ACTIVATED CARBON FIBRES FOR GAS SEPARATION

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Introduction

Carbon molecular sieves (CMS) have important applications in the chemical and petrochemical industry in separation and catalytic processes based on the different adsorption of components from gaseous or liquid phases. The work to be presented here focuses on two commercially significant separations: CO_2/CH_4 and O_2/N_2. The first is important for the recovery of CH_4 in fermentation processes [1] and in purification of natural gas [2]. The second is used worldwide for the production of nitrogen and oxygen from air by pressure swing adsorption (PSA) [3,4].

Activated carbon fibres (ACF) are a comparatively modern form of porous carbon material with a number of significant advantages over the more traditional powder or granular forms. These include high surface area and adsorption capacity, as well as very high rates of adsorption from the gas or liquid phase. The micropore size is in general uniform and can often be controlled by adjusting the conditions of preparation of the ACF or by post-preparation modifications which include CVD of suitable organic precursors, such as benzene [5] and propylene [6], thermal treatments [7] and impregnation with organic additives with subsequent carbonisation [8]. These characteristics and the fact that the micropores open directly to the exterior make ACF excellent alternatives in PSA systems because the time needed for pressurisation/depressurisation cycles can be shortened.

In this work we report a novel method of making CMS which involves the control of porosity of activated carbon fibres using thermal treatment in a microwave furnace under an inert atmosphere. This methodology leads to the production of CMS that are indicated for the separations CO_2/CH_4 and/or O_2/N_2.

The use of a microwave furnace has several advantages over conventional heating devices related to the different manner of sample heating. In conventional heating the heat source is located outside the carbon bed which is heated by conduction and/or convection. With microwave heating, on the other hand, the microwaves supply energy to the carbon particles themselves according to the mechanism of the Maxwell-Wagner effect [9].

In a microwave furnace the heating is very fast (temperatures of 900ºC can be reached in about 1 minute [10]) and the treatment time is reduced when compared with the treatment time in conventional furnaces. This leads to important savings in time, energy and gas consumption.

For carbon materials there are relatively few publications that describe the use of microwaves for producing [11,12] and regenerating [13,14] activated carbons. Surface chemistry modification of carbon materials by means of microwave heating was also studied in previous works [10,15] as was the production of molecular sieving effects [16,17].

The separations using CMS are based on kinetics and not on equilibrium. For instance the equilibrium adsorption capacities for O_2 and N_2 can be nearly identical. These different adsorption kinetics allow the adsorption of the gas that has the faster diffusion rate, in general the gas that also has the smaller molecular size, which can then be separated from other gases with slow diffusion rates. Although simple in principle, in practice it is a relatively difficult separation when compared to an equilibrium separation. Regarding the kinetic diameter of oxygen and nitrogen, 0.346 and 0.364nm [18], it is easy to see that this separation is quite an impressive feat.

The diffusion model more appropriate for the ACF used is the empirical phenomenological model for mass transfer in gas adsorption because, as can be seen in Fig. 1, the materials are not homogeneous and the particles are not spherical [19]. In this case the adsorption rate is controlled by the diffusivity into the micropores rather than by the superficial resistance to mass transfer. This model, also called the linear driving force (LDF) mass transfer kinetic model, assumes that the surface concentration of gas is constant and that the diffusion is controlled by the concentration gradient through the particle. The kinetics of diffusion can then be expressed by the empirical diffusion equation:

$$m_t/m_{inf} = kt^n \qquad (1)$$

where m_t is the gas uptake at time t, m_{inf} the gas uptake at equilibrium, t the time, n the diffusional exponent and k the constant.

The diffusional exponent can be evaluated from a plot of $\ln(m_t/m_{inf})$ vs ln t. When n=0.5 the diffusion mechanism obeys the Fick Equation. In our case n is always different from 0.5 which is coherent with our choice for the diffusional model.

