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Variable pressure adsorption and desorption by active carbon beds under PSA† conditions: A comparison of models with experimental data

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Abstract

The behaviour of active carbon beds has been investigated under dynamic conditions, for the removal of organic vapours from dry air at 293 K and 3-7 atm. A simple relation is found for the rate constant of desorption at 1 atm, taking into account the properties of the vapours and the active carbons. Previsions can therefore be made for the behaviour of the system under PSA conditions, on the basis of an analytical model and a numerical model. A good agreement is found with the experimental results.

INTRODUCTION

Pressure-swing adsorption (PSA) is a cyclic process based on pressure gradients between successive adsorption and desorption runs. This technique is nearly isothermal and it contrasts with the traditional saturation of the adsorbent bed by a stream of gas, followed by thermal desorption. Under favourable conditions, PSA can be used for the purification of gases over long periods of time.

The aim of our study was to examine the behaviour of active carbon beds in PSA, as an alternative to the classical molecular sieve adsorbents, and to determine the main parameters which play a role in the removal of an organic impurity from a stream of dry air. We compared our experimental results with an analytical model and with the numerical simulation of adsorption dynamics obtained by computer modelling (ref. 1,2).

In the case of active carbons, the static adsorption of organic vapours can be described successfully within the framework of Dubinin's theory (ref. 3,4) and it appears that the dynamics of desorption can be related to various parameters of the system. It is also hoped that the present approach can be extended later to more complicated systems, including the presence of water vapour.

EXPERIMENTAL

The PSA apparatus is shown in Fig.1 and its main characteristics are given in Table 1. It consists of two parallel columns filled with active carbon and working alternatively in the adsorption or in the desorption mode near 293 K. Synthetic air, containing 200-13000 ppm of either n-hexane, benzene or dichloromethane, is compressed to 3-7 atm and introduced into one of the columns. Adsorption takes place during the contact time of 5 minutes, kept constant in this study. The removal of the impurity is favoured by its higher relative pressure. If the concentration of the organic vapour is not too high, the column is not saturated at the end of the contact time and clean air leaves the column. Part of this stream, expanded to 1 atm through a by-pass, is used to flush the other column. One obtains a richer mixture, which can also be subjected to a similar procedure. However, the carbon bed retains a certain amount of adsorbate.

† PSA = Pressure-swing adsorption

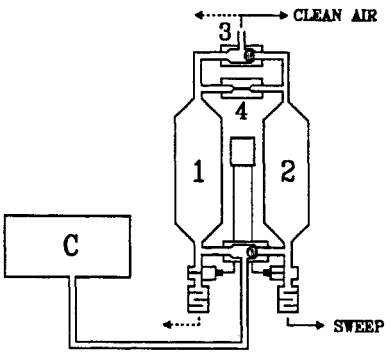

Fig. 1. Schematic view of the PSA apparatus. The compressed mixture of gases (C) is introduced alternatively into column (1) or (2). After a contact time of 5 minutes, clean air leaves the column (3). Part of the stream (4) is used to sweep the other column at 1 atm. The composition of the vapours is monitored by GSC (FID system).

After having been flushed at 1 atm, the column is returned to the adsorption mode and a new batch of the compressed mixture is introduced. This cyclic process can be repeated a number of times before a breakthrough occurs, depending on the initial concentration, the flow rate, the duration of the adsorption cycle, the adsorption pressure and the characteristics of the impurity and the carbon. Under optimum conditions, a PSA system can be used over long periods of time (up to hundreds of cycles), but diffusion through the bed and ageing of the carbon may be the ultimate limitation.

In the present study, the columns of the PSA system were used primarily for dynamic sorption and desorption studies, described below, in order to establish correlations between the various parameters. The pressure-swing technique itself was used at a later stage, in order to test the predictions of the models.

The carbons were characterized by using standard adsorption and immersion techniques (ref. 3,4). Their general properties, given in Table 2, include the micropore volume W_0, the external surface area S_e and the characteristic adsorption energy E_0, which is related to the average micropore width L (ref. 5). This quantity plays an important role in adsorption kinetics and therefore carbons with different micropore sizes were considered in the present study.

