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## Sorption kinetic studies of water vapour on activated carbon beds

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### ABSTRACT

Experimental measurements of the adsorption kinetics of water in activated carbon beds at different values of relative humidity have been made. The development of a simple theoretical model based on inter- and intra-particle mass transfer taking into account the thermal effects of sorption of water in activated carbon beds is described. The comparison of the model results with the experimental data is also presented. It is concluded that a single value of the estimated mass transfer coefficient can be used to reasonably predict the adsorption behaviour of water in activated carbon beds.

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### 1. Introduction

It is well-known that the adsorption and breakthrough behaviour of vapours through activated carbon beds is affected by the presence of water vapour in the incoming carrier gas stream [1,2]. This effect is found to be significant particularly in the case of low-boiling organic vapours where competitive adsorption of water and the organic vapour on the surface of the activated carbon takes place. For example the ratios of the experimental breakthrough times of dry *n*-propane and dry *n*-butane through an activated carbon bed to the corresponding values through a pre-humidified activated carbon bed subjected to a challenge of wet organic vapour were found to be between 12–15 and 5–7, respectively; whereas similar ratios for *n*-octane and *n*-decane were experimentally found to be between ~1.5 and ~1.1, respectively [3]. Also, the comparison between the experimental uptake of water vapour and similar-sized organic molecules showed that the kinetics

of water uptake was noticeably slower than that of organic molecules. The reason for this behaviour is still not clear.

With respect to understanding the mechanism of the sorption of water vapour on porous activated carbon surfaces, there is still some debate as to whether the sorption of water in porous carbon materials occurs through a capillary condensation mechanism or through one that involves clustering around primary adsorption centres/sites [4]. Dubinin and Serpinski [5] proposed a mechanism based on the effect of surface oxide complexes, which act as primary sites, to initiate adsorption and subsequent sorption of water molecules on the sorbed water. However, additional experimental work by Barton et al. [6,7] and Juhola [8] indicated that the surface oxides do not seem to control the adsorption of water significantly on activated carbon surface. Sircar [9] presented the development of a conceptually simple general model for adsorption and an isotherm equation accounting for the effect of physical adsorption and capillary condensation in

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microporous adsorbents. Subsequently, Mahle and Friday [10] extended the Sircar's isotherm assuming a bimodal pore distribution and capillary condensation occurring in both types of pores. Their analysis seemed to indicate that it might be possible to note the effect of capillary condensation in pores with radii as small as 2 nm. Brennan et al. [21], in their review of the adsorption of water on activated carbon, have also indicated that strong self-association of water due to hydrogen bonding limits adsorption on graphite surfaces and water condensation is stabilized by the formation of clusters in the liquid phase. However, in small pores, there are geometric constraints on the limits of cluster formation, which limits the adsorption until high relative pressure is obtained. At low coverage, water adsorption is governed by polar site interactions.

As a first step in understanding the adsorption behaviour of water vapour on activated carbon, a study of the kinetics of adsorption of water on activated carbon was undertaken. This involved some experimental measurements and development of a generic, simple model, based on inter- and intra-particle mass transfer taking into account the thermal effects associated with sorption of water vapour in activated carbon beds. There is considerable information related to the experimental sorption equilibrium data and their correlation with some form of sorption equilibrium equation [5,9-12]. Also, there have been some attempts related to correlating the kinetics of sorption of water vapour in activated carbon with a mass transfer coefficient. However, either these studies are limited to single or a very small amount of particles, wherein the thermal effects are negligible [13] or those where the thermal effects are not taken into account [14,15]. Since the phenomenon of adsorption is always associated with thermal effects that could be significant particularly in a bed of adsorbent particles, it is important to take thermal effects into account while developing a model to accurately predict the sorption behaviour.

## 2. Experimental

As a first step, the physical characterization of the ASZM/T carbon was carried out by measuring the mercury porosimetry and nitrogen adsorption measurements, from which surface area, micropore volumes, and the bulk and skeletal densities were obtained. The experimentally measured values of these parameters are given in the Table 1.