The gas uptake into CMS may be considered as a pseudo-first order mass transfer between the gas phase and the ACF. Then the rates of gas uptake can be compared in terms of the pseudo-first order rate constant (k) with the gas uptake following equation (2).

$$m_t/m_{inf} = 1-e^{kt} \qquad (2)$$

The plot $\ln(1-m_t/m_{inf})$ vs t should be a straight line with gradient equal to k that is essentially comparable to $D\pi^2/a^2$ in the Fickian diffusion model for spherical particles where $m_t/m_{inf}>0.5$.
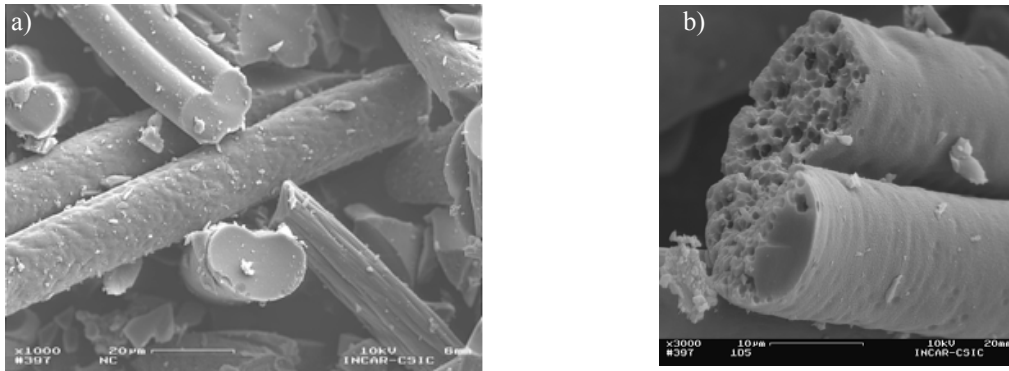

Figure 1: SEM image of a) F2-0 and b) F1-37.

EXPERIMENTAL
Materials
The precursors used for the production of ACF were three acrylic textile fibres (designed F1, F2 and F1N) provided by Fisipe (Barreiro, Portugal). According to the manufacturer all of the fibres had been polymerised from acrylonitrile (~90w%) and vinyl acetate (~10w%) monomers. For the production of the ACF about 12g of fibre and a horizontal tubular furnace were used. The fibres were carbonised at 800ºC for 1 hour under a constant N_2 flow of $85cm^3min^{-1}$ (samples F1N-0, F1N-0 and F2-0) and activated at 900ºC in a CO_2 flow of $85cm^3min^{-1}$ for 2 hours, to 37% burn-off (sample F1-37). Details of the process are given elsewhere [20].

Microwave treatments
Sub-samples (*ca.* 1-2g) sized to less than 1mm of activated carbon fibres were placed in a quartz reactor, which in turn was placed inside a multimode resonant microwave cavity. Microwave treatments consisted in subjecting the samples to microwave action for 15min. The time of treatment is indicated in the sample designation (XXXm15, means 15 minutes of microwave treatment). An inert atmosphere was maintained during treatment and cool-down intervals by passing a N_2 flow of $100cm^3min^{-1}$ through the sample bed. The input power of the microwave equipment was set at 1000W and the microwave frequency used was 2450MHz. The temperature of the carbon bed during microwave treatment was measured using an infrared optical pyrometer. Details of the microwave device as well as temperature measurements are given elsewhere [21,22].

Gas uptake experiments
The adsorption of O_2, N_2, CO_2 and CH_4 at 25ºC was determined using a classical glass adsorption apparatus. After outgassing the ACF at 300ºC, the probe molecule at an initial pressure of 955mbar was introduced and the uptake measured as a function of time.

Results and Discussion

Typical uptake curves obtained are shown in Fig.2 were the plots of volume adsorbed (in volume NPT obtained by the ideal gas equation) versus contact time are represented. From this data we can evaluate the ability of the materials for performing the separations wanted. This evaluation is done by the determination of the volume adsorbed, at a specific contact time, and the kinetic selectivity obtained by the ratio between the volumes of gas adsorbed. These data are shown in tables 1 and 2. We chose 100s for the contact time because the PSA apparatus normally uses similar times.