Static experiments showed that the adsorption of n-hexane at 293 K was not influenced by the presence of air, the final equilibrium being only a function of the partial pressure of the organic vapour, as predicted by the equation of Dubinin, given below. Dynamic saturation experiments carried out at 1, 3, 5 and 7 atm and for various concentrations lead to the same conclusion for the carbon beds.

TABLE 1. The main characteristics of the PSA system

Mass of carbon 120 - 130 g (see Table 2)	columns length 168 mm diameter 43.5 mm	Flow rates 10-60 dm^3/min	Concentrations 200-13000 ppm
Pressure 3-7 atm (ads) 1 atm (sweep)	Cycles 5 minutes	Vapours n-hexane, benzene, dichloromethane	Temperature T 293-298 K

TABLE 2. General properties of the active carbons

Carbon	W_0(cm^3/g)	E_0(kJ/mole)	L(nm)	S_e(m^2/g)	Particle Ø (mm)
U-03	0.512	17.66	1.7	60	1.0
DCG5	0.542	21.20	1.1	38	1.8
C-40	0.553	17.64	1.3	12	4.0

The numerical simulation model

A computer model has been used to predict the fraction of the organic component which is adsorbed by the active carbon bed, as well as the concentration of the stream leaving the column. A full description of the program dealing with the case of isothermal adsorption is given elsewhere (ref. 1). The model is based on equations (1)-(5), given below, and corresponding to (1) a mass balance , (2) a relation for the mass transmission between the gaseous and adsorbed phases, (the overall mass transfer coefficient k takes into account an external and an internal transfer coefficient, respectively calculated and determined experimentally), (3) the equation of Dubinin, used to describe the adsorption equilibrium in the active carbon bed, (4) a mass balance, and finally (5) an energy conservation relation

$$\frac{\partial c}{\partial t}+\frac{v(T)}{\varepsilon}\frac{\partial c}{\partial x}+\frac{\rho_b}{\varepsilon}\frac{\partial n}{\partial t}=0 \qquad \frac{\partial n}{\partial t}=k\left(c-c^*\right) \qquad (1)\ (2)$$

$$n^*=F(n,T,c)=W_0\rho_a(T)\exp\left(-\left(\frac{RT}{\beta E_0}\right)^2\log^2\left(\frac{c^*}{c_s(T)}\right)\right) \qquad (3)$$

$$\varepsilon c+\rho_b n=\varepsilon c^*+\rho_b n^* \qquad (4)$$

$$\left(\rho_b C_p^s+n\rho_b C_p^a+\varepsilon\rho_0(T)C_p^0\right)\frac{\partial T}{\partial t}+\varepsilon\rho_0(T)C_p^0\frac{v(T)}{\varepsilon}\frac{\partial T}{\partial x}=\rho_b\frac{\partial n}{\partial t}Q_i(n)+Q_e \qquad (5)$$

List of symbols

c	concentration (adsorptive)	W_0	limiting micropore volume
c^*	concentration at sorption equilibrium	x	length (in column)
c_s	concentration at vapour saturation	β	affinity coefficient
E_0	characteristic energy (Dubinin)	ε	void volume fraction
k	overall mass transfer coefficient	v	linear velocity
n	amount adsorbed (adsorbate)	ρ_0	density of carrier gas
n^*	amount adsorbed at equilibrium	ρ_a	bulk density of adsorbate
Q_i	isosteric heat of adsorption	ρ_b	bulk density of adsorbent
Q_e	heat flux through the walls	C^0_p	heat capacity of carrier
R	gas constant	C^a_p	heat capacity of adsorbate
T	temperature	C^s_p	Heat capacity of adsorbent
t	time		

The program is written in FORTRAN (PC and VAX versions) and Table 3 lists the parameters required for the simulation shown in Fig. 2.

TABLE 3. Groups of parameters used for the computer simulations shown in Fig. 2.