The next step involved measuring the water adsorption isotherm data on the ASZM/T samples at 298 K using a McBain-Bakr microbalance. The sorption isotherm measurements were repeated four times to ensure repeatability. The

Table 1 - Physical properties of the AZM/T carbon

Parameter	Value
Mesopore volume	0.14 cm <sup>3</sup> /g
Macropore volume	0.2 cm <sup>3</sup> /g
Micropore volume	0.30 cm <sup>3</sup> /g
Surface area (BET)	739 m <sup>2</sup> /g
Bulk density	0.97 g/cm <sup>3</sup>
Skeletal density	1.44 g/cm <sup>3</sup>

kinetics of adsorption as well as desorption of water on ASZM/T carbon was studied under following conditions: 170 cm<sup>3</sup> of 12 × 30 mesh ASZM/T at flow rate of 30 L/min (superficial linear velocity ~5.77 cm/s) at ~297 K with humidity values ranging between 25% RH and 80% RH. The kinetic experiments were carried out in a standard unit used to measure the performance of military canisters. The experimental procedure involved measurement of the inlet and outlet temperatures of the carrier gas stream, and the water uptake/loss as a function of time starting with a clean, dry bed containing no pre-adsorbed water till the bed reached a constant weight. The time to reach equilibrium varied between 24 h and 48 h depending on the value of the humidity.

## 3. Theoretical

A simple, generic model, taking into account inter- and intra-particle mass- and heat-balance in a packed bed, was developed based on assumptions of plug-flow, pseudo-equilibrium conditions and considering equality of temperatures between the carrier gas and the particle temperature at any point within the bed. The details about the model have been presented earlier [3]. The basic mass- and heat-balance equations can be written as

$$v_L \frac{\partial c}{\partial x} + \varepsilon \frac{\partial c}{\partial t} + \rho_b \frac{\partial n}{\partial t} = 0 \quad (1)$$

$$\frac{\partial n}{\partial t} = k_v(n^* - n) \quad (2)$$

$$v_L \rho_g c_{pg} \frac{\partial T}{\partial x} + (K) \frac{\partial T}{\partial t} = \rho_b Q_a \frac{\partial n}{\partial t} - \frac{4h_w}{d} (T - T_w) \quad (3)$$

where  $v_L$ ,  $\varepsilon$  and  $\rho_b$  denote the superficial linear velocity of the carrier gas (cm/s), voidage and bulk density (g/cm<sup>3</sup>) of the bed, respectively;  $c$  (g/cm<sup>3</sup>) and  $T$  denote the concentration and temperature of the adsorbate in the bulk carrier gas stream respectively at a distance ( $x$ ) from the inlet of the bed and time ( $t$ );  $Q_a$ ,  $c_{pg}$  and  $(K)$  denote the heat of adsorption of the adsorbate, heat capacities of the carrier gas and the adsorbent particle including the adsorbed phase respectively;  $n$  (g/g) and  $n^*$  (g/g) denote the concentration of the adsorbate in the adsorbed phase and its equilibrium value corresponding to the gas phase concentration  $c$ ; and  $k_v$  (s<sup>-1</sup>) denotes the overall mass transfer coefficient;  $h_w$  (W/cm<sup>2</sup>-K) denotes the overall heat transfer coefficient for the exchange of heat between the carrier gas and the outside air through the walls of the canister;  $d$  (cm) is the diameter of the bed and  $T_w$  denotes the temperature of the canister wall.

The adsorption equilibrium for the water-activated carbon system can be represented by the following equation proposed by Mahle [12].

$$n^* = \frac{n_{ws}}{D_{wm}} \left[ \tan^{-1} \left\{ \frac{c_w - A_{wm}}{B_{wm}} \right\} - \tan^{-1} \left\{ -\frac{A_{wm}}{B_{wm}} \right\} \right] \quad (4)$$

where  $A_{wm}$ ,  $B_{wm}$  and  $D_{wm}$  denote the coefficients;  $c_w$  and  $c_{ws}$  denote the concentration of water in the carrier gas stream and its value corresponding to 100% humidity, respectively; and  $n_{ws}$  (g/g) denotes the concentration of water in the adsorbed phase at saturation. It is to be noted that  $c$  [Eq. (1)] and  $c_w$  [Eq. (4)] are the same.

