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# INFLUENCE OF ACTIVATED CARBONS TEXTURAL PROPERTIES ON ACETAMINOPHEN ADSORPTION AT DIFFERENT TEMPERATURES

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**Abstract**

Temperature influence (20-40 ºC) on the acetaminophen adsorption onto activated carbons with different textures was studied. Different temperature dependences, not explained by kinetic effects, were observed for carbons with different micropore size distributions patterns: adsorption capacity increases for samples Pi-fa/800 and Pi-fa/900, and decreases for carbon S/700. No significant variation was seen for carbon CP. The $^{1}$H NMR spectroscopic analysis of the adsorbed phase proved that during the adsorption process exist the conditions required to promote the formation of acetaminophen oligomers which have constrained access to the narrow microporosity. The rotation energy of the dihedral angle between monomers (estimated by electronic DFT methods) showed that conformations in the planar form are less stable than the non-planar conformation (energy barrier of 70 and 23 kJ mol$^{-1}$), but have critical dimensions similar to the monomer and can access most of the micropore volume. The enthalpy change of the overall process showed that the energy gain of the system (endothermic) for Pi-fa samples (≈ 40 kJ mol$^{-1}$) was enough to allow a change in the dimer, or even larger oligomers, conformation to the planar form. This will permit adsorption in the narrow micropores, thus explaining the uptake increase with temperature. Non-continuous micropore size distributions centered at pore widths close to the critical dimensions of planar form seem to be crucial to a positive evolution of the adsorption capacity with temperature.

**Keywords**: Activated carbon, acetaminophen adsorption, temperature, oligomers, conformations.

## 1 Introduction

Activated carbons have been successfully applied as adsorbents of a variety of organic pollutants from aqueous solution.[1-3] However, despite a great number of studies are focused on the performance of the materials[2-6], only in few cases some insight into the mechanism of the adsorption process is reported.[7,8]

The mechanism of the adsorption from solution is not an easy issue to address, due to the competition of the organic compounds and water for the adsorption sites, which depend on the textural characteristics of the carbon, content and type of the surface functionalities, as well as on the structure of organic molecules. Among the experimental parameters that influence the adsorption mechanism of organic molecules, pH is probably the most studied, since the net surface charge of the carbons and the adsorbate molecular structure are dependent of the solution pH.[6, 9-24] Although less extensively, the influence of the water hardness[25], ionic strength[25], and temperature[8-16, 18, 20, 23, 26] have also been evaluated.

According to thermodynamic principles, adsorption is an exothermic phenomenon[27], thus one could expect that an increase of temperature would always lead to a decrease of the adsorption capacity. However, in the literature there are a great number of studies reporting a positive effect of the temperature on the adsorption capacity in liquid[8-11, 14, 20, 23, 26], and also gas phase processes.[28-30] In the particular case of liquid phase processes, the results obtained by Guedidi et al.[9] on the adsorption of ibuprofen onto a granular activated carbon presenting both micro and mesopores are illustrative of this

unexpected behavior. The authors found that rising the temperature in 30 ºC promoted an increase of 34 percentage points on the monolayer capacity. In the study developed by Al-Degs et al.[31], focused on the adsorption of reactive dyes onto a commercial activated carbon, a 30 ºC increase of temperature had an even more pronounced effect on the monolayer capacity that increased by a factor of 2.8. Regarding gas phase adsorption processes, an example of this type of results is the data reported by Ramos et al.[28] on benzene adsorption onto a carbon cloth, being demonstrated that for low relative pressures, benzene uptake increases when the temperature changed from 0 to 25 ºC.

To explain these thermodynamically unexpected results several hypothesis have been proposed in the literature. The most common is to consider that the higher mobility of the molecules at higher temperatures may facilitate the diffusion through the narrowest micropores of the adsorbent.[10-12,14,28] When the molecular dimensions are close to the pore size, conformation effects are also admitted to explain the uptake increase.[30] In the particular case of adsorption from solution, the unexpected effect of the temperature on the adsorption capacity is interpreted as being related with some interactions of chemical nature.[12,20,23,26]

In a recent work developed by our group, carbons prepared from pine gasification residues were tested as adsorbents of acetaminophen, and an increase of the monolayer capacity was observed when the temperature increased by 20 ºC.[32] To explain these results, we hypothesized that the positive effect of temperature on the adsorption capacity was linked to the microporosity of the materials, which seems to play a crucial role in the mechanism of acetaminophen adsorption.[32] To check the consistency of this hypothesis, in the present work we tested four carbons, with different micropore size

distributions and surface chemistry characteristics, as adsorbents of acetaminophen at three temperatures (20, 30 and 40 ºC). The discussion of the kinetic and equilibrium data was complemented by computational calculations using electronic Density Functional Theory (DFT) methods for acetaminophen adsorbed species identified by $^{1}H$ NMR spectroscopy in the back-extraction solution. The optimized structures of the most stable conformations of acetaminophen dimer and tetramer, indicated that molecular dimensions seem, indeed, to be critical for the behavior of carbons with narrow pores. The energetic barrier associated with the internal rotation of the adjacent monomers was estimated and conformations with lower critical dimensions, although less stable, seem to play a crucial role in the explanation of the experimental results.

## 2 Experimental

### *2.1 Activated carbons*

In this study four activated carbons were used, a commercial carbon (sample CP) and three lab-made samples produced from two different precursors: fly ash, obtained by pine gasification (Pi-fa); and sisal residues(S), supplied from a rope industry.

The experimental details of the materials production are detailed described in references 32 and 33. Briefly, 1 g of Pi-fa and sisal (fibers 1 cm long) were mixed with, respectively, 3 g and 0.5 g of potassium carbonate ($K_2CO_3$, Aldrich 99%). The mixtures were activated in a horizontal furnace (Thermolyne mod. 21100) under $N_2$ flow (5 $cm^3$ $s^{-1}$), Pi-fa at 800 and 900 ºC (samples Pi-fa/800 and Pi-fa/900) and sisal residues at 700 ºC (sample S/700), for 1 h. The samples obtained were thoroughly washed with distilled water and dried at 100 ºC.

