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# Adsorption dynamics measured by permeation and batch adsorption methods

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## Abstract

We have measured the adsorption equilibrium and kinetics of carbon dioxide on a commercially available activated carbon by two methods; permeation and batch adsorption. The two methods are compared and found to yield consistent results. All experiments are performed at low pressure (<5 torr) and in this range the isotherm was found to be reversible and non-linear. Because of the observed non-linearity, the batch adsorption experiments were conducted differentially in order to obtain the adsorbed phase diffusivity at local conditions. The diffusion process was described by gas phase diffusion, adsorption and adsorbed phase diffusion which was modelled using the Darken relation. Results of adsorption equilibria and kinetics will be discussed in detail in this investigation. ©2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Adsorption dynamics; Permeation adsorption; Batch adsorption

## 1. Introduction

In the commercial operation of processes based on adsorption technology, an understanding of adsorption equilibria and dynamics is required. Gaining a fundamental understanding can be valuable in assisting process prediction and optimisation [1]. To this end, it is worthwhile measuring both capacity and kinetics in experiment. This can be performed by a variety of methods each with inherent advantages and disadvantages [1]. The chosen method may influence the measured sorption rate because of intrusion of secondary rate processes such as external film resistance and heat transfer rate. For this reason the method should be chosen carefully.

Interpretation of the rate data obtained from the chosen experimental method is often not straightforward. This is especially true for materials such as activated carbon which possess a distribution of pore sizes. Micropores usually provide the bulk of the adsorption capacity but due to the nature of molecular interaction, can provide a highly resistant path for diffusion of the adsorbed phase. Molecular simulation studies have shown this [2,3]. Mesopores can also contribute to the adsorption capacity as well as allowing some through flux of the adsorbed phase at high relative pressures where the amount adsorbed is high. This may occur by surface diffusion or an activated gaseous translation [4]. Macropores usually allow transport of the free gas phase which is often the significant contributor to the total through flux in adsorbent pellets. The nature of the through flux itself has been the focus of many studies [4,5] which have been undertaken in an effort to elucidate the activated nature of the measured flux. This is worthy of consideration as detailed evaluation of the pore network can often be achieved through using Lennard-Jones potential after having evaluated the necessary energetic features from experiment [5]. These studies have the added advantage that direct evaluation of the through flux is made. This is not possible with standard adsorption techniques such as batch adsorption experiment and such evaluation is usually obtained from optimisation. However, steady state permeation experiment will allow direct measure of the total flux and helium permeation is used to evaluate gas phase flux. The adsorbed phase flux is obtained simply from difference and this procedure provides an accurate means of measurement even for species with relatively low affinity, provided the flow of the adsorbed phase is not significantly less that of the gas phase. The batch adsorption experiment can provide information about the amount adsorbed at equilibrium, information which cannot be gained from steady state measurements. By this means it is possible to forge an accurate relationship between the through flow diffusion processes and the loading of adsorbate within the adsorbent material. Over a large range of loading this relationship may reveal possible pellet scale heterogeneity [6]. In this investigation, we utilise the method of permeation (for a review see [7]) and batch adsorption to investigate adsorption dynamics in a commercial activated carbon pellet and characterise such a relationship.

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## 2. Mass balance

When considering the dynamics of fluid transport in a porous adsorbent the process of adsorption and adsorbed phase diffusion have been shown to contribute significantly to the measured kinetics of mass transfer [8,9]. The contribution may be made in the form of adsorbed phase diffusion and possibly activated gaseous transport [4]. Because of the ill defined nature of the structure of many porous materials including activated carbon, the adsorbed phase transport process and its relationship with loading is not well understood. Several interpretations of this relationship are found in the literature, all generated from different views of the physical nature of the molecular motion through the porous solid. This is discussed in a review by [10]. Whatever the interpretation, the actual measurement of the adsorbed phase flux cannot be undertaken without measurement of the gas phase transport which occurs in parallel with the adsorbed phase transport. When local equilibrium is established quickly between the adsorbed phase and fluid phase, the mass balance can be represented as:

$$\varepsilon\frac{\partial C}{\partial t}+(1-\varepsilon)\frac{\partial C_\mu}{\partial t}=-\frac{1}{r^m}\frac{\partial}{\partial r}(\varepsilon r^m J+(1-\varepsilon)r^m J_\mu), \quad (1)$$

where $\varepsilon$ is the volume fraction allowing gas phase transport, $C_\mu$ and $J_\mu$ are the adsorbed phase concentration and flux, respectively and $m=0$ for slab, 1 for cylindrical and 2 for spherical geometry.

It is important to consider the representation of the adsorbed phase flux as various differing forms are presented in the literature [11]. It is usually related to the adsorbed phase concentration through a general Fickian type relation:

$$J_\mu=-D_{\mathrm{ads}}(C_\mu)\frac{\partial C_\mu}{\partial r}, \quad (2a)$$

where the adsorbed phase diffusivity, $D_{\mathrm{ads}}$ (representing the mobility of the adsorbed phase) is often dependent upon the adsorbed phase concentration. A general relationship between the two which is dependent on isotherm shape, is the Darken equation expressed as:

$$J_\mu=-D^0_{\mathrm{ads}}\frac{C_\mu}{C}\frac{\partial C}{\partial r}, \quad (2b)$$

where $D^0_{\mathrm{ads}}$ is the limiting diffusivity of the adsorbed phase occurring at very low loading.

