.6.2 Parameters for adsorption onto CS-15

The parameters estimated as described above for acetic acid and furfural are tabulated below:

Table 4.2
Parameters for Carbon Type CS-15

Parameter		Acetic Acid	Furfural
D_s^*	$[m^2.s^{-1}] \times 10^{12}$	100.0	4.28
β	[-]	0.2	1.45
σ	[s]	1 681.0	41 221.4

Comparisons between calculated concentration histories and experimental measurements for acetic acid and furfural adsorption may be found in Figs. 4.3 and 4.4 respectively.

4.6.3 Comparison to literature values.

Although the parameter D_s^* is very dependent on the grade and even the method of preparation of activated carbon, it would still be useful to compare the values obtained above with those from the literature derived from the same model. Suzuki and Kawazoe (1975) estimated the parameter D_s^* , though no dependence on θ was allowed, for fifteen different organic compounds. They successfully correlated surface diffusion coefficients with boiling point of each compound. The values calculated using their correlation are as follows:

Table 4.3
Literature values for D_s^*

Compound	$D_s [m^2.s^{-1}] \times 10^{12}$
Acetic Acid ¹	9.8
Furfura ¹	4.8

The parameters fitted work are acceptable, since orders

of magnitude variation are commonly found with different adsorbent grades.

4.6.4 A check on the applicability of the parameters to adsorption in a two-component solution.

The parameters fitted in sections 4.6.1 and 4.6.2 were used in the multicomponent homogeneous surface-diffusion model - see section 4.4 - to predict the concentration histories of acetic acid and furfural in a stirred-tank. Unfortunately, in attempting to perform the two-component stirred-tank batch-adsorption experiment, the rate of decomposition of furfural was far too high to be able to obtain meaningful results. The reason for the high rate of decomposition can be ascribed to the combination of the following factors:

- dissolved oxygen in the solution
- continuous transfer of oxygen to the solution via the surface of the vigorously agitated solution
- the presence of acetic acid. Along with the attempt to check the validity of the multicomponent adsorption isotherm theory by experiment - see section 2.5, this is the only occasion on which furfural was exposed to both acetic acid and sulphur dioxide. It would appear that the acetic acid is responsible for catalysing the rapid breakdown of furfural.

Since furfural has been measured in appreciable quantities in the complete plant effluent - see section 1.1 - the components not included in the experimental solutions could exert a stabilising influence on furfural. The chemistry of furfural decomposition in multicomponent solutions is well beyond the scope of this research, though studies in this area are required if investments are to be made in effluent treatment equipment.

4.7 Estimation of Parameters for the Simplest Model

Parameters for the simplest model as described in section 3.3.3 were fitted by the method described in section 4.5;

since there is no value of β for this model all that was required was to find the best time-scaling factor σ . Note that since all the measured isotherms are concave downwards, the linearised isotherms all predict too large an adsorbance at high concentrations. Thus it was necessary to compromise when fitting the linearised model to experimental data, and so the model predictions have been placed between the two sets of experimental measurements. The parameter estimation for this linear model could have been biased to best match the initial rates of adsorption rather than the overall concentration history. To summarise, there is no unique, 'correct' criterion for fitting the model response to experimental data.

4.7.1 Parameters for adsorption onto CS-10

The fitted parameters are tabulated below.

Table 4.4		
Linearised-model Parameters for Carbon Type CS-10		
Parameter	Acetic Acid	Furfural
D_s^* [$m^2.s^{-1}$] $\times 10^{12}$	21.9	4.69
σ [s]	34 615.0	161 538.0