The adsorption kinetics analysis shows that for all samples the uptake of O_2 and CO_2 is faster than the adsorption of N_2 and CH_4, respectively. The uptake at 100s contact time is greater for O_2 and CO_2 than for N_2 and CH_4. This behaviour is typical for CMS but opposite to other molecular sieves like zeolites 5A or 13X that have more affinity for N_2 than for O_2, with the faster adsorption of the first gas [23].

The results show that the microwave treatments lead to important changes in the values of gas adsorbed and selectivities. It can be seen in tables 1 and 2 that after microwave treatment the adsorption of the larger molecules N_2 and CH_4 was, in almost every case, reduced to zero. On other hand, the adsorption of the smaller molecules CO_2 and O_2 was less pronounced leading to significant increase of the selectivities.

For samples F1-0 and F1-37 the treatment caused a decrease in the mean width of the micropores [22] and consequently a decrease of the adsorption capacity. For sample F1-0m15 this results in null adsorption of CH_4, N_2 and O_2. Despite the reduction of 80% in the CO_2 adsorption the fast adsorption obtained makes this sample a good CMS for the separation of CO_2. The sample F1-37 improved the CMS characteristics after the treatment with the selectivity values for the separations CO_2/CH_4 and O_2/N_2 changing from 2.3 to 13.9 and from 0.9 to 13.9, respectively, as can be seen in the tables.
For samples F1N-0 and F2-0 the treatment caused an increase in the mean micropore diameter [22] and also an increase in the adsorption capacity. These samples have much amorphous carbon which was in part burnt-out during the microwave treatment with the opening of the micropores. We can say that the micropores still have some constrictions after the treatment because the uptake curves show a slower approximation to equilibrium adsorption, which leads to smaller values of k when compared with F1-0m15 (tables 1 and 2). The sample F1N-0m15 is very interesting because the null adsorption of methane and nitrogen lead to infinite selectivities for the separations CO_2/CH_4 and O_2/N_2.
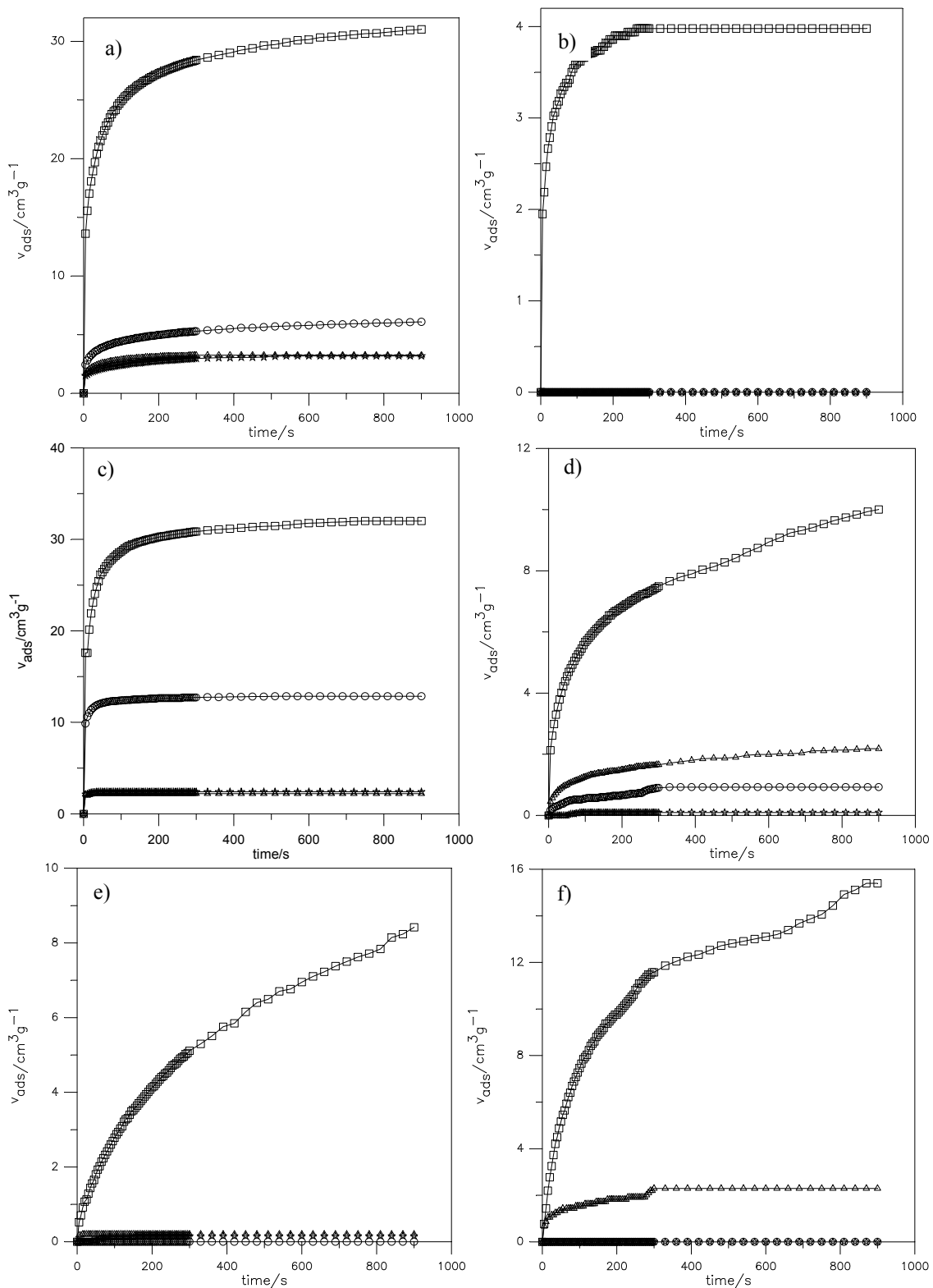
Figure 2: Uptake curves at 25ºC of CO_2(□), CH_4(O), O_2(△) and N_2(✶).a) F1-0, b)F1-0m15, c)F1-37, d)F1-37m15, e)F1N-0, f)F1N-0m15.