Column	PSA NE		Adsorptive	n-hexane	
diameter	0.0435	m	molecular weight	86.177e-3	kg/mol
length	0.168	m	affinity coefficient	1.30	
heat transfer	13.3	J/K m^{2}s	molar volume	126.7e-6	m^3/mol
			critical temperature	507.43	K
Carrier gas	air				
critical pressure	30.12e 5	N/m^2	critical density	232.98	kg/m^3
molar volume	20.1e-6	m^3/mol	critical parameter	7.256	
molar weight	0.02896	kg/mol	heat capacity	2186.5	J/kg/K
viscosity	17.9e-6	Ns/m^2			
Initial conditions			Adsorbent	carbon U-03	
initial conc. (t=0)	0	kg/m^3	micropore volume	0.512e-3	m^3/kg
challenge conc.	342.2e-3	kg/m^3	charact. energy	17.7	kJ/mol
initial load (t=0)	0	kg/kg	particle Ø	0.8e-3	m
linear velocity	0.336	m/s	bulk density	493	kg/m^3
pressure	709.1e 3	N/m^2	apparent density	924	kg/m^3
temperature	295.15	K	heat capacity	800	J/kg/K

Simulation parameters: maximum time 2000 s, number of column elements 30

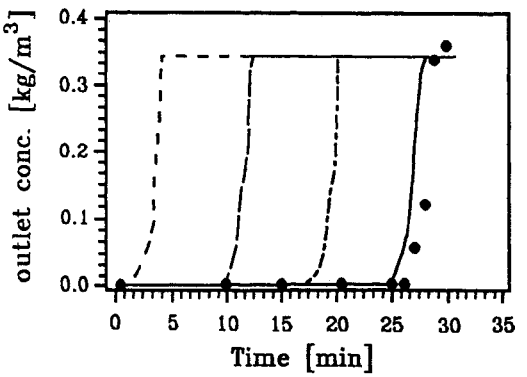

Fig. 2. Isoplanes for the dynamic adsorption of n-hexane on carbon bed U-03 (total pressure 7 atm and c = 0.3422 kg/m^3 at 293K, 1 atm). The simulations correspond, from left to right, to bed depths of 22, 73, 128 and 168 mm (end of the column). The points represent the experimental data for the breakthrough of the bed.

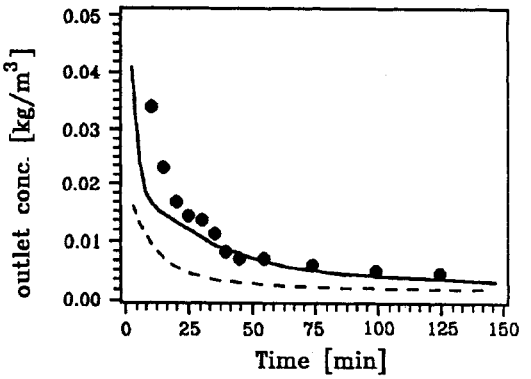

Fig. 3. Isoplanes for the dynamic desorption of n-hexane by air at 1 atm, following saturation as shown in Fig 2. Situation at a depth of 50 mm (– – –) and at the exit (——), with the experimental points determined by GSC.

RESULTS AND DISCUSSION

The data obtained for the dynamic desorption of hexane, benzene and dichloromethane from carbon beds saturated under different conditions (see Table 4) can be fitted to the simple equation

$$N_d(t) = N_a\left[1-\exp\left\{-(k_p t)^{1/2}\right\}\right] \qquad (6)$$

$N_d(t)$ represents the amount desorbed at time t and N_a is the total amount initially present in the bed.

The kinetic constants k_p themselves could be fitted to the following empirical relation containing the properties of the vapours and the carbon beds,

$$k_p\left(\text{min}^{-1}\right) = f^{7/2}\cdot(\beta E_0)^{-2}\cdot(p_s/1\ \text{atm})^3\cdot\theta^4\cdot 4.35\cdot 10^{-15} \qquad (7)$$

where f is the flow rate (dm^3/min) at which the column is swept at 1 atm; β and p_s are the affinity coefficient and the saturation pressure of the organic vapour and θ represents the degree of micropore filling of the carbon, i.e. N_a/N_a^o (N_a^o itself is equal to the micropore volume W_o of the carbon, divided by the molar volume V_m of the liquid-like adsorbate). As seen in Table 4, the experimental and fitted values of k_p are in good agreement.

As expected, k_p depends on the average pore width and on the size of the adsorbed molecule, since E_o is an inverse function of L, and the affinity coefficient β increases with the molar volume of the adsorbate.