*2.2 Characterization techniques*

The textural characterization of the samples was made by $N_2$ adsorption isotherms at -196 ºC measured on a Micromeritics ASAP 2010 apparatus, and $CO_2$ adsorption isotherms at 0 ºC obtained on a conventional volumetric apparatus equipped with a MKS-Baratron (310BHS-1000) pressure transducer (0–133 kPa). Before the isotherms acquisition the samples (≈ 50 mg) were outgassed overnight at 120 ºC, under vacuum better than $10^{-2}$ Pa. From $N_2$ adsorption data, the apparent surface area, $A_{BET}$, and microporosity were evaluated through, respectively, BET equation ($0.05 < p/p^0 < 0.15$)[34] and $\alpha_S$ method, taking as reference the isotherm reported by Rodríguez-Reinoso et al..[35]

The surface chemistry of the solids was characterized by the determination of the pH at the point of zero charge ($pH_{PZC}$), following the reverse mass titration methodology proposed by Noh and Schwarz.[36] The pH measurements were made with a Symphony SP70P pH Meter.

*2.3 Liquid phase adsorption*

The effect of the carbons microporosity characteristics on their behavior as adsorbents of acetaminophen (Aldrich – lot. 535764-326) from liquid phase was studied through kinetic and equilibrium assays at three different temperatures: 20, 30 and 40 ºC.

For kinetic studies, *ca.* 6 mg of adsorbents, were mixed with 20 $cm^3$ of acetaminophen solution (120 mg $dm^{-3}$) prepared with ultra-pure water obtained from Milli-Q water purification systems. A magnetic stir bar was introduced, the vials were placed in a water bath (Grant GD100 controller) at the desired temperature, and the solution was added. The stirring at 700 rpm (multipoint agitation plate from Variomag

Poly) and the time recording were then started, and samples were collected between 1 min and 24 h. The residual concentration of solute was determined by UV-vis spectrophotometry (Genesys 10S UV-Vis spectrophotometer) at $\lambda_{max}$ = 243 nm.

The equilibrium adsorption studies were carried out maintaining the adsorbent dose (*ca.* 6 mg) and varying the solution volumes (10-20 $cm^3$) and the acetaminophen solution concentration (120-480 mg $dm^{-3}$). After stirring for 5 h (equilibrium time selected from kinetic results), the concentration of the acetaminophen remaining in solution at equilibrium was determined and the uptake calculated. All the equilibrium adsorption assays were made in triplicate. The pH was monitored, at the beginning and at the end of all the assays, using a Symphony SP70P pH Meter.

*2.4 Back-extraction assays and $^1H$ NMR spectroscopy*

To identity the adsorbed acetaminophen species, a back-extraction assay using the commercial sample was made following the procedure reported in the literature for efficient back-extraction of other pharmaceutical compounds adsorbed onto activated carbons[37,38]. Briefly *ca.* 90 mg of carbon CP were mixed with 450 $cm^3$ of acetaminophen solution (300 mg $dm^{-3}$) at 30 ºC. After stirring (700 rpm) for 17 h, the exhausted activated carbon was recovered by filtration under vacuum (Whatman 5) and dried overnight at 100 ºC. For back-extraction the carbon was placed in a glass vial containing 50 $cm^3$ of a 50:50 (v:v) mixture of methanol:acetonitrile, both Merck analytical grade reagents. After stirring (700 rpm) for 2.5 h the liquid fraction was collected by filtration and placed in a Schlenk flask and the stripping solvent was evaporated under vacuum until total dryness.

NMR data was collected in a Bruker Avance 400 spectrometer. The $^{1}$H NMR spectrum was recorded at 400.13 MHz in acetone-d6, at 20 ºC. A standard pulse sequence from Bruker library was used and 64 scans were accumulated with 8,278 spectral width and 64k data points. Topspin software from Bruker was used for acquisition and processing (versions 2.6 and 3.0 respectively) and the spectrum was referenced to the residual signal of the solvent at 2.05 ppm from TMS.

*2.5 Computational methods*

The molecular modelling of acetaminophen species identified in the $^{1}$H NMR spectrum of the back-extracted adsorbed species was accessed with Gaussian-09 software[39], considering the molecules in the liquid phase (polarizable continuum model for water) using the non-local hybrid three parameters B3LYP density functional approach[40,41] with the 6-31 G (d) basis set. Geometry optimizations were performed without constrains to obtain the most stable molecular geometry (conformation) of the dimer and tetramer. van der Waals size of the various oligomers was estimated considering the radius given by the Universal Force Field model[42] centered on the optimized atomic positions. The minimum energy of the different conformations with several dihedral angles between the two monomers was obtained by performing a relaxed potential energy surface scan, rotating (5º step) the dihedral angle between the two monomers (Figure S1 in SI) and full optimization of the structure at each rotation step. The heat capacity at constant volume ($C_v$) was estimated by performing frequency and thermochemistry calculations on the optimized minimum energy conformer.

