THE INFLUENCE OF MESOPORES ON THE KINETICS OF ORGANIC VAPOUR ADSORPTION BY ACTIVATED CARBONS

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Introduction

It is a "well known fact" amongst people in the activated carbon business that an enhanced mesoporosity improves the kinetics of the physisorption of vapours [1,2]. The actual adsorption taking place in, essentially, the micropore system, the mesopores are considered to be the highways from the external surface towards these micropores. However, very little factual proof has been published to support this theory. The purpose of this research project is twofold: determine if the mesopore system really influences the adsorption kinetics and, if this is the case, try to evaluate and model this influence.

Theoretical

The adsorption of the majority of organic vapours can be modeled by the Wheeler-Jonas equation [3] (Eq. 1):

$$t_b = \frac{W_e \cdot M}{Q \cdot c_o} - \frac{\rho_b \cdot W_e}{k_v \cdot c_o} \ln\left(\frac{c_o - c_x}{c_x}\right) \quad \text{(Eq. 1)}$$

It expresses the breakthrough time t_b (min) as the difference between the adsorption capacity and the effect of the adsorption rate, i.e. the fact the adsorption is not instantaneous. The different parameters are the equilibrium adsorption capacity W_e (g_{vapour}/g_{carbon}), the mass of the carbon M (g_{carbon}), the volumetric flow rate Q (cm^3/min), the vapour concentration in the air c_o (g_{vapour}/cm^3), the breakthrough concentration c_x (g_{vapour}/cm^3), the bulk density of the carbon (g_{carbon}/cm^3) and the overall adsorption rate coefficient of the adsorption k_v (min^{-1}). W_e can easily be calculated from the micropore volume W_o of the carbon by means of the Dubinin-Radushkevich (DR) equation [4].
In previous work an equation has been established to estimate the kinetic parameter k_v [5](Eq. 2):

$$k_v = 800 \, \beta^{0.33} \, v_L^{0.75} \, d_p^{-1.5} \, (W_e/M_w)^{0.5} \quad \text{(Eq. 2)}$$

Where k_v is the adsorption rate coefficient [min^{-1}], β the similarity constant of the Dubinin-Radushkevich Eqn [-], v_L the linear velocity [cm/s], d_p the mean diameter of the activated carbon particles [cm], W_e the equilibrium adsorption capacity [g_{vapour}/g_{carbon}] and M_w the molecular weight of the vapour [g/mole]. As one can see, the mesopore volume is not accounted for in this model. However, the majority of the carbons that were investigated to establish Eq. 2 were highly microporous. Therefore it is possible the influence of mesoporosity was underestimated or it is "hidden" in the constant term (800) as it is the case for the dependency on the temperature [X].

Experimental

Three activated carbon beads with comparable micropore distributions but different mesopore systems were manufactured: TE-3, 5 and 7. Subsequently, breakthrough tests were carried out with cyclohexane under the following experimental conditions: inlet concentration – 1000 ppmv, breakthrough concentration – 10 ppmv, flow rate – 1200 cm^3/min, temperature – 293 K, filter diameter – 2 cm. In order to distinguish the kinetics from the capacity, two different bed depths were used: 1 cm and 2 cm. This was equivalent to carbon masses of respectively 1.26 / 2.59 g (TE-3), 0.83 / 1.64 g (TE-5) and 0.60 g and 1.21 g (TE-7). The mean values of the respective breakthrough times, as well as the linear trend lines are presented in Fig 1 and 2.
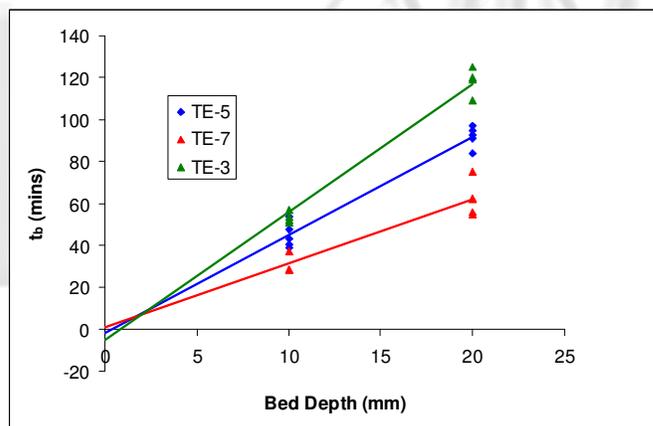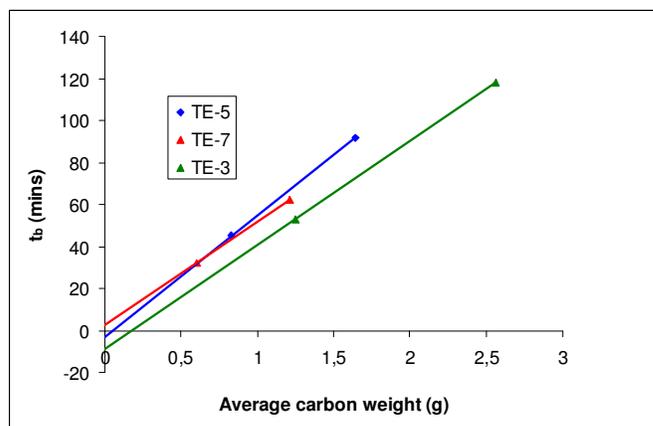

Fig. 1 Breakthrough versus bed depth.

Fig. 2 Breakthrough versus carbon weight.

Results and Discussion

The breakthrough time versus carbon weight curves in Fig 2 indicate there is a difference in micropore volume between the three carbons: the slope of the trend lines being related to the capacity W_e (through Eq. 1) and hence to W_o by the DR-equation. This is in contradiction with the original idea of having carbons with the "same" micropore structure. The differences are however not very significant and will be verified by nitrogen adsorption at 77K.

Y-axe intercepts are very close to zero, which indicates a very rapid adsorption mechanism (= big k_v in the right hand part of Eq. 1). According to Eq. 2, this is probably a direct effect of the small size of the beads (250-500 μm). Eq. 2 will be used to calculate theoretically the values of k_v for the three carbons. Discrepancies between the calculated values and the experimentally determined ones could be an indication of an influence of mesoporosity on the adsorption kinetics.

Conclusions

More modeling and experimental work (e.g. Nitrogen isotherms) has to be done to reach quantitative conclusions. But from the experimental data it is clear that if there is an influence on adsorption kinetics, it seems to be very small.

References

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