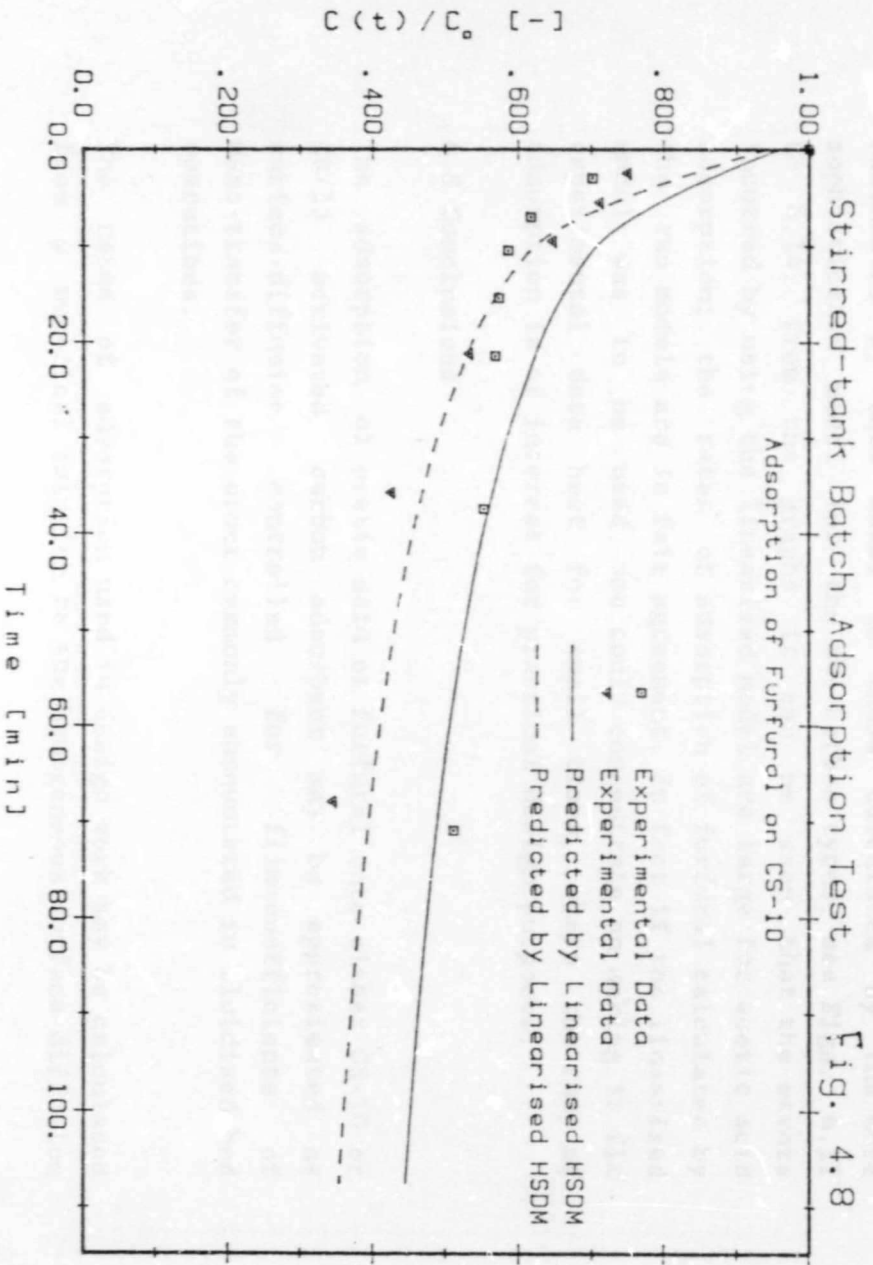
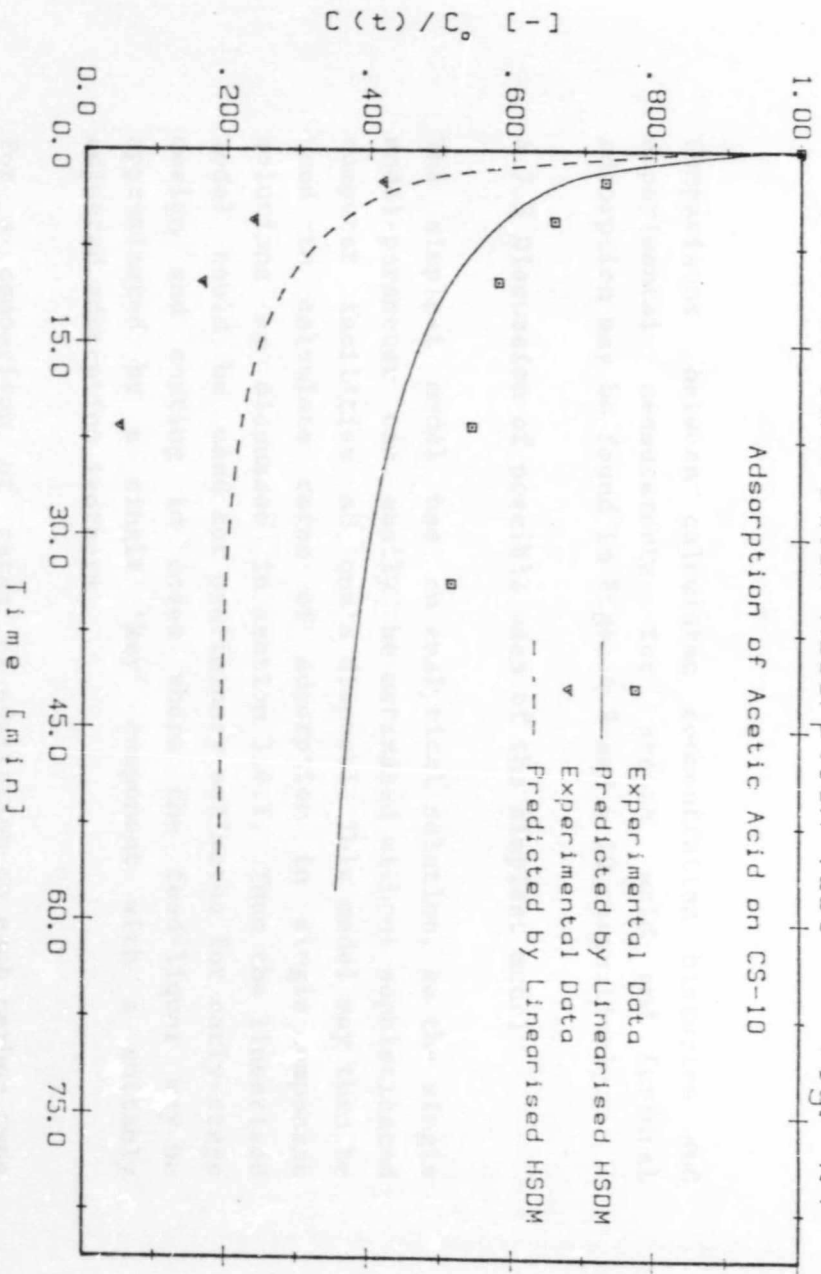
Comparisons between calculated concentration histories and experimental measurements for acetic acid and furfural adsorption may be found in Figs. 4.7 and 4.8 respectively.