## 3 Results

### *3.1 Nanotextural and chemical characterization of samples*

The textural characteristics of the carbons used in this study were already presented and detailed discussed in previous works[24,32,33], but it should be noted that sample S/700 corresponds to a different batch of that used in ref. 33. Nevertheless for data interpretation purposes, the main textural parameters estimated from the analysis of the $N_2$ adsorption isotherms are reported in Table 1. The results show that the Pi-fa based carbons present a higher porosity development, specially sample Pi-fa/900 where an apparent surface area of around 1100 $m^2\ g^{-1}$ was achieved. The experimental conditions used to prepare this sample originated a developed mesopore structure ($V_{meso}$ = 0.26 $cm^3\ g^{-1}$) and a micropore network formed almost exclusively by larger micropores, *i.e.* supermicropores (widths between 0.7 and 2.0 nm). The values reported in Table 1 reveal that, in fact, for sample Pi-fa/900 the volume of supermicropores ($V_{\alpha\ super}$) is significantly larger than that of $V_{\alpha\ ultra}$, *i.e.* the volume of narrow micropores (ultramicropres - width < 0.7 nm). In the case of carbons Pi-fa/800 and S/700 the micropore network is composed by similar amounts of narrow and larger micropores ($V_{\alpha\ ultra} \approx V_{\alpha\ super}$), while the commercial carbon CP has a slightly higher volume of larger micropores.

The surface chemistry of the materials was evaluated by the $pH_{PZC}$ values, which reveal the different chemical properties of the carbons: Pi-fa/800 and Pi-fa/900 are neutral carbons, while S/700 is acidic, and the commercial carbon is basic.

**Table 1.** Nanotextural parameters and $pH_{PZC}$ values of lab-made and commercial carbons.

| Sample | $pH_{PZC}$ | $A_{BET}$ ($m^2 g^{-1}$) | $V_{meso}$ [a] ($cm^3 g^{-1}$) | $\alpha_s$ method | | | Reference |
|---|---|---|---|---|---|---|---|
| | | | | $V_{\alpha\ total}$ [b] ($cm^3 g^{-1}$) | $V_{\alpha\ ultra}$ [c] ($cm^3 g^{-1}$) | $V_{\alpha\ super}$ [d] ($cm^3 g^{-1}$) | |
| Pi-fa/800 | 7.0 | 954 | 0.08 | 0.41 | 0.19 | 0.22 | 32 |
| Pi-fa/900 | 7.4 | 1171 | 0.26 | 0.45 | 0.02 | 0.43 | 32 |
| S/700 | 5.3 | 834 | 0.01 | 0.36 | 0.18 | 0.19 | This study |
| CP | 10.3 | 907 | 0.03 | 0.40 | 0.16 | 0.24 | 24 |

[a] $V_{meso}$ – difference between the volume adsorbed at $p/p^0 = 0.975$ (total pore volume) and $V_{\alpha\ total}$;
[b] $V_{\alpha\ total}$ – obtained by back extrapolation of the high relative pressure region ($\alpha_S > 1$);
[c] $V_{\alpha\ ultra}$ – intercept of the linear range defined the region $p/p^0 \geq 0.02$ ($\phi < 0.7$ nm);
[d] $V_{\alpha\ super}$ – difference between $V_{\alpha\ total}$ and $V_{\alpha\ ultra}$ (0.7 nm < $\phi$ < 2 nm)

*3.2 Liquid-phase adsorption*

To evaluate the influence of the temperature on the acetaminophen adsorption process on activated carbons, kinetic and equilibrium assays were made for all the carbons at three different temperatures: 20, 30 and 40 ºC.

The kinetic data displayed in Figure 1 reveal that for all the carbons, and regardless the temperature, a very marked decay is observed in the first 5 minutes of contact time. Afterwards the adsorption process proceeded slowly until 4 h, time at which the equilibrium was attained. No increase in the acetaminophen uptake was observed even after 24h of contact time (data not shown).

The results obtained show that, in the case of Pi-fa based carbons (Figure 1 (a) and (b)), acetaminophen uptake increased with the increase of the temperature, *i.e.*, the overall process shows an endothermic character. According to Acemioğlu[14] these unexpected results can be explained considering that the mobility of the molecules increases with temperature. If this was the solely possible explanation for these results,

then it would be expected that the increase of temperature would accelerate the adsorption process.