Table 1. Adsorption kinetics (k/s^{-1}) and uptakes (v/cm^3g^{-1}) of O_2 and N_2 at 25ºC.

Sample	V(O₂)	V(N₂)	V(O₂)/V(N₂)	k(O₂)	k(N₂)
F1-0	2.8	2.4	1.2	0.020	0.009
F1-0m15	0	0	id	0	0
F2-0	0.1	0	inf	0.039	0
F2-0m15	0.3	0	inf	0.035	0
F1N-0	0	0	id	0	0
F1N-0m15	1.5	0	inf	0.008	0
F1-37	2.2	2.4	0.9	0.097	0.096
F1-37m15	1.3	0.1	13.9	0.010	0

Note: Uptakes after 100s of contact time, nd=not determined, id=indeterminate, inf=infinite

Table 2. Adsorption kinetics (k/s^{-1}) and uptakes (v/cm^3g^{-1}) of CO_2 and CH_4 at 25ºC.

Sample	V(CO₂)	V(CH₄)	V(CO₂)/V(CH₄)	k(CO₂)	k(CH₄)
F1-0	24.9	4.4	5.6	0.015	0.012
F1-0m15	3.6	0	inf	0.025	0
F2-0	0.7	0	inf	0.004	0
F2-0m15	1.4	0	inf	0.004	0
F1N-0	2.8	0	inf	0.003	0
F1N-0m15	7.5	0	inf	0.008	0
F1-37	28.7	12.4	2.3	0.025	0.030
F1-37m15	5.7	0.5	13.9	0.011	0.011

Note: Uptakes after 100s of contact time, nd=not determined, id=indeterminate, inf=infinite.