Such a relationship has proven useful in describing the adsorbed phase transport of oxygen and nitrogen in activated carbon [12].

The fluid phase transport when known to be represented by Knudsen or molecular diffusion can reliably be represented by the pore diffusivity $D_{\mathrm{p}}$, making the flux expression as follows:

$$J=-D_{\mathrm{p}}\frac{\partial C}{\partial r}. \quad (3)$$

Using Eqs. (2a) and (3) to relate the flux to the concentration, the mass balance now becomes

$$\left(\varepsilon+(1-\varepsilon)\frac{\partial C_\mu}{\partial C}\right)\frac{\partial C}{\partial t}=\frac{1}{r^m}\frac{\partial}{\partial r}\left[r^m\frac{\partial C}{\partial r}\left(\varepsilon D_{\mathrm{p}}+(1-\varepsilon)D^0_{\mathrm{ads}}\frac{C_\mu}{C}\right)\right]. \quad (4)$$

Once a relationship between the adsorbed phase and gas phase concentrations is established the mass balance can be solved. This equilibrium relationship is usually ascertained by measurement via batch adsorption experiment.

### 2.1. Batch adsorption

In order to determine the amount adsorbed, it is the usual case that the adsorbent material will be placed in a bath of fluid and the amount adsorbed will be calculated by measurement of bulk concentration change in the batch reservoir. This set-up is widely used for measurement and has been termed batch adsorption experiment. The necessary boundary conditions, when a significant change is made in the bulk concentration, are represented as:

$$\frac{V}{A}\frac{\mathrm{d}C_R}{\mathrm{d}t}=\left[\varepsilon J+\varepsilon_\mu J_\mu\right]_{\partial\Omega}, \quad (5)$$

where $V$ is the volume of the bath and $A$ the contact area of the solid with the bath. After some time the bath concentration will reach equilibrium with the adsorbent making this method useful for determining the adsorption equilibrium isotherm. When the kinetics of adsorption are monitored for each equilibrium point, the dynamic parameters can be evaluated. The advantage offered by this method is that it allows measurement over a small increment in concentration, an approach commonly known as differential measurement. Over the small range of concentration that is being measured, the change in the adsorbed phase will be approximately linearly related to the change in the gas phase concentration, even when the adsorption isotherm is non-linear. This allows the mass balance to be linearised and solved analytically. The analytical solution of the mass balance is presented in the text of [13] for different geometries. In this paper, we experiment with cylindrical pellets and the solution in cylindrical geometry subject to the initial conditions

$$C(r,t=0)=C_{\mathrm{ini}}, \quad (6a)$$

$$C(r=R,t=0)=C_0, \quad (6b)$$

is given as

$$\frac{m}{m_{\mathrm{equ}}}=1-\sum_{n=1}^{\infty}\frac{4\alpha(1+\alpha)}{4+4\alpha+\alpha^2q_n^2}\exp\left(-\frac{D_{\mathrm{app}}q_n^2t}{R^2}\right), \quad (7)$$

where the $q_n$'s are the positive, non-zero roots of

$$\alpha q_n J_0(q_n)+2J_1(q_n)=0, \quad (8a)$$

$$\alpha=\frac{(C_\infty-C_{\mathrm{ini}})}{2\,(C_0-C_\infty)}, \quad (8b)$$

and $C_\infty$ is the final equilibrium concentration. Often the relevant equation is fitted to the data by error minimisation procedure. Alternatively, we may note from Eq. (7) that at large values of uptake only the first term in the series is dominant, and as a result the slope of the plot of $\ln(1-m/m_{\mathrm{equ}})$ vs. time will be

$$\mathrm{slope} = -\frac{D_{\mathrm{app}} q_1^2}{R^2}. \tag{9}$$

The variable of interest which characterises the dynamics, the apparent diffusivity ($D_{\mathrm{app}}$) is defined as:

$$D_{\mathrm{app}} = \frac{D_p + \frac{1-\varepsilon}{\varepsilon}\frac{C_\mu}{C} D_{\mathrm{ads}}^0}{1 + \frac{1-\varepsilon}{\varepsilon}\frac{\partial C_\mu}{\partial C}}. \tag{10}$$

When measured over many increments, the apparent diffusivity obtained from the slope of the above mentioned plot can be determined as a function of the concentration at which it is measured. The relationship between the diffusivity and the concentration can be determined by this means without the need for assuming any particular description of the diffusivity. This is the approach we adopt in this investigation and we will compare the results with those obtained by integral measurement taken over a large pressure increment where a mathematical description of the relationship is required and optimisation is usually used to justify the use of the description. However, it is possible by separate and independent measurement to determine this relationship accurately before batch measurements are taken. In this investigation, we use permeation method to achieve this.

