# CHARACTERIZATION OF ACTIVATED CARBONS OBTAINED FROM POLYETHYLENE TEREPHTHALATE

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## Introduction

Polyethyleneterephthalate (PET) is a polymer material developed to replace glass in soft drinks and containers. Nevertheless its elimination after being used is an environmental problem. However, this type of waste with a high carbon fraction can be recycled into activated carbons [1-4].

The objective of this work is to propose a novel treatment of the precursor that allow to diminish the mass loss and the elimination of volatile compounds in the process of pyrolysis. In addition the aim is to establish the influence of the activation time on the textural characteristics of the obtained activated carbons.

Adsorption of $N_2$, $CO_2$ and benzene has been used to study the microporous system of the samples. The adsorption isotherms have been analysed by the application of the BET equation for nitrogen adsorption and Dubinin-Radushkevich equation for the adsorption of nitrogen, $CO_2$ and benzene.

## Experimental

Polyethyleneterephthalate (PET) has been submitted to basic hydrolysis in aqueous solutions of two concentrations of sodium hydroxide (10 % and 30 %). The final product of the hydrolysis is a mixture of sodium terephthalate and sodium hydroxide. This was pyrolyzed in $N_2$ flow at 923 K for different soak times: 1, 4 and 8 hours. As the precursor was mixed with NaOH, the pyrolysis process can be considered as a chemical activation. The obtained samples are labelled 10%-T650 (NaOH 10%, 1hour at 923K), T650, T650-4 and T650-8 (NaOH 30%, 1, 4 and 8 hours at 923K respectively).

Table 1. Physical properties of the adsorptives

| Adsorptive | dimension (nm)[a] | $\beta$[b] | $\rho$ (g/cm$^3$) | molecular area (nm$^2$) |
|---|---|---|---|---|
| nitrogen | 0.3[c] | 0.34 | 0.808 | 0.162 |
| carbon dioxide | 0.28[c] | 0.42 | 1.030 | 0.187 |
| benzene | 0.37(t) 0.67(w) 0.74(l)[d] | 1.00 | 0.877 | |

[a] t = thickness; w = width; l = length.
[b] From ref [5]; [c] From ref [6]; [d] From ref [7]

The textural characteristics of the four carbons were determined by the analysis of adsorption isotherms of $N_2$ (77 K), $CO_2$ (273 K) and benzene (303 K). The $N_2$ and $CO_2$ isotherms were obtained in a conventional volumetric system whereas these of benzene were measured in a gravimetric one.

Some of physical properties of adsorptives assumed in this work are shown in Table 1 [5-7].

**Results and discussion**

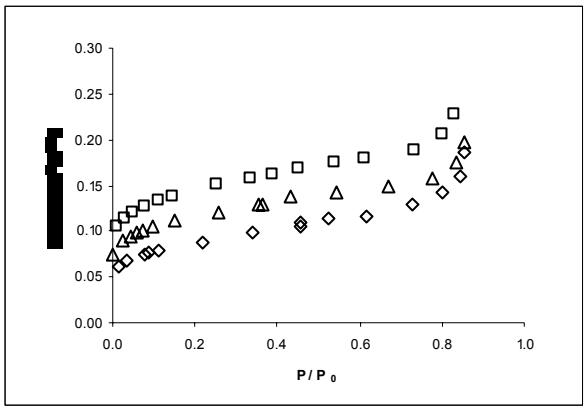


Figure 1. Adsorption of nitrogen at 77 K on: ◇ T650, △ T650-4, □ T650-8

The adsorption isotherms of $N_2$ on these samples are plotted on Figure 1. These type II isotherms are typical of solids with microporosity associated with an appreciable external surface. Because of the contribution from the microporosity, they have a steep initial portion

Table 2 shows the textural parameters of the samples. $S_{N2}$ is the surface area accessible to $N_2$ which has been obtained by using the BET equation. Moreover the application of the Dubinin-Radushkevich equation to the $CO_2$ adsorption isotherms [8] has been used to obtain the values of micropore volume (Wo), adsorption energy (Eo) and average micropore width (Lo).

Table 2. Textural parameters derived form adsorption of $N_2$ (77K) and $CO_2$ (273K)

| Sample | $S_{N2}$ ($m^2\ g^{-1}$) | $S_{CO2}$ ($m^2\ g^{-1}$) | Wo ($cm^3\ g^{-1}$) | Eo ( $kJ\ mol^{-1}$) | Lo (nm) |
|---|---|---|---|---|---|
| 10%-T650 | 205 | 369 | 0.131 | 28.41 | 0.78 |
| T650 | 199 | 350 | 0.124 | 29.07 | 0.76 |
| T650-4 | 269 | 342 | 0.122 | 28.46 | 0.78 |
| T650-8 | 336 | 341 | 0.121 | 28.73 | 0.77 |

The textural parameters of samples 10%-T650 and T650 are very similar. This means that the effect of both concentrations of sodium hidroxide (10 % and 30 %) is the same with respect to these parameters. The only difference found was related with the hydrolysis process which was faster for 30 % NaOH concentration. For this reason the latter was preferred for the preparation of other samples.

