

APPLICATION OF THE WHEELER-JONAS EQUATION FOR THE CALCULATION OF CARBON MONOLITH BREAKTHROUGH TIMES

Peter Lodewyckx¹, Teresa Valdés-Solís², Marco J. G. Linders³ and Freek Kapteijn⁴

¹Royal Military Academy, Renaissancelaan 30, 1000 Brussels, Belgium

²Instituto Nacional del Carbón, Francisco Pintado Fe 26, 33011 Oviedo, Spain

³Prins Maurits Laboratory, TNO, P.O. Box 45, 2280 AA Rijswijk, The Netherlands

⁴Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

Corresponding author e-mail address: Peter.Lodewyckx@rma.ac.be

INTRODUCTION

Recently some of the authors have focused on gas adsorption of carbon-ceramic monoliths [1-2]. They developed a mathematical model, based on the solution of the subsequent phases in the physical adsorption process: axially dispersed plug flow in the monolith channels, mass transfer to the channel walls, diffusion into the carbon layer and, finally, adsorption by the carbon micropore system. The results were very good as the complete breakthrough curves obtained by the model were very close to the experimental ones. A downside of the model is the fact that it requires an estimation of the shape of the radial gas velocity profile, severely compromising its use as a tool. Lodewyckx *et al.* have recently shown that the scope of the Wheeler-Jonas (or Reaction Kinetic) equation can be extended largely beyond its commonly accepted boundaries of organic vapour adsorption on granular activated carbon, e.g. by applying it to adsorption by Activated Carbon Fibres (ACF) [4]. The downside of this model is that it only yields a single breakthrough time and does not provide a complete breakthrough curve. So its usefulness is limited to applications where only the first part of the breakthrough curve is important, e.g. protective filters. It is clearly not suited for other applications such as gas separation. But as most of its parameters are macroscopic and readily available, it is often possible to use the Wheeler-Jonas equation to perform breakthrough calculations.

The aim of this work is to show the applicability of the Wheeler-Jonas equation to gas adsorption by carbon monoliths. In a first phase to describe laboratory results under varying environmental conditions, and if possible, to calculate breakthrough times without any parameter estimation.

THEORETICAL

The Wheeler-Jonas equation [5,6] (see Eq 1) permits the estimation of the breakthrough time of an adsorption bed, based solely on measurable and readily available macroscopic parameters:

$$t_b = \frac{M \cdot W_e}{Q \cdot c_{in}} - \frac{W_e \cdot \rho_b}{k_v \cdot c_{in}} \ln \left(\frac{c_{in} - c_{out}}{c_{out}} \right) \quad (1)$$

Where t_b is the breakthrough time to reach c_{out} (min), M the weight of the carbon bed (g_{carbon}), W_e the equilibrium adsorption capacity (g/g_{carbon}), Q the volumetric flow rate (cm^3/min), c_{in} the contaminant concentration in air (g/cm^3), c_{out} the chosen breakthrough concentration (g/cm^3), ρ_b the bulk density of the carbon bed (g_{carbon}/cm^3) and k_v the overall adsorption rate coefficient (min^{-1}). This equation is the result of a semi-empirical approach. It is originally based on a continuity equation of the mass balance between the vapour entering the carbon bed and the sum of the amount adsorbed by this bed plus the amount penetrating through it. This model makes several assumptions:

- the flow pattern is a perfect plug flow
- only physisorption in the micropores is considered
- the kinetics of the reaction are of a pseudo-first order

A perfect plug flow implies the absence of any axial dispersion and/or wall effects. Previous work [1] suggests this condition is not completely satisfied. However, in a first approximation, we can work with this assumption, as the Wheeler-Jonas model will not focus on individual channels but has to be seen as an average adsorption front advancing through the monolith.

Only physisorption in the micropores excludes any chemisorption and/or interactions with other gases or vapours present on the carbon. The vapour used in this study (n-butane) is known to be exclusively physically adsorbed in the micropore system of the activated carbon coating.