### 2.2. Permeation method

Another method of monitoring the dynamics of diffusion is to mount the permeable material to form a porous barrier to penetrating fluid. This method maintains its unique advantages over the batch adsorption experiment [7]. Often the concentration is kept constant at the point of contact of the permeable barrier and the fluid, one point at a defined value, $C_0$, the other usually kept small in comparison. The boundary conditions of this permeation method can be represented as:

$$C(r=0) = C_0, \tag{11a}$$

$$C(r=L) = 0. \tag{11b}$$

Because the concentration difference is large across the permeable barrier, the time lag permeation technique is by definition, an integral method. Therefore measurement over a small increment and subsequent linearisation of the mass balance is not possible as it is with differential measurement. However, it has been shown that the steady state rate ($S_\infty$) and time lag ($t_{\mathrm{lag}}$) provide a useful method of characterisation without the need for solving the mass balance numerically when the isotherm is non-linear [14]. Integrating the mass balance by a method similar to that presented by [15] we obtain the following time lag

$$t_{\mathrm{lag}} = \frac{L^2 \int_0^{C_0} (\varepsilon C + (1-\varepsilon) C_\mu) H(u) \left(\int_u^{C_0} H(w)\,\mathrm{d}w\right) \mathrm{d}u}{\left(\int_0^{C_0} H(u)\,\mathrm{d}u\right)^3}, \tag{12a}$$

and steady state rate $S_\infty$,

$$S_\infty = \frac{A}{VLC_0} \int_0^{C_0} H(C)\,\mathrm{d}C, \tag{12b}$$

where, for the description of the adsorbed phase flux given by Eq. (2a), the function $H$ is defined as:

$$H = \varepsilon D_{\mathrm{p}} + (1-\varepsilon)\frac{C_\mu}{C} D_{\mathrm{ads}}^0. \tag{12c}$$

Because the steady state rate is directly related to the adsorbed phase mobility, it is possible to obtain direct evaluation of the adsorbed phase diffusivity when the effective diffusivity has been evaluated by permeation of inert gas.

## 3. Experimental

The permeation experiments were conducted as discussed in a previous publication [16]. However, a modification of the system was made to allow batch adsorption dynamics and equilibrium to be measured. Hollowed copper housing containing the extruded activated carbon pellets was attached to the commercially supplied Conflat flanged fittings. This allowed the option of undertaking permeation experiment or batch adsorption experiment at any time simply by opening/closing valves. The modified apparatus appears in Fig. 1.

In the permeation experiment, a cylindrical pellet of Ajax activated carbon was studied. Similar pellets but of shorter length (1 cm) were used for the batch adsorption study. Details of the pellet properties are summarised in Table 1.

The procedure for the batch adsorption experiment involved initially charging the receiving volume (or outgassing in the case of the desorption experiment) with the required amount of fluid. At $t=0$ the valve is opened, fluid fills the adsorption chamber and adsorption begins. The kinetic process is monitored by change in pressure. The ability to measure pressure changes at low pressures requires high vacuum components permitting very low static vacuum leak rates. For this reason all fittings in the apparatus have VCR (a Cajon fitting) or Conflat (a Varian fitting) face seals.

Outgassing of the pellet before each experiment occurred at $10^{-6}$ torr for a minimum of 48 h, a period much greater than the time required for the actual dynamic experiment.

Table 1
Pellet details

| Length of mounted slab ($L$) | Pellet macroporosity | Pellet radius ($R$) | Mean pore size |
|---|---|---|---|
| 1.4 cm | 0.31 | 0.1 cm | 0.8 μm |

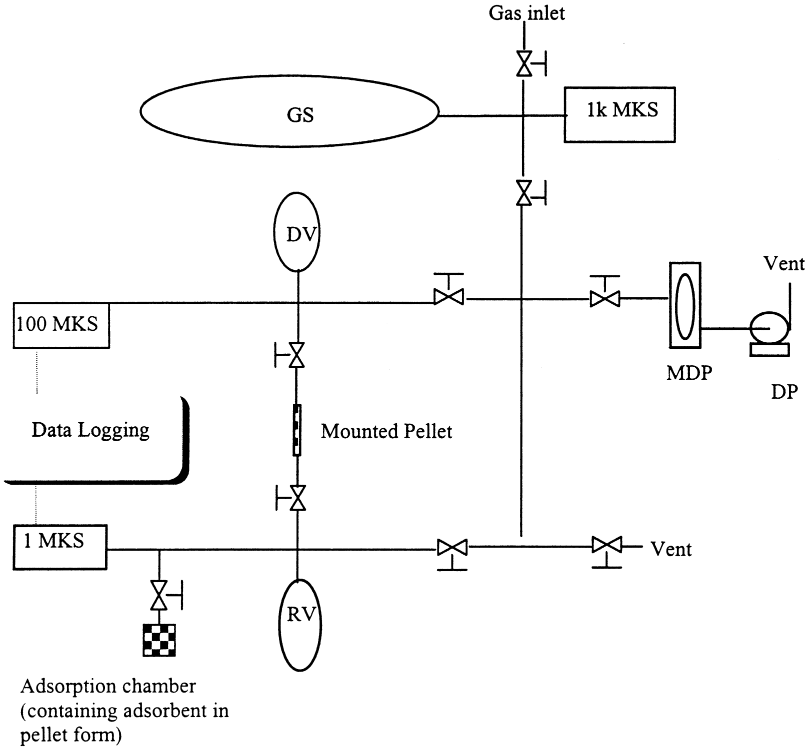

Fig. 1. Schematic of experimental apparatus.

Integral measurement of kinetics and equilibria requires this outgassing procedure before each experimental run. This makes it a time consuming method. Differential measurement requires one outgassing stage and many data points may be determined depending on the increment taken. It is obvious that this is an inherent advantage of the differential operation and is the primary reason for performing batch experiment in this manner.