The overall mass transfer coefficient can be correlated to the effective diffusivity,  $D_{eff}$  (cm<sup>2</sup>/s), of the water vapour in

the activated carbon pores and the radius of the adsorbent particle as per Glueckauf assumption [16] as equal to  $15 D_{eff}/R_p^2$ . The effective diffusivity can be calculated from effective diffusion coefficients for pore and surface diffusion as per the following equation [17].

$$D_{eff} = \frac{1}{\alpha} \left[ D_{Ag} + \frac{(1 - \epsilon_p)}{\epsilon_p} K D_{As} \right] \quad (5)$$

where  $\alpha$  and  $\epsilon_p$  denote the tortuosity factor and the porosity of the carbon particles, respectively, and  $K$  denotes the slope of the adsorption isotherm. The effective pore diffusion coefficient  $D_{Ag}$  is a function of the molecular and Knudsen diffusion coefficients as given below [16].

$$\frac{1}{D_{Ag}} = \frac{1}{D_{mA}} + \frac{1}{D_{Kn}} \quad (6)$$

The correlations to calculate molecular diffusion coefficient,  $D_{mA}$ , from the molecular properties of the adsorbate, pressure

and temperature, and Knudsen diffusion coefficient,  $D_{Kn}$ , from the pore radius, molecular weight and temperature, are available in any reference book [17].

$$D_{mA} = \left[ \frac{(3.03 - \frac{0.98}{M_{AB}^{0.25}}) T^{1.5} * 10^{-3}}{P M_{AB}^{0.5} \sigma_{AB}^2 \Omega_D} \right] \quad (7)$$

and

$$D_{Kn} = 9700 r_p \sqrt{\frac{T}{M_A}} \quad (8)$$

The effective surface diffusion coefficient  $D_{As}$  can be calculated from the heat of adsorption, temperature and a polarity-dependent coefficient by the following correlation proposed by Sladek et al. [18].

$$D_{As} = 0.016 \exp \left[ -\frac{0.45 Q_a}{mRT} \right] \quad (9)$$

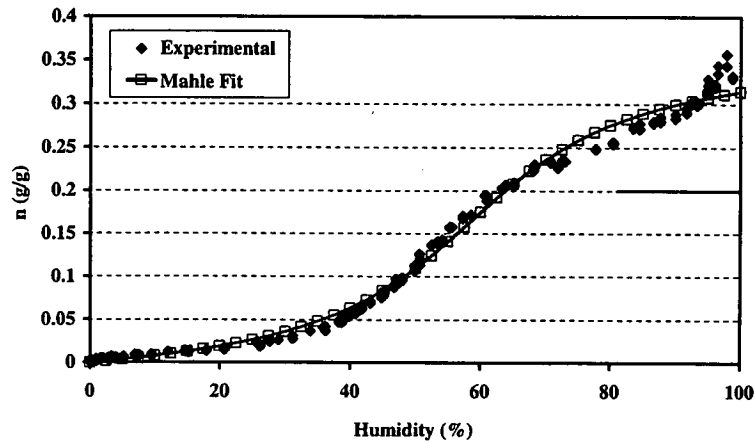


Fig. 1 - Water-ASZM/T adsorption isotherm.

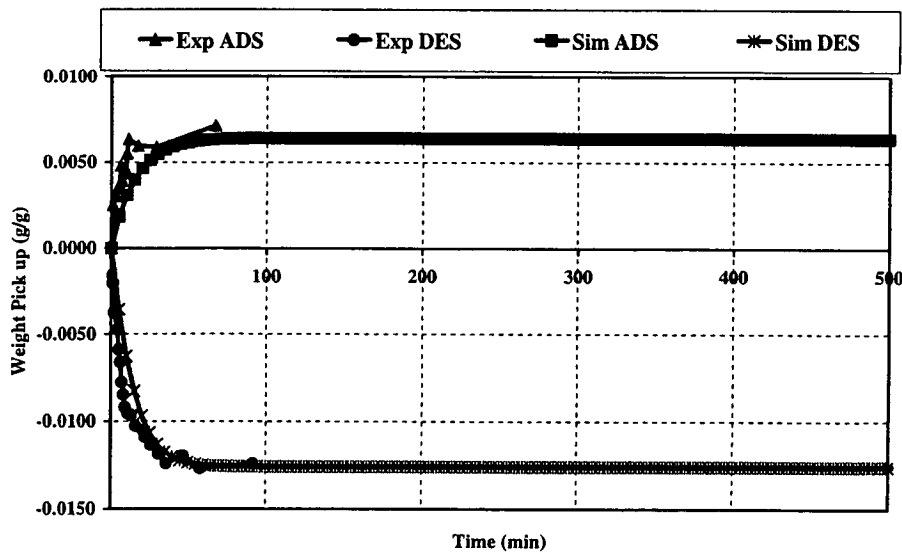


Fig. 2 - Water-ASZM/T sorption [25% RH].