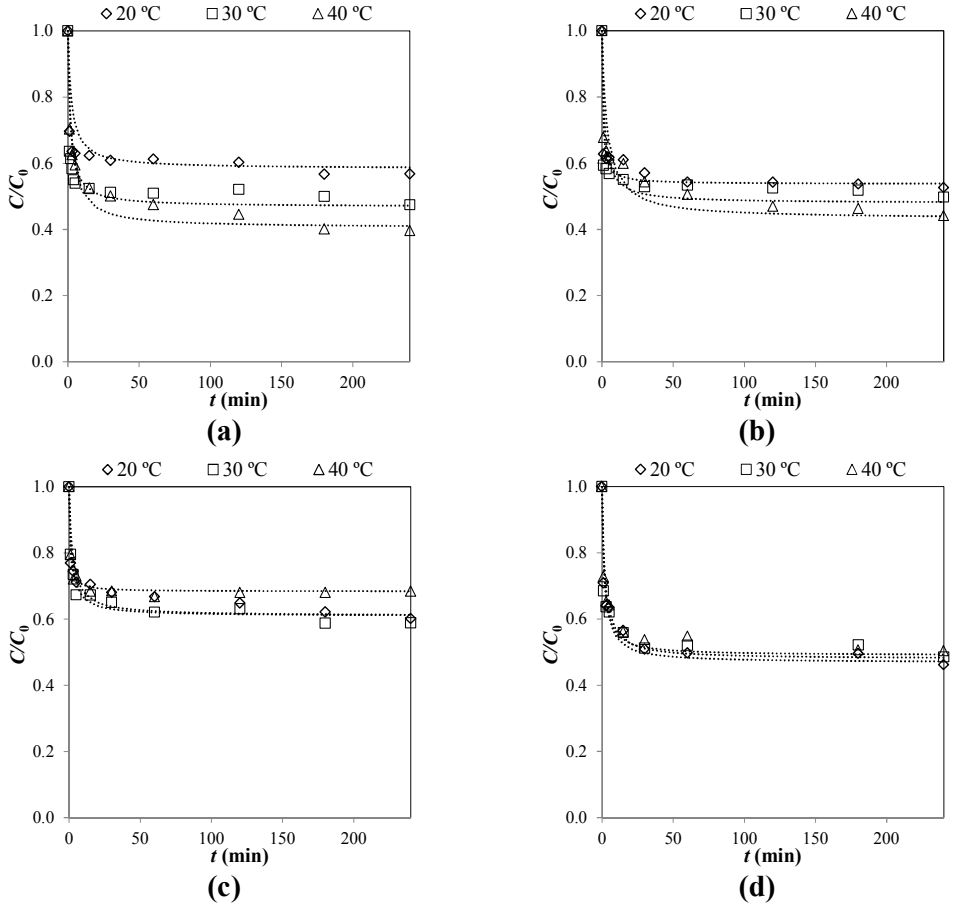


**Figure 1.** Kinetic results of acetaminophen obtained at 20, 30 and 40 ºC for (a) Pi-fa/800, (b) Pi-fa/900, (c) S/700 and (d) CP ($C_0$= 120 mg dm$^{-3}$, 6 mg of carbon, and 20 cm$^3$ of solution). Symbols correspond to the experimental data, whereas lines represent the fitting to the pseudo-second order kinetic equation.

However, the kinetic parameters obtained from the fitting of the kinetic data to pseudo-second order model[43] (Table 2), particularly the initial adsorption rates ($h$) evaluated by the product of $k_2 q_e^2$, show exactly the opposite trend. This behavior is specially marked in the case of sample Pi-fa/900, where the initial adsorption rate

decreased one order of magnitude when the temperature rose from 20 up to 40 ºC.

Contrarily to the behavior of Pi-fa based carbons, in the case of sample S/700 the expected influence of temperature in the adsorption kinetics was observed. Actually, a slight decrease of acetaminophen uptake and a pronounced increase of the initial adsorption rate are observed. In the case of sample CP, there is no significant change, neither in the uptake, nor in the adsorption kinetic parameters.

Despite the discussion presented above, it must be mentioned, that the physical meaning of the estimated kinetic constant $k_2$ is uncertain in the cases studied in the present work because the observed process is not a only an adsorption process, but other simultaneous chemical and physical process are occurring, as we will discuss bellow.

**Table 2.** Pseudo-second order acetaminophen adsorption parameters for the lab-made and commercial samples at 20, 30 and 40 ºC.

| Sample | $R^2$ | $k_2 x10^{-4}$ (g mg$^{-1}$ min$^{-1}$) | $h$ (mg g$^{-1}$ min$^{-1}$) | $q_{e,calc}$ (mg g$^{-1}$) |
|---|---|---|---|---|
| *Pi-fa/800* | | | | |
| 20 ºC | 0.997 | 50 | 145 | 167 |
| 30 ºC | 0.997 | 30 | 127 | 213 |
| 40 ºC | 0.996 | 20 | 104 | 238 |
| *Pi-fa/900* | | | | |
| 20 ºC | 0.997 | 70 | 256 | 185 |
| 30 ºC | 0.999 | 30 | 123 | 208 |
| 40 ºC | 0.999 | 10 | 66 | 227 |
| *S/700* | | | | |
| 20 ºC | 0.996 | 30 | 82 | 156 |
| 30 ºC | 0.997 | 30 | 91 | 156 |
| 40 ºC | 0.996 | 120 | 196 | 127 |
| *CP* | | | | |
| 20 ºC | 0.999 | 27 | 120 | 213 |
| 30 ºC | 0.999 | 32 | 132 | 204 |
| 40 ºC | 0.999 | 25 | 108 | 208 |

This diversity of results points out that the increase of the species mobility, which obviously occurs when the temperature rises, is not the only parameter ruling the complex process of acetaminophen adsorption onto activated carbons.

The acetaminophen adsorption isotherms presented in Figure 2 show the completely different behavior of the samples assayed when the temperature increases from 20 up to 40 ºC. In fact, all the possible dependences of the adsorption capacity with temperature were observed. An increase of the adsorption capacity as the temperature rises is observed for both Pi-fa derived carbons, being especially pronounced in the case of sample Pi-fa/900. Conversely, with carbon S/700 the increase of the temperature led to a continuously decrease of the adsorption capacity, and no significant dependence is observed in the results obtained with the commercial carbon CP.

From the analysis of the isotherms configuration it is also possible to conclude that the highest adsorption capacity was achieved with sample Pi-fa/900 when the adsorption process was carried out at 40 ºC. On the other hand, the stepper isotherms obtained with carbon CP, reveal the higher affinity of acetaminophen for this sample.

The results were fitted to the linear forms of Langmuir[44] and Freundlich[45] models, equations 1 and 2, respectively.

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m} \quad (1)$$

$$\log(q_e) = \log(K_F) + \frac{1}{n}\log(C_e) \quad (2)$$

where, $q_e$ (mg g$^{-1}$) and $C_e$ (mg dm$^{-3}$) are, respectively, the solute uptake and the solution concentration at equilibrium and $q_m$ (mg g$^{-1}$) is the monolayer adsorption capacity. The $K_L$ (dm$^3$ mg$^{-1}$) and $K_F$ (mg$^{1-1/n}$ (dm$^3$)$^{1/n}$ g$^{-1}$) are, respectively, the Langmuir and

Freundlich constants, and $1/n$ is related to the adsorption affinity and surface heterogeneity[45]. The data obtained are presented in Table 3, along with the linear regression determination coefficients and the $\chi^2$ values, evaluated following the method used by Ho[46], both proving a better fitting of the experimental values to the Langmuir model.