In the Wheeler-Jonas model it does not matter which step in the adsorption process is rate controlling, as long as the rate constant is of a first order with respect to the number of gas molecules ($= c_{in}$). This is only true in the first, convex, part of the sigmoidal breakthrough curve [9], i.e. for values of $c_{out}/c_{in} < 4\%$. As the breakthrough criterion used in this study is 0.1 %, equation 1 is valid.

In summary, there is a strong possibility the Wheeler-Jonas model can indeed be applied to these experiments.

In the case of pure physisorption, especially for organic vapours, equation 1 needs two parameters of the carbon-adsorbate system to be calculated: the static adsorption capacity W_e and the overall adsorption rate coefficient k_v . The first one is usually calculated from the Dubinin-Radushkevich equation (Eq. 2) [7] and does not pose any major problems.

$$W_e = W_o d_L \exp \left[\frac{-BT^2}{\beta^2} \log^2 \left(\frac{c_s}{c_{in}} \right) \right] \quad (2)$$

Where W_e is the adsorption equilibrium capacity ($\text{g/g}_{\text{carbon}}$), W_o the micropore volume ($\text{cm}^3/\text{g}_{\text{carbon}}$), d_L the liquid density of the organic vapour (g/cm^3), B the structural constant of the carbon (K^{-2}), T the test temperature (K), β the affinity coefficient of the organic vapour (-), c_s the saturated vapour concentration (g/cm^3) and c_o the contaminant concentration in air (g/cm^3).

The estimation of the second parameter, the overall adsorption rate coefficient k_v , is less straightforward. Initially some very crude estimations were developed, based on theoretical diffusion models. An alternative way was the experimental determination of k_v by means of a single breakthrough experiment [8]. Since then, several authors have proposed semi-empirical equations [9-12]. The most recent one has been put forward by Lodewyckx and Wood [12] (Eq. 3):

$$k_v = 800 \cdot \beta^{0.33} \cdot v_L^{0.75} \cdot d_p^{-1.5} \cdot \sqrt{\left(\frac{W_e}{M_w}\right)} \quad (3)$$

With k_v the overall adsorption rate coefficient (min^{-1}), W_e the adsorption equilibrium capacity ($\text{g/g}_{\text{carbon}}$), M_w the molecular weight of the vapour (g/mol), d_p the average diameter of the carbon particle (cm), β the affinity coefficient of the organic vapour (-) and v_L the linear velocity through the bed (cm/s).

Both equations (2 and 3) have been applied to many different granular activated carbons and a broad range of gases and vapours. Some difficulties arise in the application of the model for gases with low molecular weights. However, in most cases it shows excellent results for organic vapours, both low and high boiling. Therefore, the use of the Wheeler-Jonas equation is widespread in both theoretical research and industrial applications [13].

EXPERIMENTAL & RESULTS

Experiments

Breakthrough curves of n-butane were measured on ceramic monoliths with the channels (called cells) coated with activated carbon. The experimental set-up as well as the monolith preparation has been described previously [1-3]. The main focus has been on a series of monoliths with 4 different cell densities: 200 – 400 – 600 and 900 cells per square inch (cpsi). Some tests included non-standard environmental conditions such as the presence of water vapour or pulsed flow.

As the Wheeler-Jonas model only works with breakthrough times, as opposed to complete breakthrough curves, the criterion for breakthrough was fixed at an outlet concentration of 3 ppmv. This is 0.1 % of the inlet concentration and is, as such, clearly situated in the region of (supposed) applicability of the Wheeler-Jonas equation.

Applicability to monoliths

In order to test the applicability of the Wheeler-Jonas equation to monoliths, the breakthrough times were plotted against the mass of the activated carbon present in the monoliths (Fig 1). If the equation is applicable, the data for each individual type of monolith (a certain cpsi) should be situated on a straight line. The capacity and rate coefficient (W_e and k_v) can be calculated from the slope and intercept of these lines (see Eq 1). Furthermore, as we presume that all types of monoliths have the same carbon characteristics, i.e. the same microporosity due to the same activation process, and only differ in the number and size of the channels, these lines should be parallel to each other: the slope being solely influenced by W_e and not by the kinetics of adsorption (see Eq 1). Fig 1 shows that all 4 types yield a straight line, and in three cases these lines are fairly parallel to each other. The fourth one (900 cpsi) however, is not parallel. This would indicate that this type has a different micropore volume (see Eq 2), which could be explained by differences in the activation process of the monoliths. Possibly the very narrow channels of the 900 cpsi-type have led to a different type of activation (different micropore volume for a same degree of burn-off) during the steam activation of the carbon. At this time N_2 - and CO_2 -isotherm measurements are conducted on the 900 cpsi samples in order to confirm a deviation from the micropore data derived for the other samples.