## 4. Adsorption isotherm

When the batch adsorption process reaches equilibrium, the total amount adsorbed can be calculated and the process repeated over a range of pressures. By this means, we may establish a relationship between the pressure and the amount adsorbed. This was undertaken for $CO_2$ adsorption onto Ajax activated carbon over a range of pressures less than 5 torr at 20°C. The relationship represented on Fig. 2 was fitted to several isotherm equations including Unilan, Dubinin-Radushkevich and Toth but the best fit determined by the smallest sum of squares error was that of the Langmuir-Freundlich (or Sips) equation represented as:

$$C_\mu = C_{\mu s}\frac{(bC)^{1/n}}{1+(bC)^{1/n}}. \tag{13}$$

Although the isotherm is often used to determine heterogeneous features of the porous solid, our aim in fitting the isotherm equation is merely to obtain the most accurate analytical description for predicting and correlating the dynamics of adsorption. For this reason discussion and interpretation of the isotherm is not warranted. However, the values for the parameters of the Sips equation obtained from optimisation are $n = 1.76$, $C_{\mu s} = 0.56$ mmol/cc, $b = 28.3$ cc/mmol. The desorption experiment was also performed upon a loaded sample yielding similar results to the adsorption experiment as is shown on Fig. 2. This indicates that most of the adsorbed molecules are essentially adsorbed reversibly which is common for many physical adsorption processes.

## 5. Adsorption dynamics

The dynamics of adsorption can be measured by a variety of methods each having their own advantages [1]. In this paper we use two of these methods: batch adsorption and permeation, both of which evaluate the apparent diffusivity. The definition of the apparent diffusivity has been presented in Eq. (10) and includes the pore diffusivity term. We have shown in a previous publication that the mechanism of mass transfer in the gas phase is one of pure Knudsen diffusion for pressures less than 5 torr [16] in this porous carbon. The Knudsen diffusivity was evaluated and it is predicted that for carbon dioxide the pore diffusivity would be $D_p = 0.2\ \mathrm{cm^2/s}$.

### 5.1. Permeation dynamics

The two parameters characterising permeation through the pellet are the previously mentioned steady state rate and time

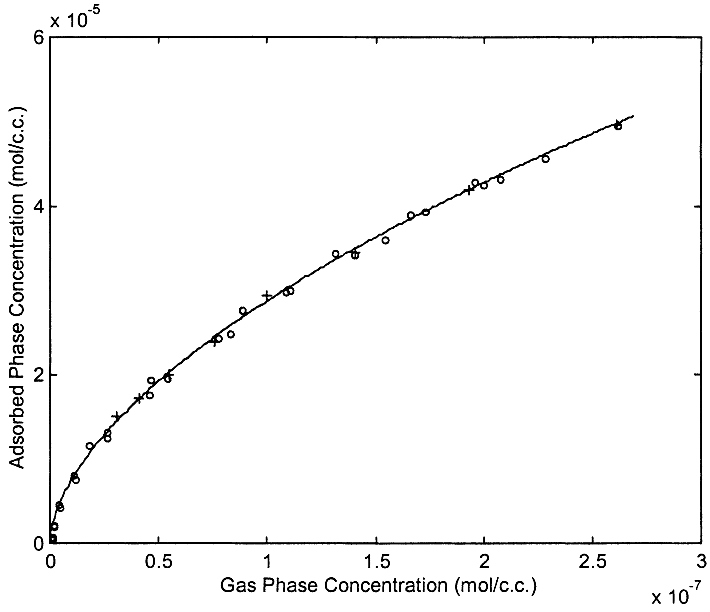

Fig. 2. Adsorption equilibrium isotherm for carbon dioxide and Ajax activated carbon at 20°C. Open circle indicates those points obtained from adsorption, cross indicates those obtained via desorption.

lag. Having determined the isotherm relationship and evaluated the effective diffusivity the time lag and steady state rate can be predicted when the adsorbed phase diffusivity is known. At this point we must use an optimisation/fitting procedure to evaluate $D^0_{\mathrm{ads}}$ from the data because at this stage it is unknown. The measured time lag and steady state slope are presented in Fig. 3 and the best fit of Eqs. (12a) and (12b) respectively is shown. The two equations are evaluated numerically using the Sips isotherm equation. It should be noted here that the equation for steady state slope can be evaluated analytically using the Sips isotherm. It is given as:

$$S_\infty = \frac{A}{VL}\{\varepsilon D_{\mathrm{p}} + (1-\varepsilon) n D^0_{\mathrm{ads}} \delta \ln[1 + (\lambda)^{1/n}]\}, \tag{14a}$$

where the parameters are defined as:

$$\lambda = bC_0, \tag{14b}$$

$$\delta = \frac{C_{\mu s}}{C_0}. \tag{14c}$$

The time lag cannot be exactly evaluated analytically so numerical methods are required. Before evaluation we non-dimensionalise the expression and obtain:

$$t_{\mathrm{lag}} = \frac{L^2 \int_0^1 \left(z + \frac{(1-\varepsilon)\delta}{\varepsilon} \frac{(\lambda z)^{1/n}}{1+(\lambda z)^{1/n}}\right) W(z) \left(\int_z^1 W(u)\mathrm{d}u\right) \mathrm{d}z}{D_{\mathrm{p}} \left(\int_0^1 W(z)\mathrm{d}z\right)^3}, \tag{14d}$$

where the function $W$ is defined as:

$$W = 1 + \frac{(1-\varepsilon) D^0_{\mathrm{ads}}}{\varepsilon D_{\mathrm{p}}} \frac{bC_{\mu s} (\lambda z)^{1/n-1}}{1 + (\lambda z)^{1/n}}. \tag{14e}$$

The expressions for both time lag and steady state rate fit the data reasonably well, verifying the use of the Darken equation to describe the adsorbed phase diffusion process. The value of the diffusivity obtained from optimisation is $D^0_{\mathrm{ads}} = 1 \times 10^{-6}$ cm$^2$/s. This value compares well with that obtained by measurement of carbon dioxide permeation at 303 K through a microporous material [4]: $1.5 \times 10^{-6}$ cm$^2$/s.