Though it is expected that the heat of adsorption will vary as a function of surface coverage due to its energetic inhomogeneity, a single value has been used in the present case to facilitate ease of calculation. The variation of heat of adsorption as a function of surface coverage will be taken into account in a comprehensive model under development.

Eqs. (1)–(4) were solved numerically by application of finite-difference technique to determine the values of  $c$ ,  $n$ ,  $n'$  and  $T$  as functions of  $t$  and  $x$ .

#### 4. Results and discussion

The experimental results and their comparison with those obtained from the model are presented and discussed in this section.

##### 4.1. Sorption isotherm

The sorption equilibrium equation proposed by Mahle was fitted to the experimental data by least-square minimization technique to estimate the coefficients  $A_{wm}$ ,  $B_{wm}$  and  $n_{ws}$ . The applicability of the Mahle equation to predict the water sorption equilibria can be confirmed by the comparison between the experimental and theoretical results as shown in Fig. 1. The values of  $n_{ws}$ ,  $A_{wm}$  and  $B_{wm}$  were determined to be 0.3143 g/g, 0.5845 and 0.1895, respectively.

##### 4.2. Sorption kinetics

To ensure the applicability of the Glueckauf assumption, it was important to determine the ratio of the resistance of

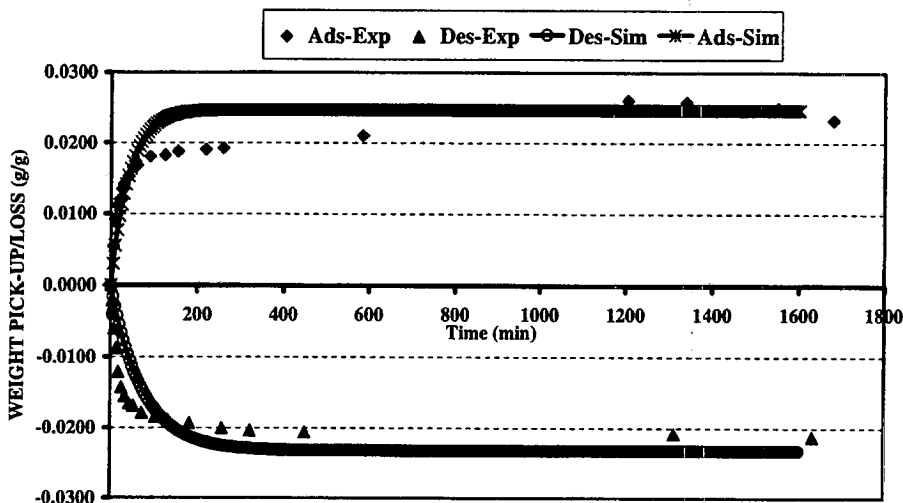


Fig. 3 - Water-ASZM/T sorption [35% RH].

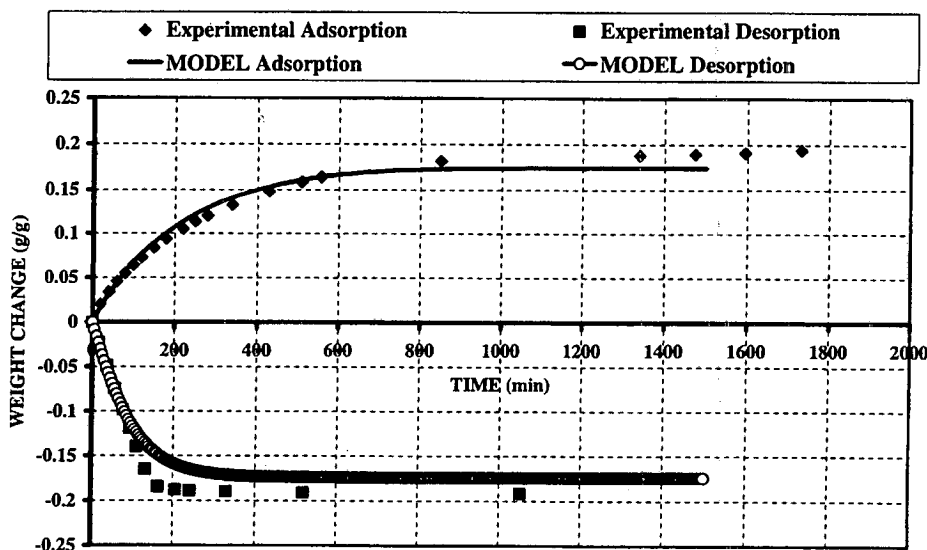


Fig. 4 - Water-ASZM/T sorption [60% RH].