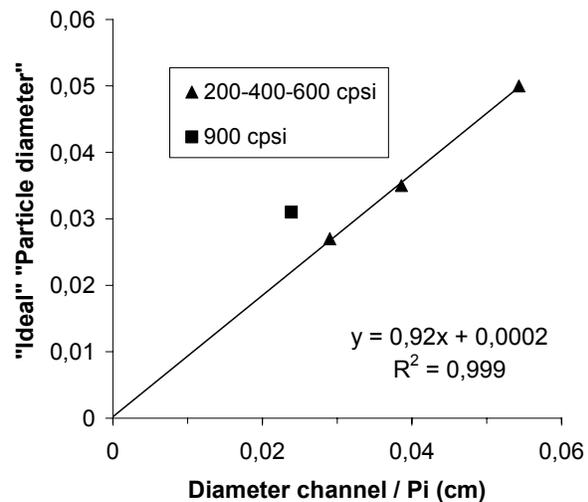
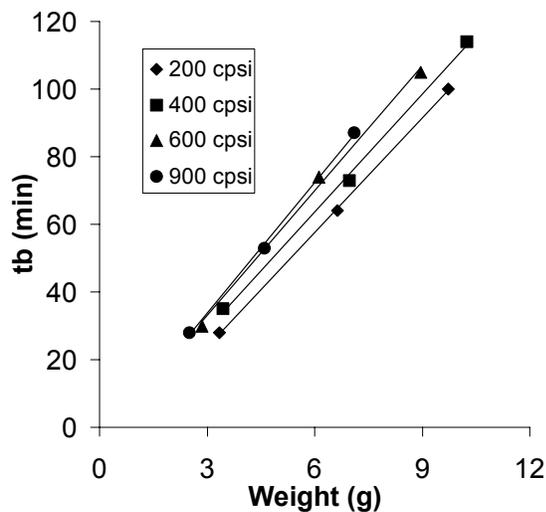


Fig 1: Breakthrough time vs. Carbon weight Fig 2: Calculated "ideal" d_p vs. $d_{channel}/\pi$

Breakthrough calculations

From Fig 1 we can assume that the Wheeler-Jonas equation applies to monoliths. To demonstrate it however, extrapolation to various conditions and even first principles calculations, based on readily available parameters, should be possible. Therefore, the experimental values of W_e and k_v were derived from Fig 1 and compared to the theoretical values calculated by equations 2 and 3. The results are presented in Table I.

Type monolith	Exper. W_e (g/g)	Calculated W_e (g/g)	Exper. k_v (min ⁻¹)	Calculated k_v (min ⁻¹)
200 cpsi	0.12	0.12	5800	5200
400 cpsi	0.13	0.12	10300	8700
600 cpsi	0.13	0.12	16600	14800
900 cpsi	0.14	0.12	13400	19400

Table I: Experimental vs. calculated values of W_e and k_v

Even though the application of equation 2 proved to be rather straightforward, the calculated values of W_e differ slightly from the experimentally determined ones. The initial assumption that all four types of monoliths have the same micropore volume, does not seem to hold. An increasing number of channels seems to lead to an increase in the micropore volume (to account for the increase in W_e), especially for the 900 cpsi samples. No doubt the estimation of W_e can be improved by using the exact measured micropore volume for each of the different types of monoliths.