Published work using the same type of experimental method that we have used indicates that for O_2/N_2 separation a selectivity of about 10 with O_2 uptake of about $4cm^3g^{-1}$ after 100s contact time can be considered reasonable for a laboratory sample [24,25]. Verma has reported higher selectivities, of about 20, but only at the expense of much lower O_2 uptake [26], while Villar-Rodil et al. have reported higher O_2 uptakes but with slightly lower selectivities [27]. Other authors have reported results for commercial CMS which are inferior both in relation to selectivity and to O_2 uptake [24,25]. The results obtained by us, and shown in tables 1 and 2, therefore appear to be quite reasonable in comparison with other published work. Of the microwave treated samples, the best results were obtained with F1-37 and F1-0, which both had higher selectivities, although the O_2 uptakes were lower than ideal.

For CO_2/CH_4 separation various authors have reported selectivities greater than 40 with CO_2 uptakes as high as $45 cm^3 g^{-1}$ [24,27]. The best result in table 2 was obtained with F1N-0 and is comparable to the results reported by Vyas et al. [28]. However, it is clear that a more detailed study is still necessary in order to achieve a higher CO_2 uptake necessary to improve the productivity of the process.

The application of the phenomenological model for adsorption kinetics to the gas uptake (eq. 2) is shown in Fig. 3. As expected the plots show good linear regions. For samples F1-0, F1-37m15, F1N-0m15 and F1-37 (in the last sample only for CO_2 and CH_4 uptake) it is possible to observe two linear regions for contact times less than and greater than 100s. In these cases we only considered the first region because, as explained before, the PSA instruments use short cycle times and it is therefore more useful to evaluate the k value for these conditions.

The pseudo-first order rate constant, k, for the uptake of oxygen (table 1) is in general comparable with the values reported in previous work with similar materials. In some cases the values found for our samples are 10 times higher. Hu and Vansant [29] reported for the best sample studied for O_2/N_2 separation (selectivity=9.2) a k value of $0.0008s^{-1}$. In comparison, for sample F1-37m15 (table 1) we report here selectivity=13.9 and $k=0.008s^{-1}$.

In the samples that after the microwave treatment have increased the gas uptake as a consequence of micropore enlarging, F2-0 and F1N-0, the rate constant also increased because it is easier for the probe molecules to enter the micropores. On the other hand, for samples F1-0 and F1-37 where the treatment caused a decrease in micropore mean width the rate constant values also decreased.

The rate constant for the CO_2 uptake is also comparable to the values already reported in previous works. Reid and Thomas reported values between 0.004 and $0.012s^{-1}$ for commercial CMS [30] and Prasetyo and Do reported values in the range 0.0013-0.0030 in modified CMS [31].

The comparison with reported values is sometimes not totally meaningful because the linear ranges chosen for the application of the model are not the same. In several cases the authors don't refer the linear range used, which can lead to misleading comparisons.

Conclusions

The results presented here suggest that microwave heating could be a useful alternative to more commonly used methods for introducing molecular sieve properties into activated carbon adsorbents. One of the advantages of the microwave method is that, unlike conventional heating, where there can be temperature gradients from the outside towards the centre of the carbon bed, in the microwave furnace the carbon bed is uniformly heated throughout. It should therefore be possible to scale up the process while still obtaining highly homogeneous products. Furthermore, the heating time is

considerably shorter which would result in significant energy and process gas cost savings.