The sensitivity of techniques used for adsorption dynamics measurement is an important issue when considering evaluation of adsorbed phase flux. This is because the flux is often only a small percentage of the total flow. Fig. 3c shows the predicted fraction of average adsorbed phase flux through the pellet to the total flux for carbon dioxide permeation measured in this investigation. It can be seen that at low pressures this fraction is greater due to the favourable shape of the isotherm. The magnitude of this fraction (around 10%) is typical for many adsorbates in this material [17]. With such a small percentage of adsorbed flow accurate measurement of the flux is vital. Direct measurement of the total flux is the most accurate means of evaluation because "transient" effects such as heat transfer, outgassing effects, dead end porosity etc. which are captured by "transient" measurement techniques such as time lag and batch adsorption, have no effect on direct steady state measurement.

### 5.2. Batch dynamics

Measurement of the adsorption isotherm required dynamic monitoring of the pressure changes in order to determine when equilibrium was truly reached. The dynamic adsorption experiment was performed differentially for several reasons including:

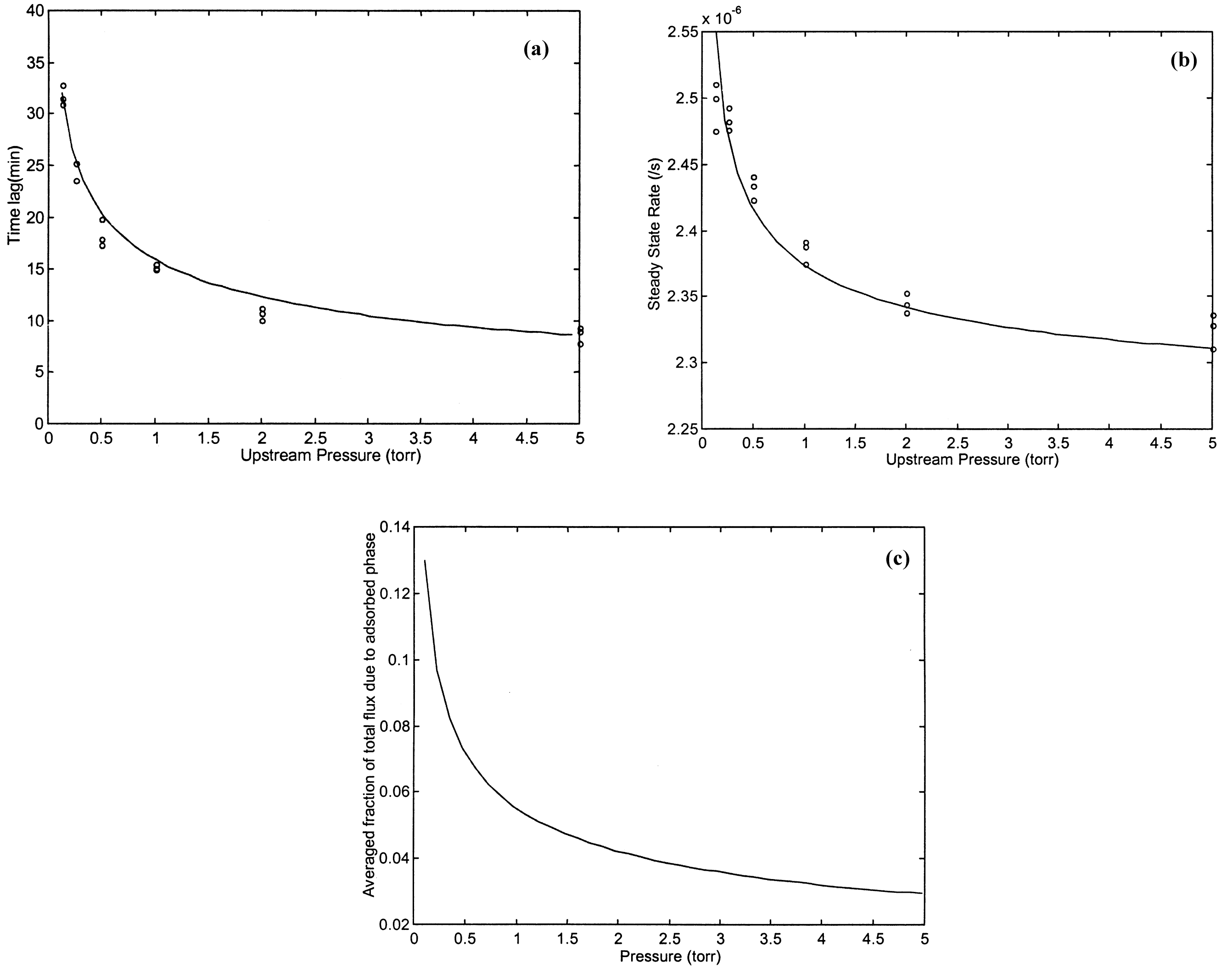

Fig. 3. (a) Change in the time lag with upstream pressure for carbon dioxide on Ajax activated carbon at 293 K. (b) Change in the steady state rate with upstream pressure for carbon dioxide on Ajax activated carbon at 293 K. (c) Predicted fraction of average adsorbed phase flux through the pellet and its relationship with the upstream pressure.