4.7.2 Parameters for adsorption onto CS-15

The fitted parameters are tabulated below.

Table 4.5		
Linearised-model Parameters for Carbon Type CS-15		
Parameter	Acetic Acid	Furfural
D_s^* [$m^2.s^{-1}$] $\times 10^{12}$	40.5	3.64
σ [s]	4 153.0	46 153.0

Stirred-tank Batch Adsorption Test Fig. 4.7



Comparisons between calculated concentration histories and experimental measurements for acetic acid and furfural adsorption may be found in Figs. 4.9 and 4.10 respectively.

4.7.3 Discussion of possible uses of the simplest model

The simplest model has an analytical solution, so the single model-parameter can easily be estimated without sophisticated computer facilities at one's disposal. This model may then be used to calculate rates of adsorption in single component solutions as discussed in section 3.4.1. Then the linearised model could be used for preliminary estimates for early-stage design and costing in cases where the feed-liquor may be approximated by a single 'key' component with a suitably adjusted adsorption isotherm.

For a comparison of rates of adsorption on each carbon type calculated by this model to those calculated by the more sophisticated model for the two carbon types, see Figs. 4.11 to 4.14. From the graphs it can be seen that the errors incurred by using the linearised model are large for acetic acid adsorption; the rates of adsorption of furfural calculated by the two models are in fair agreement. In fact if the linearised model was to be used, one could concentrate on making it fit experimental data best for small times, where the rate of adsorption is of interest for practical design purposes.

4.8 Conclusions

The adsorption of acetic acid or furfural onto either CS-10 or CS-15 activated carbon adsorbent may be approximated as surface-diffusion controlled for film-coefficients of mass-transfer of the order commonly encountered in fluidised-bed operations.

The rates of adsorption used in design work may be calculated from a numerical solution to the homogeneous surface-diffusion

Author Anderson Paul

Name of thesis The Modelling And Design Of An Activated Carbon Adsorber For The Recovery Of Organic Components From A Cellulose-plant Effluent. 1986

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