As usual, the problem in applying the Wheeler-Jonas equation lies in the calculation of k_v . Equation 3 presents two unknown parameters: the linear velocity v_L and the particle diameter d_p . The linear velocity can be calculated quite easily, but one has to take into account the specific nature of a monolith: as the ceramic structure is impassable to the air stream, the effective surface is not calculated from the diameter of the monolith, but from the sum of the surface areas of the individual channels perpendicular to the air stream. Hence all four types of monoliths are subjected to a different v_L .

The biggest problem however, lies in the choice of the equivalent diameter d_p . For carbon granules this is the real, physical, mean diameter of the particles. For extrudated particles, or activated carbon fibres, good correlations have been obtained between d_p and the total external surface area of the “cylinders” [14,15]. However, in the case of monoliths, the situation is a bit different: the probability of a butane molecule to enter the activated carbon is not directly related to an external surface. It is linked to the probability of a molecule, flowing through one of the channels, to hit the channel wall. Up to this moment, no theoretical expression has been derived. Fig 2 shows a very tight relation between d_p (calculated from the measured values of k_v) and the diameter of a channel divided by π . This result is similar to the solution of Buffon’s needle problem, which is not at all surprising, as the problem itself is very similar [16]. However, one could argue that the inner surface of the channels plays essentially the same role in the adsorption mechanism for monoliths as the external surface for granular activated carbon (i.e. the granule is turned inside out). In this way, the physical meaning of d_p in both cases becomes more similar.

However, the relation between d_p and the channel diameter is not valid for the 900 cpsi type monolith. This was to be expected given its different behaviour (see Fig 1). Moreover, from 200 to 600 cpsi one can see an increase in adsorption kinetics with decreasing channel diameter, as one would expect instinctively. For 900 cpsi one observes a sudden, important, decrease in kinetics. This phenomenon is still under investigation, but it could be related to the difference in activation, similar to the observed irregularities in the micropore volume of this type of monolith.

The influence of the linear velocity was tested by performing a breakthrough test with a 400 cpsi monolith at 3.3 litres/min, keeping all other parameters identical. As a result of the higher v_L , the calculated value of k_v increased from approx. 8700 to 15000 min^{-1} , leading to an estimated breakthrough time of 45 min (Experiment = 47 minutes). If the influence of v_L is not taken into account, i.e. using Equation 3 with the same value of v_L as calculated for a flow rate of 1.5 litres/min, the estimation becomes worse (41 min).

Parameter	Value			
	200 cpsi	400 cpsi	600 cpsi	900 cpsi
Temperature [K]	298			
Volumetric flow rate [cm^3/min]	1500			
Micropore Volume [cm^3/g]	0.44			
Structural Constant B (DR-Eqn) [10^{-7}K^{-2}]	4.5			
“Particle diameter” (d_{channel}/π) [cm]	0.054	0.039	0.029	0.024
Bulk density of the carbon [g/cm^3]	0.506			
Mass of activated carbon [g]	3.0; 6.6; 9.7	3.4; 7.0; 10.2	2.9; 6.1; 9.0	2.5; 4.6; 7.1
Monolith length (= bed depth) [cm]	5 ; 10 ; 15			
Monolith diameter [cm]	4.3			
Linear velocity [cm/s]	2.43	2.40	2.84	2.79
n-Butane vapour pressure [mbar]	2100			
n-Butane liquid density [g/cm^3]	0.58			
n-Butane β (DR equation) [-]	0.8			
n-Butane molar weight [g/mol]	58.12			
n-Butane inlet concentration [ppmv]	3100			
n-Butane breakthrough conc. [ppmv]	3			

Table II: Parameters used to calculate breakthrough times with the Wheeler-Jonas eq