The textural parameters obtained from the $CO_2$ adsoption isotherms indicate that the accesible microporosity to this molecule at 273K is not affected by the activation process as it can be deduced from the values of volume ($W_0$) and average micropore

widths ($L_0$). From the adsorption of nitrogen at 77K it can be seen that this adsorbate is not able to acces to the microporosity on sample T650 which is usually attributed to the existence of constrictions in the micropores. But the adsorption of nitrogen increases when the activation time incrases from 1 to 8 hours as it is shown in Figure 1. The textural parameter for samples T650-4 and T650-8 obtained from the application of Dubinin-Radushkevich equation to the corresponding isotherms are in Table 3. Although $L_0$ values indicate that $N_2$ is adsorbed on pores much wider than those where $CO_2$ is adsorbed, the $W_0$ values for $N_2$ are only slightly higher than for $CO_2$, which could mean that both adsorbates are measuring very different range of microporosity; while $CO_2$ is covering the ultramicroporosity, $N_2$ is covering supermicroporosity (betwen 0,7 and 2 nm). These data show that activation time above 1 hour develops porosity in the range of supermicropores where the nitrogen is adsorbed, but in which the $CO_2$ is not adsorbed because the highest relative pressure attained at the adsorption temperature (273K) of $CO_2$ is very low to fill these pores [9].

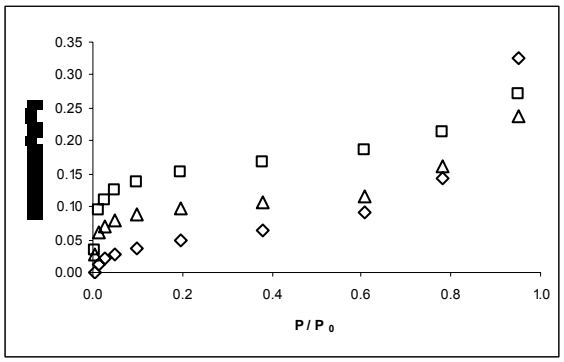


Figure 2. Adsorption of benzene at 303 K on: ◇T650, △ T650-4, □ T650-8

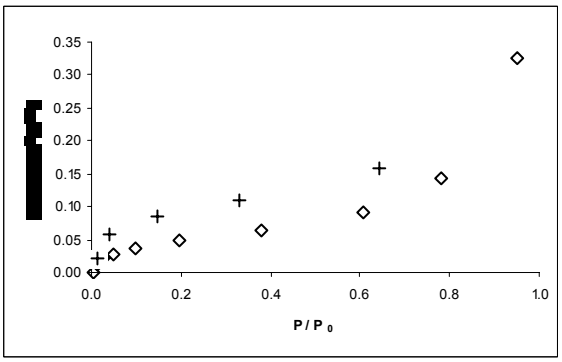


Figure 3. Adsorption and desorption of benzene at 303 K on T650. ◇adsorption process, + desorption process

Table 3. Parameters of Dubinin-Raduskevich equation for the adsorption isotherms of nitrogen (77 K) and benzene (303 K).

| Sample | adsorbate | Wo ($cm^3\ g^{-1}$) | Eo ($kJ\ mol^{-1}$) | Lo (nm) |
|---|---|---|---|---|
| T650 | nitrogen | 0.096 | 9.32 | - |
| | benzene | 0.057 | 9.03 | - |
| T650-4 | nitrogen | 0.114 | 14.38 | 1.79 |
| | benzene | 0.104 | 14.79 | 1.73 |
| T650-8 | nitrogen | 0.141 | 15.56 | 1.64 |
| | benzene | 0.157 | 15.57 | 1.64 |

The adsorption isotherms for benzene are plotted on Figure 2. These isotherms present small hysteresis loops at low relatives presures when desorption process is carried out which means that the very small amount of benzene adsorbed on the smallest pores can not be desorbed; the adsorption-desorption isotherm of benzene on sample T650 is shown Figure 3.

The textural parameters obtained from the adsorption isotherms of benzene (Table 3) are in good agreement with that of nitrogen which support the proposed effect of the activation time on the textural properties of the samples.

## Conclusions

A novel treatment is proposed for recycling of PET into activated carbons which decrease the elimination of volatile compounds in the pyrolysis process.

Activated carbons derived from the final product of the basic hydrolysis of PET show different microporous systems depending on the time of activation. For the less activated sample, T650, the micropore system is limited to ultramicropores and the adsorption of $N_2$ and benzene appeared to occur almost exclusively on external surface. This means that there are strong constrictions for the adsorption of these adsorbates on the ultramicropore system measured with $CO_2$. For samples with a much longer activation time, T650-4 and T650-8, the ultramicropore system seems not to be altered but a new range of micropores with a larger mean width ($\approx$ 1.6 nm) is created which is only covered by $N_2$ and $C_6H_6$ adsorption.

## Acknowledgements

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