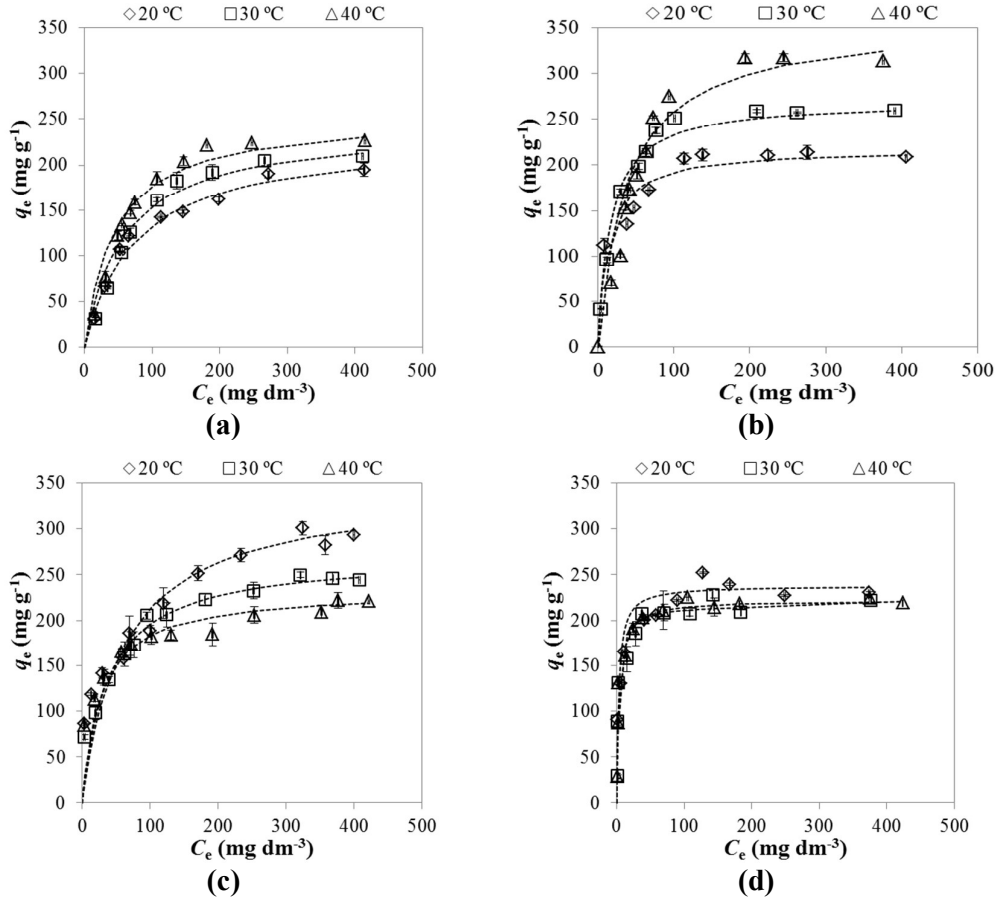


**Figure 2.** Acetaminophen adsorption isotherms at 20, 30 and 40 ºC on (a) Pi-fa/800, (b) Pi-fa/900, (c) S/700 and (d) CP. Symbols correspond to the experimental data, and dotted lines to the fitting to the Langmuir equation. Error bars are included.

The values of the monolayer capacities allow to quantify the influence of the temperature on acetaminophen adsorption on the various carbons. Curiously, in the case of the samples for which a significant effect of the temperature on the maximum adsorption capacity ($q_m$) was verified, an increase (sample Pi-fa/900) or decrease (sample S/700 ) of almost the same amount (≈120 mg $g^{-1}$ ) is detected. In other words, for each sample, the percentual difference between its higher and lower $q_m$ values is 60 % of the lower $q_m$ value.

**Table 3.** Langmuir and Freundlich isotherm parameters for the adsorption of acetaminophen onto the mentioned samples at 20, 30 and 40 ºC. Determination coefficients, $R^2$, and chi-square test analysis, $\chi^2$, for the fittings are also presented.

| System | Langmuir equation | | | | Freundlich equation | | | |
|---|---|---|---|---|---|---|---|---|
| | $q_m$ (mg $g^{-1}$) | $K_L$ ($dm^3$ $mg^{-1}$) | $R^2$ | $\chi^{2a}$ | 1/n | $K_F$ | $R^2$ | $\chi^{2a}$ |
| *Pi-fa/800* | | | | | | | | |
| 20 ºC | 232.6 | 0.013 | 0.990 | 4.08 | 0.515 | 11.0 | 0.884 | 26.35 |
| 30 ºC | 243.9 | 0.016 | 0.989 | 19.14 | 0.589 | 8.4 | 0.884 | 50.24 |
| 40 ºC | 256.4 | 0.022 | 0.994 | 21.70 | 0.532 | 13.3 | 0.850 | 62.10 |
| *Pi-fa/900* | | | | | | | | |
| 20 ºC | 217.4 | 0.073 | 0.997 | 4.73 | 0.187 | 75.6 | 0.892 | 9.26 |
| 30 ºC | 270.3 | 0.061 | 0.999 | 6.27 | 0.373 | 38.4 | 0.866 | 76.67 |
| 40 ºC | 344.8 | 0.032 | 0.993 | 15.30 | 0.469 | 30.6 | 0.809 | 95.61 |
| *S/700* | | | | | | | | |
| 20 ºC | 344.8 | 0.016 | 0.992 | 5.16 | 0.266 | 60.1 | 0.974 | 7.66 |
| 30 ºC | 270.3 | 0.026 | 0.999 | 1.92 | 0.283 | 48.9 | 0.961 | 11.65 |
| 40 ºC | 232.6 | 0.037 | 0.996 | 3.56 | 0.210 | 65.2 | 0.961 | 5.16 |
| *CP* | | | | | | | | |
| 20 ºC | 232.6 | 0.240 | 0.999 | 1.83 | 0.184 | 95.5 | 0.936 | 9.28 |
| 30 ºC | 227.3 | 0.370 | 0.999 | 2.40 | 0.245 | 69.1 | 0.774 | 54.60 |
| 40 ºC | 222.2 | 0.276 | 0.999 | 3.54 | 0.285 | 62.5 | 0.718 | 92.41 |

[a] $\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}}$

In the case of sample CP, the decrease of $q_m$ values with the temperature increase is not significant (10 mg $g^{-1}$). So, as it was already pointed out by the kinetic results, the acetaminophen adsorption onto this particular sample, does not seem to be affected by the temperature in the range assayed.