mass transfer between the external film and the internal pore diffusion in order to verify that the internal mass transfer rate was controlling the overall rate of mass transfer. As described by Ruthven [17] and Yang [16], the Biot number,  $Bi$  expressed as  $(R_p k_f / D_{eff})$ , is a good measure of the relative importance of external and internal resistances. The value of the film mass transfer coefficient was calculated from the following correlation for Sherwood number,  $Sh [=2k_f R_p / D_{m,A}]$ , given by Wakao and Funazkri [19].

$$Sh = 2.0 + 1.1Sc^{1/3}Re^{0.6} \quad (10)$$

where  $Sc [= \mu / \rho D_{m,A}]$  and  $Re [= 2\rho v_1 R_p / \mu]$  denote the Schmidt and Reynolds numbers, respectively, and  $\mu$  and  $\rho$  denote the

viscosity and the density of the carrier gas at the temperature of operation respectively, and  $R_p$  denotes the radius of the particle. From the available values of the various parameters, the values of  $Sc$  and  $Re$  were calculated as 0.566 and 5.43, respectively at the operating conditions of the filter. Using these values, the Biot number was calculated as 101.93 indicating thereby the effect of external film mass transfer resistance was not significant compared to the internal mass transfer resistance as per Do [20]. Similarly, quantitative analysis of the various terms in Eq. (3) indicated that the effect of the heat transfer through the wall of the canister was negligible.

The calculated values of  $D_{eff}$  were then used to determine the values of the overall mass transfer coefficient at different

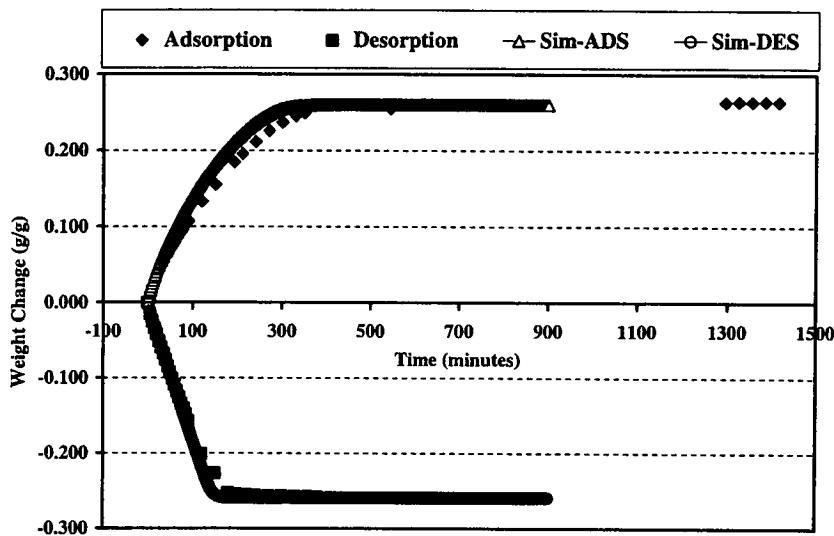


Fig. 5 - Water-ASZM/T sorption [80% RH].