1. Often the amount adsorbed has a non-linear relationship with pressure. Over a small pressure increment, such non-linear relationships can be effectively linearised. As a result, analytical solution of the mass balance is possible and the diffusivity determined by asymptotic methods (as discussed earlier). Using a large pressure increment would require numerical solution of the mass balance with subsequent model fitting. This is usually a cumbersome procedure.
2. Under high vacuum the process of heat transfer from the pellet to the surrounds is very slow. Any energy gained from the exothermic process of adsorption cannot be released quickly and may interfere with the adsorption dynamics. A small increment in pressure will correspond to a small change in the amount adsorbed and over a long period of time the effect of temperature rise will be negligible. A simple calculation taking into account the worst case scenario of a closed adiabatic system reveals the maximum possible temperature rise of the pellet. If we assign the maximum temperature rise to be no greater than 1°C and use typical values for heat of adsorption and heat capacity for a carbon pellet (as presented by [18]) then a change in pressure of around 10 torr should not be exceeded for $CO_2$ measurement.
3. More data can be obtained in a shorter time period because outgassing of the pellet occurs once only.

As discussed earlier, it is the slope of the logarithmic uptake plot in which we are interested. The slope was determined from the data by linear regression and the apparent diffusivity determined by Eq. (9). The result is shown on Fig. 4 which clearly shows the dependence of the diffusivity upon the concentration. The solid line represents that predicted by Eq. (10) using values previously obtained from permeation measurement. The prediction is an accurate one as the plot shows. This indicates that both methods, permeation and batch adsorption, are providing measurements

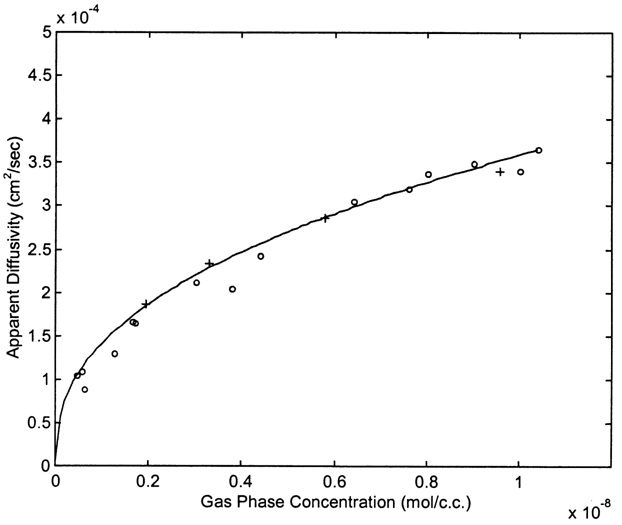

Fig. 4. Change in the apparent diffusivity for carbon dioxide on Ajax activated carbon at 20°C with gas phase concentration. Open circle indicates those points obtained from adsorption, cross indicates those obtained via desorption.

consistent with each other. Because the permeation experiment is conducted with a slab and the batch adsorption with a pellet of cylindrical geometry, it further implies that the mathematical description is consistent across both geometries. Fig. 4 also shows the value of the measured diffusivity for some desorption experiments performed differentially. There appears to be little difference between the kinetics of adsorption and desorption, just as there was little difference in the measurements of the amount adsorbed from both type of experiment. This reinforces the observation made from measurement of the amount adsorbed from the desorption experiment that the physical process being monitored is truly a reversible action.

In order to further validate the results obtained from permeation and differential batch adsorption we have measured the uptake over a large change in pressure in which the isotherm relation is not linear. This is known as integral measurement and analysis of data requires solving the mass balance numerically. We aim to solve our non-linear mass balance in cylindrical geometry, represented by Eq. (4) with $m=1$. Using the symmetry conditions we will define a new spatial co-ordinate, non-dimensional time and concentration as is shown in Table 2. Also defining some parameters in Table 2 allows us to represent the mass balance as:

$$\frac{\partial y}{\partial \tau} = 4EP(y)x\left(\frac{\partial y}{\partial x}\right)^2 + 4M(y)x\frac{\partial^2 y}{\partial x^2} + 4M(y)\frac{\partial y}{\partial y}. \tag{15a}$$

This non-linear equation is solved by the numerical method of lines with the boundary and initial conditions:

$$x = 1;$$

$$\frac{\partial y}{\partial \tau} = \frac{-2\varepsilon AR}{V}\left[1 + ED\frac{\lambda^{1/n}\delta y^{1/n-1}}{1+(\lambda y)^{1/n}}\right]\sqrt{x}\frac{\partial y}{\partial x}. \tag{15b}$$