The properties of samples F1N-0m15 and F1-37m15 (reasonably good O_2 adsorption capacity, very good selectivity and interesting adsorption rate) altogether make these samples the best ones for O_2/N_2 separation.
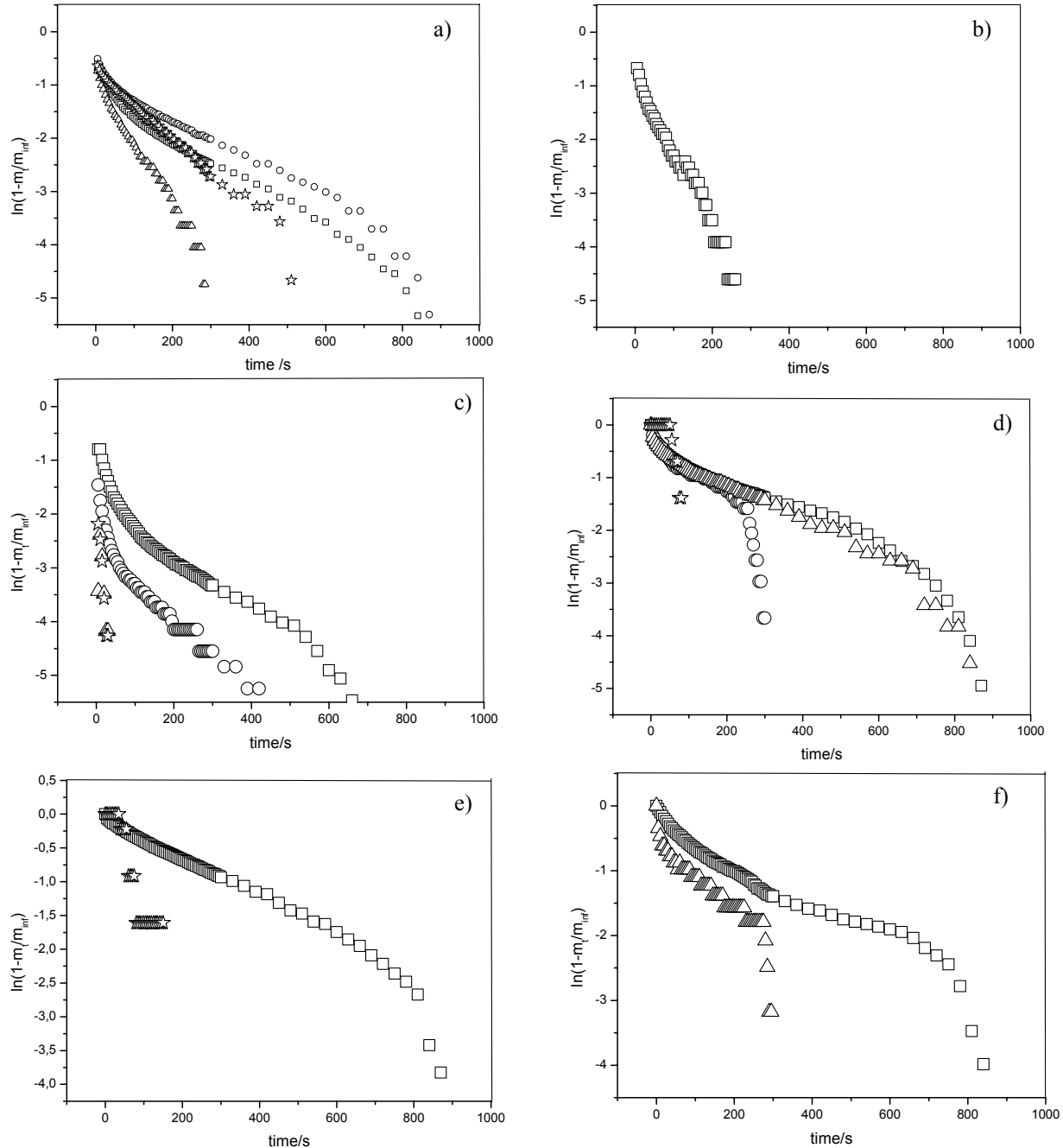

Figure 3: Representation by phenomenological model for adsorption kinetics for the uptake of CO_2(□), CH_4(O), O_2(△) and N_2(✶).a)F1-0, b)F1-0m15, c)F1-37, d)F1-37m15, e)F1N-0, f)F1N-0m15.

Despite the relatively low CO_2 uptake ($3.6cm^3g^{-1}$), the sample F1-0m15 can be a good choice for the CO_2 separation from CH_4, O_2 and N_2 because the only probe molecule taken up was CO_2 with a relatively good adsorption rate ($0.025s^{-1}$). For the CO_2/CH_4 separation we must refer also to samples F1N-0m15 and F1-37m15 that can be very promising alternatives.

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