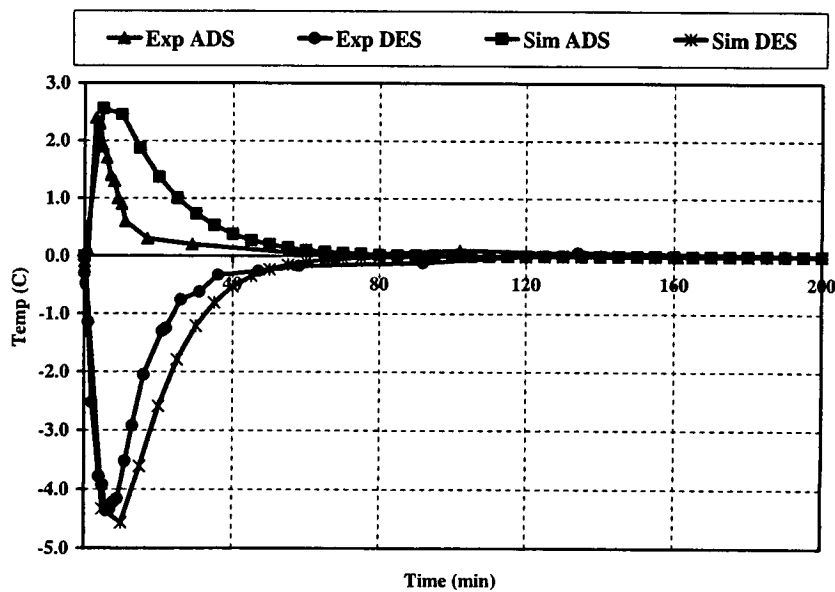


Fig. 6 - Water-ASZM/T sorption [25% RH] temperature profile.

values of humidity. The  $k_w$  and the fitted values of the coefficients from the water isotherm data were then used in the model described by the Eqs. (1)-(4) to predict the uptake (or loss) of water [g/g] in the bed and the temperature of the carrier gas in the exit stream as a function of time. A set of results at different values of humidity (25%, 35%, 60% and 80% RH), showing the change in weight of the canister and temperature of carrier gas stream, are shown in Figs. 2-9. The values of  $k_w$ , determined theoretically, used in the model to compare the experimental and simulation results are given in the Table 2.

Compared to the estimated value of  $D_{Ag}$  [ $\sim 4.25E-03$  cm<sup>2</sup>/s], which remains the same, the contribution of surface diffusion is determined to be significant [ $\sim 8$  times] even at a low RH [25%]. It is interesting to note that though the actual value of surface diffusion coefficient is expected to increase contin-

uously with increasing amount of adsorption, the contribution of surface diffusion itself to the overall mass transfer decreases at greater than 60% RH. This is because the slope of the adsorption isotherm decreases at higher RH. This might change if the variation of heat of reaction as a function of surface coverage was also taken into account. Also, it can be seen that the variation in the values of  $k_w$ , needed to compare the simulation and experimental results reasonably, is not very significant. Therefore, it can be concluded that using a single value of the mass transfer coefficient, it might be possible to predict the uptake behaviour of water vapour on activated carbon. Considering that the contribution of surface diffusion is fairly significant and a single value of mass transfer coefficient is adequate to predict the uptake behaviour reasonably well, it can be hypothesized that the sorption of water on the surface of impregnated activated carbons can

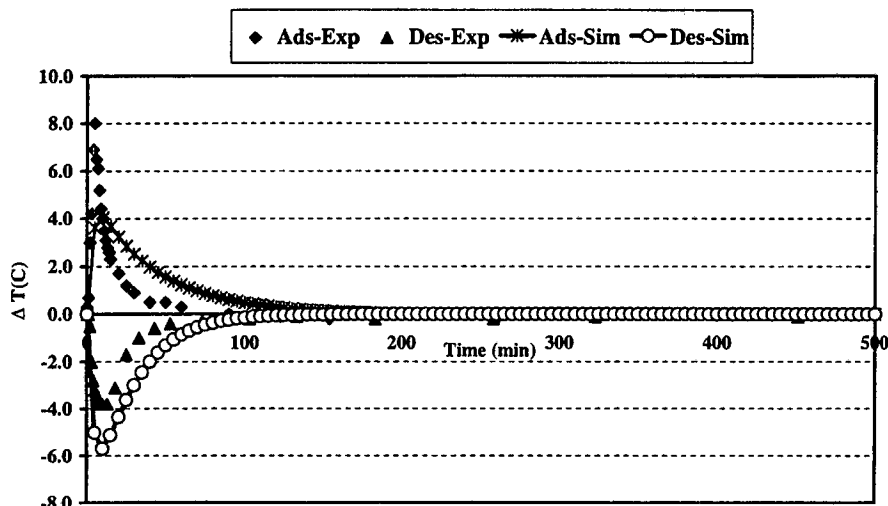


Fig. 7 - Water-ASZM/T sorption [35% RH] temperature profile.