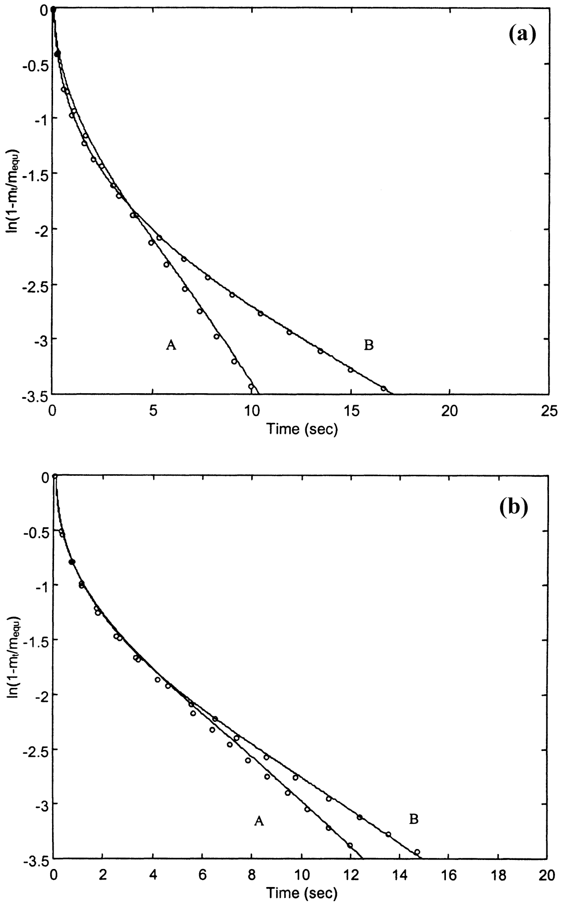

Fig. 5. (a) The amount adsorbed varies with time in the "integral" measurement from initially outgassed pellets. Open circles represent data points and solid line represents model fit. Curve A has a starting pressure ($P_0$) 0.4 torr and curve B has a starting pressure of 0.05 torr. (b) The amount adsorbed varies with time in the "integral" measurement from initially outgassed pellets. Open circles represent data points and solid line represents model fit. Curve A has a starting pressure ($P_0$) of 0.2 torr and curve B has a starting pressure of 0.1 torr.

$$At\ t = 0;\quad y(x=1) = 1\ and\ y(x<1) = C_{ini}/C_o. \tag{15c}$$

The method of lines requires discretisation of the mass balance and a series of ODEs are generated which are solved by a "stiff" ODE solver. This numerical method has been shown to be useful for dynamic adsorption simulation [19]. The result of the numerical analysis is the dynamic uptake simulation for a given pressure ($P_0$) and this can be compared to the measured pressure change with time. In all the experiments undertaken in this manner the pellet was initially outgassed ($P_{\mathrm{old}}=0$) meaning that at higher pressures the total pressure change may be large and hence that the heat released upon adsorption may be significant. However, Fig. 5a and b show the experimental and simulated dynamic change for the pressures indicated using previously obtained values for equilibrium isotherm and diffusivity. Once again the agreement of the data and simulation is good, indicating that the effect of heat released is minimal in this range.

Table 2
Non-dimensional parameters and variables for simulation

| Non-dimensional variable | Non-dimensional parameter |
|---|---|
| $x=\left(\frac{r}{R}\right)^2$ | $E=\frac{\varepsilon_\mu}{\varepsilon}$ |
| $\tau=\frac{\mathrm{D_P}}{\mathrm{R}^2}t$ | $D=\frac{D_{\mu 0}}{D_{\mathrm{P}}}$ |
| $y=\frac{C}{C_0}$ | $M(y)=\left[1+\frac{ED\lambda^{1/n}\delta y^{1/n-1}}{1+(\lambda y)^{1/n}}\right]\left\{1+\frac{E\lambda^{1/n}\delta y^{1/n-1}}{n[1+(\lambda y)^{1/n}]^2}\right\}^{-1}$ |
|  | $P(y)=D\frac{\lambda^{1/\mathrm{n}}\delta y^{1/n-2}}{[1+(\lambda y)^{1/n}]^2}[1-\frac{1}{n}-(\lambda y)^{1/n}]\left\{1+\frac{E\lambda^{1/n}\delta y^{1/n-1}}{n[1+(\lambda y)^{1/n}]^2}\right\}^{-1}$ |

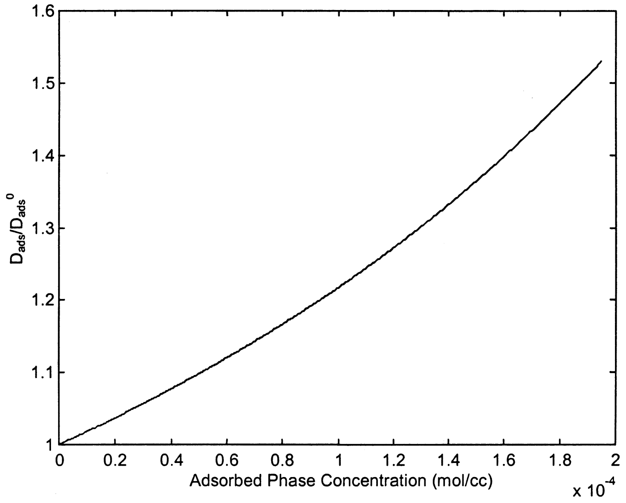

Fig. 6. The relationship between the adsorbed phase diffusivity ratio and the adsorbed phase concentration (for carbon dioxide on Ajax activated carbon at 20°C) as predicted by the Darken relation.