Equations (6)-(7) are still limited to the desorption from a given bed and at single temperature, but they already provide an insight into the main parameters to be considered when changing the carbon and/or the adsorptive. We also used these equations to predict the PSA behaviour of the active carbon bed on the basis of a simple analytical model, assuming rectangular adsorption profiles within the carbon bed. (Under these conditions, the degree of micropore filling θ is calculated for the portion of the column which is actually filled, and not for the entire column). This is a reasonable approximation of the typical isoplanes shown in Fig. 2 and confirmed by X-ray computer tomography of carbon beds (ref. 2).

Fig. 4 shows the experimental results obtained for a limited PSA behaviour, leading to a rapid breakthrough. These results are compared with the predictions of the analytical model based on equations (6)-(7) and from the computer simulations. The different approaches are in good agreement, which means that a prediction of the PSA behaviour of active carbon beds is possible.

TABLE 4. Dynamic desorption by dry air at 293 K and 1 atm from carbon beds saturated at 3-7 atm

Carbon/vapour		loading (ppm)	p(atm)	sweep 1 atm (dm^3/min)	k_p (calc.) (min^{-1})	k_p (exp.)
U-03	hexane	12983	7	55	0.0202	0.0156
	hexane	13225	5	37	0.00467	0.00641
	hexane	12397	3	26	0.00112	0.00119
	benzene	7095	7	60	0.0120	0.0126
	benzene	6300	5	46	0.00426	0.00306
	benzene	7105	3	28	0.00063	0.00076
	CH_2Cl_2	2908	5	46	0.1702	0.1436
DCG5	hexane	11931	7	49	0.0121	0.0128
	hexane	3900	5	34	0.00237	0.00271
	hexane	4094	3	17	0.00018	0.00024
C-40	hexane	3377	7	64	0.0349	0.0308
	hexane	2236	5	46	0.00946	0.00957
	hexane	3674	3	30	0.00175	0.00159

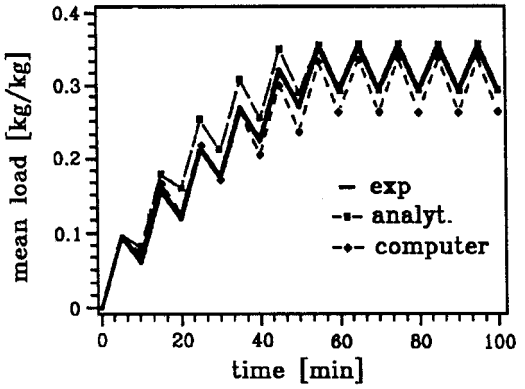

Fig. 4. PSA carried out on carbon bed U-03 with n-hexane in air at 7 atm, and c = 0.3422 kg/m^3 at 293 K, 1 atm. Adsorption/sweep flow rate of 60/40 dm^3/min. The graph shows the mean load of the bed as a function of time.

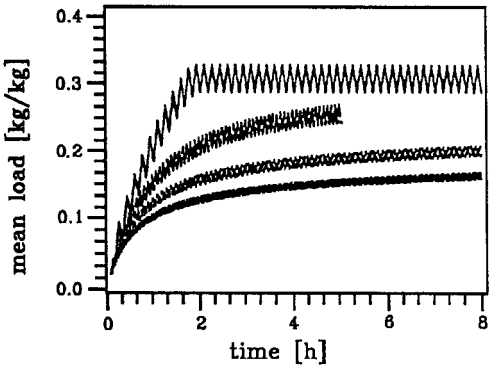

Fig. 5. Effect of the length of the adsorption/desorption cycle on the PSA system. Conditions as in Fig. 4, but adsorption/sweep flow rates of 30/20 dm^3/min. Cycles of 300, 150, 90 and 60 seconds from top to bottom.

The effect of the length of the adsorption/desorption cycles on the PSA behaviour has not been examined yet from the experimental point of view, but the predictions based on the computer simulations (Fig. 5) are probably quite accurate. In this representation mode, the breakthrough is reflected by a steady load pattern as observed for the 300 s cycles after 2h.

Although it is limited to a given PSA system, the present study reveals the main parameters which play a role in the case of organic vapours adsorbed by active carbon beds. On the basis of the two models (analytical and computer simulation), it becomes possible to assess the conditions under which the system can operate. The present approach will be expanded to more complicated situations, including the presence of water.

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