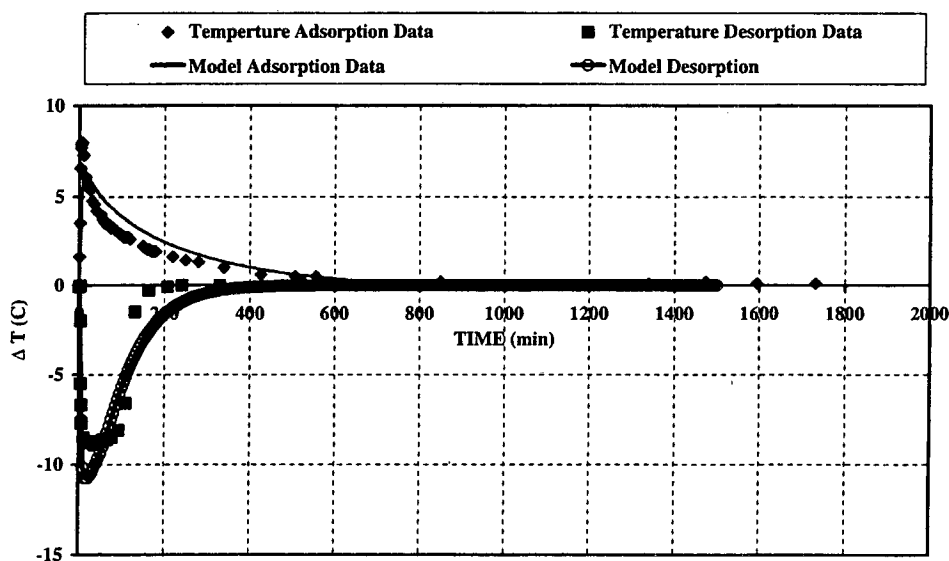


Fig. 8 - Water-ASZM/T sorption [60% RH] temperature profile.

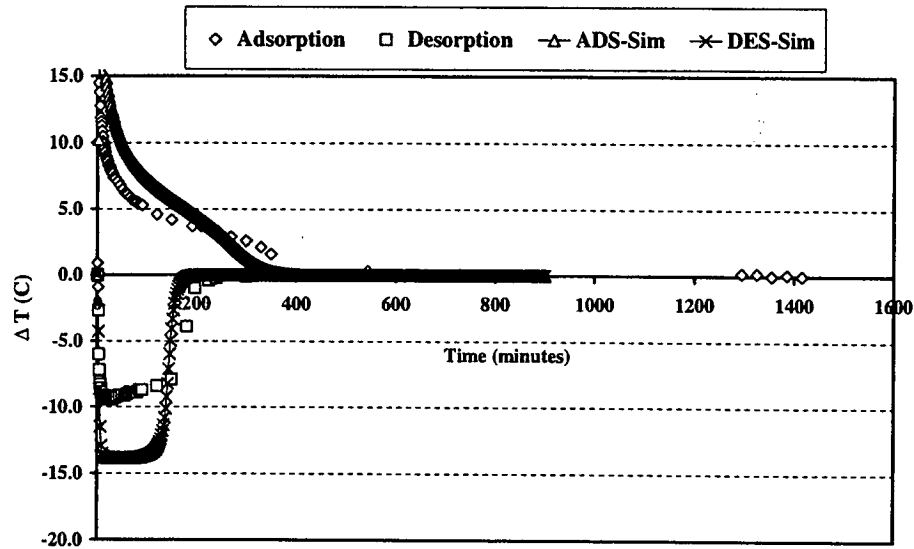


Fig. 9 – Water-ASZM/T sorption [80% RH] temperature profile.

Table 2 – Summary of  $k_v$  values

% RH	$K \cdot D_{As}$ (cm <sup>2</sup> /s)	$k_v$ (s <sup>-1</sup> )
25	1.53E-02	5.08E-4
35	2.49E-02	6.10E-4
60	6.26E-02	7.52E-4
80	2.75E-02	6.07E-4

be considered similar to condensation on a free surface of liquid water. The rate of adsorption on a free surface is expected to be constant at a constant value of humidity signifying a single value of overall mass transfer coefficient, similar to what is observed in this case.

### 5. Conclusions

A simple, generic model taking into account inter- and intra-particle mass- and heat-balance in a packed bed has been successfully developed. The model has been tested to predict the temperature and water uptake/loss profiles through ASZM/T carbon beds at different RH values. A single value of the overall mass transfer coefficient can be used to reasonably predict the adsorption behaviour of water in activated carbon beds.

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