The higher affinity of acetaminophen for carbon CP, suggested by the analysis of the isotherms configuration, is demonstrated by the $K_L$ values which are one order of magnitude higher than those observed for the other samples. This behavior may be related to the surface chemistry of the samples. Carbon CP is the only sample with basic surface chemistry properties (see $pH_{PZC}$ in Table 1) thus, at the experimental pH (≈ 5) its surface will present a higher density of positive charges than the other carbons. In these conditions, the interaction with acetaminophen will be favored, since this molecule is a weak base with nitrogen atoms presenting lone electron pairs.

If the acetaminophen affinity can be justified considering the surface chemistry properties of the carbons, the same is not valid for the adsorption capacity dependence with temperature. In fact, considering the $pH_{PZC}$ values of the lab-made samples (see Table 1), the opposite behavior observed for Pi-fa based carbons and sample S/700 would not be expected. Thus, as we hypothesized in a previous study[32] microporosity can be a determinant factor in the acetaminophen adsorption that must be considered when a deeper understanding of the different temperature dependences observed is intended.

To test this hypothesis, the microporosity of the samples was further characterized by $CO_2$ adsorption. The micropore size distributions were obtained from the isotherms data with the methodology adopted by Pinto et al..[47] The results presented in Figure 3,

reveal that the carbons have different micropore structures although, in all the cases, a bimodal distribution is observed. The curves reveal that samples Pi-fa/900 and S/700 have micropores in all the range of pore width, while carbons Pi-fa/800 and CP do not present pores in the region of 0.8 – 0.9 nm and 0.9 – 1.1 nm, respectively. The maximum observed at small pore width is also different: 0.44 nm for Pi-fa/900; 0.52 nm for Pi-fa/800 and S/700; and 0.61 nm for CP carbon.

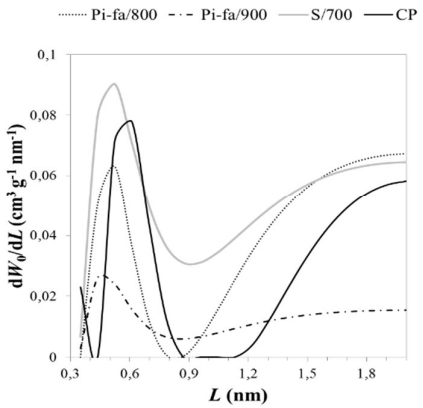


**Figure 3.** Micropore size distribution of mentioned samples.

If we assume that the acetaminophen is adsorbed as discrete molecules it is not possible to explain the different patterns observed for the monolayer capacity with temperature increase. In fact, the critical dimension of acetaminophen molecule is 0.46 nm[32] allowing us to conclude that its accessibility to the pore network of all the samples is identical. So, some unexpected phenomenon may occur in the reaction media that results into the opposite behaviors observed.

Searching for an explanation, we considered the study developed by Nemattolahi et al.[48], where it was shown that at pH ≈ 5 and in oxidative conditions acetaminophen forms a dimer. This species and more five other acetaminophen oligomers were

identified by Potter et al.[49] when acetaminophen reacted with $H_2O_2$ in the presence of horseradish peroxidase. On the other hand, in a recently published study developed by Velasco et al.[50] it is demonstrated that nanoporous carbons can convert low energy photon from the visible spectrum into chemical reactions, as is the case of phenol photooxidation. Merging these information we can assume that at experimental pH of the assays (≈ 5), in the presence of activated carbon acetaminophen can form oligomers. To test this hypothesis, we needed to analyze the adsorbed species and for that we selected the commercial sample to perform back-extraction assays. The $^1$H NMR spectrum of the adsorbed phase components obtained from the exhausted commercial sample is presented in Figure S1 of Supplementary Information. As it is detailed discussed in SI, besides the acetaminophen monomer other oligomers already identified by Potter et al.[49] were also detected in the back-extracted solution. This result demonstrates that the conditions required to promote the oxidation and consequent formation of acetaminophen oligomers are met during the adsorption process, and so the presence of these species cannot be disregarded when analyzing adsorption data.

According to DFT results, the critical dimension of low energy conformation of the smaller and larger acetaminophen oligomers, i.e. dimer and tetramer, are 0.66 nm[32] and 1.10 nm (see Figure S2 in Suplementary Information).

Considering the micropore size distribution of the samples it can be concluded that the tetramer in the lowest energy conformation can be accommodated only in the larger micropores of all the materials. On the other hand, the dimer's critical dimension is very close to the maximum of the micropore size distribution of only carbon CP. In this case the interaction between this carbon and the adsorbed specie will be enhanced, which

corroborates the higher affinity of acetaminophen for carbon CP and justifies the temperature independence of this system in the range assayed.

On the contrary of CP carbon, lab-made carbons present the micropore size distribution maxima at smaller widths. So, to explain the complexity of the acetaminophen adsorption mechanism onto the lab-made carbons, a different approach is needed. One possibility is to consider the presence of species with conformations having smaller critical dimensions than the lowest energy conformation, then closer to that of the maximum of the micropore size distributions of the samples.

To simplify the data analysis, in the following we will only consider the acetaminophen dimer, since being the smaller oligomer it is the one where a slight change towards a less stable, but with smaller critical dimesion conformation, will allow a more efficient packing in the the narrowest micropores of the samples.