### *5.3. Mobility of the adsorbed phase*

The description of the diffusion of the adsorbed phase at low concentrations is highly dependent upon the nature of the interaction between the adsorbed species and the solid itself. Currently, most of these descriptions proposed in the literature relate the mobility to a mechanism of transfer useful for homogeneous solids e.g. hopping model, random walk, statistical mechanical treatment [10]. The approach used here to describe the flow of the adsorbed phase is based upon the work of [20]. As a thermodynamic treatment, the Darken relation expresses the change in mobility of the adsorbed phase and relates it to the amount adsorbed, as presented earlier. This dependence is presented graphically in Fig. 6 which shows the non-dimensional adsorbed phase diffusivity $D_{\mathrm{ads}}/D_{\mathrm{ads}}^0$ vs. adsorbed phase concentration. It can be seen that for this case the Darken relation predicts a steady rise in mobility with concentration. The magnitude of the change is relatively small in comparison to that at concentrations approaching saturation where sharp changes and magnitudes of the ratio $D_{\mathrm{ads}}/D_{\mathrm{ads}}^0$ as high as 10 may be possible [10].

Implicitly, in the use of the Darken relation, we have treated the relationship between adsorbed phase flow and loading semi-empirically and ignored pellet scale heterogeneity inherent in the permeation/adsorbed phase diffusion process. For materials such as most activated carbons which are highly heterogeneous with respect to pore size and structure, modifications have been applied to the analysis to incorporate such effects [6]. However, the Darken relation provides an adequate description in our range of measurement, implying that these heterogeneous effects if present intrude little into the diffusion process or remain static over the range of pressure we have measured. In order to fully investigate such effects, a larger pressure range over which these effects will be more pronounced, should be scrutinised. Furthermore, the dependence of the adsorbed phase flux upon temperature can provide additional information about heterogeneous features.

## 6. Conclusions

The measurement of adsorption dynamics for carbon dioxide on activated carbon was undertaken with batch adsorption and permeation experiments. The data obtained from both methods is consistent and the mathematical description is shown to be appropriate due to the fact that consistency is obtained from measurement with pellets of different geometry and from integral and differential experiment. In this description, we have used the Darken relation to model the diffusion of the adsorbed phase. In the range of measurement undertaken, this relation provides an adequate description. We have also shown that the adsorption is reversible and desorption dynamics are equivalent to the adsorption dynamics under differential conditions.

## 7. Nomenclature

|  |  |
|---|---|
| $A$ | cross-sectional area of medium |
| $b$ | parameter of isotherm equation |
| $C$ | concentration of diffusing species |
| $C_{\mathrm{ini}}$ | initial concentration |
| $C_0$ | upstream concentration |

| | |
|---|---|
| $C_{\mu s}$ | saturation capacity |
| $D$ | diffusivity |
| $D_{\mathrm{ads}}$ | adsorbed phase diffusivity |
| $D_{\mathrm{p}}$ | pore diffusivity |
| $D^0_{\mathrm{ads}}$ | adsorbed phase diffusivity at zero loading |
| $J$ | flux |
| $L$ | length of the pellet |
| $n$ | parameter of isotherm equation |
| $P$ | pressure |
| $R$ | gas constant |
| $S_\infty$ | steady state rate |
| $T$ | absolute temperature |
| $t$ | time |
| $t_{\mathrm{lag}}$ | time lag |
| $V$ | volume of vessel in which measurement takes place |
| $\lambda$ | parameter defined by Eq. (14b) |
| $\delta$ | parameter defined by Eq. (14c) |

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## References

[1] M. Bulow, A. Micke, J. Adsorption 1 (1995) 29–48.
[2] D. Ford, E. Glandt, J. Phys. Chem. 99 (1995) 11543.
[3] J. MacElroy, N. Seaton, S. Freidman, in: W. Rudzinski, W. Steele, G. Zgrablich (Eds.), Equilibria and Dynamics of Gas Adsorption on Heterogeneous Solid Surfaces, Elsevier, Amsterdam, 1997.
[4] W. Bakker, L. van den Brooke, F. Kapteijn, J.A. Moulijn, AIChE J. 43 (1997) 9.
[5] A. Shelekhin, A. Dixon, Y. Ma, AIChE J. 41 (1995) 1.
[6] D.D. Do, Chem. Eng. Sci. 51(17) (1996) 4145.
[7] S.W. Rutherford, D.D. Do, J. Adsorption 3 (1997b) 283.
[8] D.M. Ruthven, Principles of Adsorption and Adsorption Processes, Wiley, New York, 1984.
[9] R.T. Yang, Gas Separation by Adsorption Processes, Butterworths, Boston, MA, 1987.
[10] A. Kapoor, R.T. Yang, C. Wong, Cat. Rev. Sci. Eng. 31 (1989) 129.
[11] D.D. Do, Adsorption Analysis; Equilibria and Kinetics, Imperial College Press, London, 1998.
[12] D.M. Ruthven, Chem. Eng. Sci. 47(17/18) (1992) 4305–4308.
[13] J. Crank, The Mathematics of Diffusion, 2nd ed., Clarendon Press, Oxford, 1975.
[14] S.W. Rutherford, D.D. Do, Chem. Eng. Sci. 52(5) (1997a) 703.
[15] H.L. Frisch, J. Phys. Chem. 61 (1957) 93.
[16] S.W. Rutherford, D.D. Do, Ind. Eng. Chem. Res. 38 (1999) 565–570.
[17] X. Hu, Ph.D. Thesis, The University of Queensland, 1993.
[18] Y.D. Chen, R.T. Yang, P. Uawithya, AIChE J. 40 (1994) 4.
[19] Y. Liu, J. Delgado, J. Ritter, J. Adsorption 4 (1998) 337–344.
[20] L. Darken, Trans. AIME 174 (1948) 184.