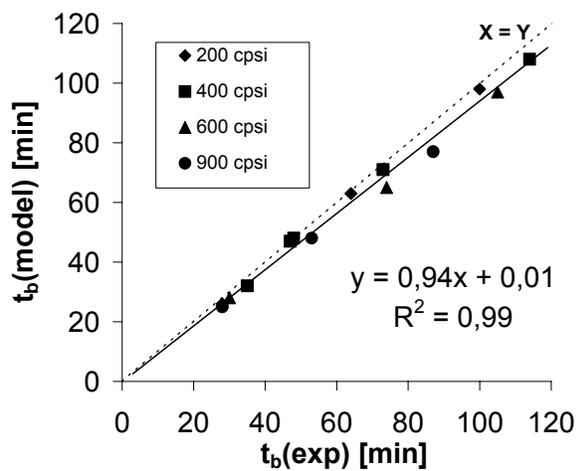


Fig 3: Experimental vs. calculated breakthrough times

The only parameter from equation 3 from which the influence on k_v has not been demonstrated yet, is the nature of the vapour (through β). However, as its influence on the adsorption kinetics is clearly linked to the specific carbon-vapour interactions (β), there is no reason why this dependence of k_v on β should be any different for carbon monoliths compared to granular activated carbon. So, it is safe to conclude that equation 3 is also valid in the case of carbon monoliths. Finally, simulations were performed, substituting the available data (see Table II) in equations 2, 3 and 1. The results are shown in Fig 3 where the calculated breakthrough times have been compared to the experimental ones. The slope of the regression line is very close to 1 (0.94), indicating a very reliable model ($r^2 = 0.99$). The slight underestimation of t_b (slope < 1) is mainly due to an underestimation of W_e for the 600 and 900 cpsi monoliths. As explained earlier, this probably could be overcome by using the exact (measured) micropore volumes instead of a general W_e (derived from the 400 cpsi sample).

Sensitivity to changing environmental parameters

During the experiments two “environmental” parameters were changed: the humidity of the air stream and the type of flow through the monolith.

Several experiments were carried out with air stream humidities up to 50% RH. These showed that n-butane breakthrough times were hardly influenced. This indicates a low water uptake at this relative humidity. As no water isotherm data are available yet, it was impossible to carry out breakthrough time predictions using the Wheeler-Jonas equation adapted for water-organic vapour co-adsorption [17,18]. To verify this model, one should also carry out experiments at higher relative humidities and with high values of water pre-adsorption by the monoliths.

There has been much debate about the influence of the flow type on breakthrough times of activated carbon beds: in some cases experimentally determined breakthrough times with a “breather” flow (discontinuous or half-sine flow) have been shown to be significantly shorter than the corresponding breakthrough times with a continuous flow [19,20]. It has been demonstrated that this difference is primarily due to a change in the overall mass transfer coefficient k_v [4,21]. The experiments with the monoliths of type 400 cpsi showed no significant difference between the breakthrough times under continuous flow (48 min) and discontinuous flow (47 min). The model adequately describes this: due to the high values of k_v (and hence of the low values of the kinetic, or right hand part, of equation 1) compared to activated carbons, breakthrough times are determined rather by the adsorption capacity of the monoliths (up to 95% of equation 1) than by the mass transfer effects. The diminished mass transfer (12900 min^{-1} vs. 14500 min^{-1}) in the case of the discontinuous flow leads effectively to a difference in calculated breakthrough times of about one minute. I.e. essentially the calculated breakthrough times are the same for both continuous and discontinuous flow, completely in agreement with the experimental data.

CONCLUSIONS

This work shows that the Wheeler-Jonas equation, and the annex equations to calculate W_e and k_v , can be applied to extrapolate breakthrough times of carbon monoliths for organic vapours. Furthermore, at least for the monoliths used in this study, it is possible to estimate these breakthrough times solely on the basis of known carbon and environmental parameters. A better knowledge of the carbon parameters (e.g. the individual micropore volume of each of the different types of monolith) will, probably, lead to even more accurate calculations.

The model also correctly predicts the behaviour of these monoliths when using a discontinuous airflow. The available experimental data do not permit to evaluate the predictive capacity of the model in case of vapour-water co-adsorption. In order to do so it would be necessary to conduct supplementary experiments and to measure the water isotherms of the monoliths.

Finally, one has to bear in mind that the model presented here can only calculate low concentration breakthrough times, and is not capable of predicting complete breakthrough curves. When interested in these curves, or in higher ($> 1\%$ of c_{in}) breakthrough concentrations one has to revert to more sophisticated (but also more complicated) models such as the one described in Refs. 1 and 2.

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