Assuming that the temperature increase could, in fact, modify the acetaminophen dimer conformation, the energy barrier resulting from the rotation between the two monomers was computed, using electronic DFT computational methods (see section 2.4 for details, and Figure S3 for the atoms took into account that define the dihedral angle), and the results are displayed in Figure 4. The obtained conformations with several dihedral angles between the two monomers correspond to the energy minima of the molecule with given dihedral angles, and the energy profile in Figure 4 can thus be regarded as the minimum energy necessary to rotate the two monomers.

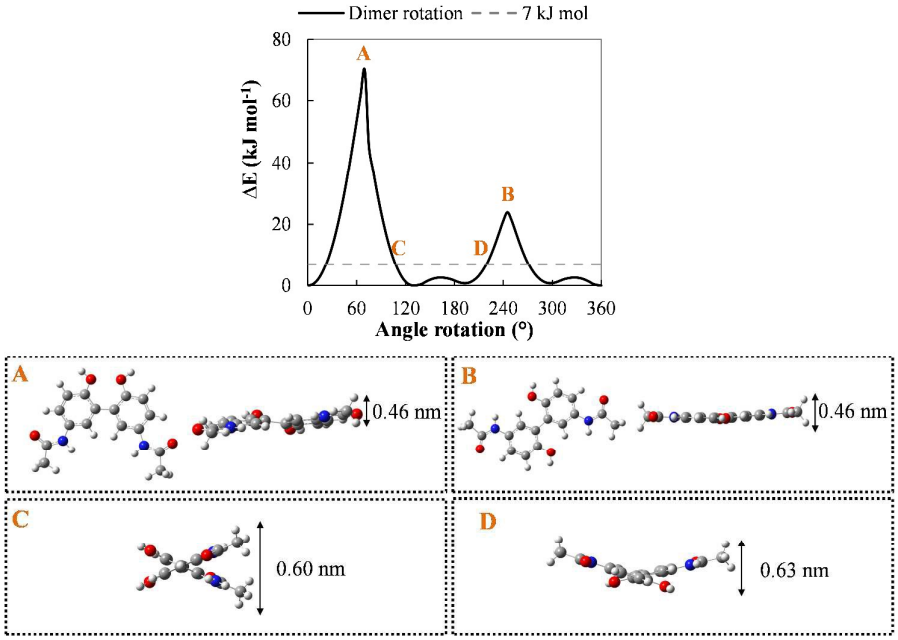


**Figure 4.** Energy profile of the different dimer conformation considering the rotation between two monomers, and conformations of the dimer associated to the energy states A, B, C and D (oxygen in red, nitrogen in blue, carbon in gray, and hydrogen in white).

The existence of two planar conformations, A and B, with different energies is demonstrated by the theoretical calculations. The conformation A is less stable due to the repulsion between the oxygens of the hydroxyl group, whereas in conformation B only some repulsion between the benzene hydrogens and the oxygens of the hydroxyl group is present, due to a very close proximity. Both these acetaminophen dimer conformations have critical dimensions around 0.46 nm, and in these conditions almost all of the microporosity of the carbons becomes accessible to the species. But could conformations A and B be present in the adsorbed phase?

To answer this question the change in the internal energy of the dimer molecule associated to an increase of the temperature from 20 up to 40 ºC was determined, using

the $C_v$ estimated from DFT calculations (see section 2.5). Considering an increase of 20 ºC and the estimated $C_v$ value, the internal energy associated is only 7 kJ mol$^{-1}$ (see SI for details). This energy gain is however much lower than the energy barrier correspondent to the formation of the species A (≈ 70 kJ mol$^{-1}$), and B (≈ 23 kJ mol$^{-1}$) but would be enough to slightly modify the lowest energy conformation of the acetaminophen dimer, and to lower its critical dimension.

Boltzmann distributions were considered to assess the effect of the increase of temperature from 20 to 40 ºC in the population distribution of the species presenting different dihedral angles (see details in SI, and results in Figure S4). The higher increase was observed in the species that correspond to the conformations associated to the energy change of about 7 kJ mol$^{-1}$, in line with the internal energy change calculations. These species (noted as points C and D in Figure 4) have critical dimensions of 0.60 and 0.63 nm, respectively. These dimensions are still significantly above the maxima of the pore size distributions of samples Pi-fa/800 and Pi-fa/900 and cannot alone justify the increase in the adsorbed amounts with temperature, in these particular cases.

Despite theoretical results point out that no significant decrease of the average critical dimension of dimer is associated to the energy gain resulting from the temperature increase from 20 to 40 ºC; the experimental data indicate that a significant number of species with near planar confromation should be present in the adsorbed phase. The lack of energy necessary to overcome the energy barrier for the formation of the planar conformations has to be linked to the adsorption process, which is an exothermic phenomenon, and can itself provide some energy to the conformational change of the molecules.

The apparent isosteric heat of adsorption, $\Delta H_{st,a}$, was determined using the Clausius-Clapeyron equation (3), adapted to the liquid-phase system:

$$\frac{dlnC_e}{d\mathrm{T}} = -\frac{\Delta H_{st,a}}{\mathrm{RT}^2} \quad (3)$$

or

$$\Delta H_{st,a} = \mathrm{R}\frac{dlnC_e}{d(1/\mathrm{T})}\Bigg|_{q_e} \quad (4)$$

For Pi-fa and S based carbons, the equilibrium concentration ($C_e$, mmol dm$^{-3}$) at constant adsorbed acetaminophen amount ($q_e$ = 1.32 mmol g$^{-1}$) was obtained from the adsorption isotherm at different temperatures, and $\Delta H_{st,a}$ were calculated from the slope of the ln $C_e$ versus (1/$T$) plots (Figure 5) and are presented in Table 4. For sample CP, $\Delta H_{st,a}$ was not calculated since no temperature dependence was observed.

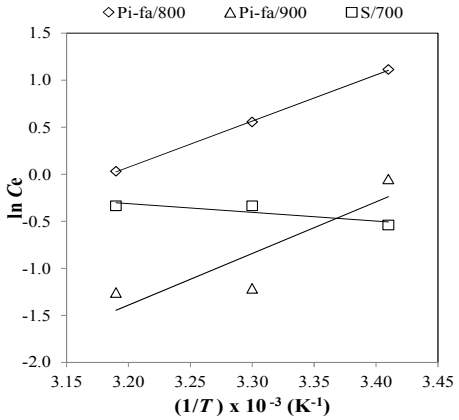


**Figure 5.** Adsorption isosters for determining the apparent isosteric heat of acetaminophen adsorption onto the mentioned samples, for surface coverage of 1.32 mmol g$^{-1}$.

**Table 4.** Apparent isosteric enthalpy of acetaminophen adsorption onto the mentioned samples, for surface coverage of 1.32 mmol $g^{-1}$.

| Sample | $\Delta H_{st,a}$ (kJ $mol^{-1}$) | $R^2$ |
|---|---|---|
| Pi-fa/800 | 41 | 0.999 |
| Pi-fa/900 | 47 | 0.793 |
| S/700 | -8 | 0.766 |

The apparent isosteric enthalpy values obtained allowed us to quantify the energy involved in the global process for the different carbons: energy gain in the systems presenting an overall endothermic process, *i.e.* when Pi-fa based carbons were used, and energy release when carbon S/700 was applied. Considering the relative high amount of energy involved in the case of the global endothermic processes one can admit the presence of the planar acetaminophen dimer conformation B (see Figure 4 (b)). In fact, the estimated gain of energy needed to reach the energy state corresponding to conformation B (23 kJ $mol^{-1}$) is much smaller than the values of the apparent isosteric enthalpies of the overall process onto Pi-fa based samples (41 and 47 kJ $mol^{-1}$ for, respectively, Pi-fa/800 and Pi-fa/900). So, under the experimental conditions used, it seems that in the system there is sufficient energy to overcome the energy barrier associated to the rotation between the two monomers, from the lowest energy configuration to the planar conformation B. In this case, the observed enthalpy change cannot be attributed only to the adsorption process, but to a combined process of adsorption and conformation change of the species adsorbed in the micropores. Thus, the experimental results are not contradicting the expected exothermic behavior of adsorption, but are in fact indicating that a very complex mechanism is taking place besides simple adsorption.

It must be noted that the complexity of the overall process that occurs when

acetaminophen interacts with carbons Pi-fa/800 and Pi-fa/900 was the reason to designate the $\Delta H_{st,a}$ values as "apparent isosteric entalpy" and not simply "isosteric entalpy" that would be associated to a solely adsorption process in the same adsorption space.

The critical dimension of the planar conformation B of acetaminophen dimer (around 0.46 nm) is very close to the maximum of the micropore size distributions of sample Pi-fa/900 (see Figure 3). Thus, a very strong interaction between the species in the planar form and the micropore network of sample Pi-fa/900 will be stablished, favouring the adsorption and leading to the unexpected evolution of the adsorption capacity with the temperature.

Despite these results, we cannot discard that larger oligomers, besides dimer, can acquire smaller conformations and access to a larger volume of narrow micropores, contributing to the increase of the adsorption capacity with temperature. This is the case of tetramer, whose planar conformation has a critical dimension idential to that of the dimer (0.66 nm), showing that a larger volume of narrow micropores can become available. Considering dihedral angles between monomers identical to that of conformers C and D of the dimer, the tetramer has critical dimension of 0.66 nm (see Figure S5 of SI). In these cases, the energetic barrier for the rotation of the monomers is identical to those discussed above for the dimer. Thus, oligomers of higher molecular weight can acess narrow micropores in a similar way as disccussed above for the dimer, and the temperature increase is expected to promote the adsorption of the oligomers.

It is interesting to observe that, although both Pi-fa carbons present rather similar values of isosteric enthalpies, the increase of the adsorption capacity with temperature

was not so marked when Pi-fa/800 sample was used. This is most likely due to the fact that the maximum of the micropore size distribution of sample Pi-fa/800 is not coincident with the critical dimension of the conformation B. In fact, the maximum of the micropore size distribution of sample Pi-fa/800 is centered at the 0.52 nm, which curiously is the same value of sample S/700. However, the influence of temperature in the acetaminophen adsorption onto these samples follows opposite trends. This result must be related with the fact that, contrary to sample Pi-fa/800, carbon S/700 has a continuous micropore size distribution with a considerable volume of pores in all of the microporosity range. Thus, the high volume of micropores with apertures much larger than the critical dimension of conformation B will influence the adsorption process because, when pores are sufficiently wide, the acetaminophen dimer, or even tetramer, can be adsorbed without having to change to the planar conformation. In this situation, the interaction of the adsorbate and the surface of those pores will be much weaker, leading to an adsorption process ruled essentially by thermodynamics of a simple adsorption process, *i.e.* without the need of conformational changes. In the case of sample Pi-fa/800, there is a gap of micropores with widths between 0.8 – 0.9 nm that seems to be the reason for the adsorption process to be ruled mainly by the texture. In fact, the results point out that in this case the temperature increase permits an access to the narrow micropores, most probably due to the possible conformation change in the dimer molecule. The amount that can be adsorbed in the porosity that becomes accessible at the higher temperature will then overlap the eventual decrease in the uptake in the larger micropores.

The results of sample CP show no dependence with the temperature. This can be

considered as an intermediate situation in which the decrease of the uptake due to the temperature increase is compensated by the increased access of the dimer to the narrow micropores.

## 4 Conclusions

In the experimental conditions used acetaminophen adsorbed species can be not only monomers but also oligomers as large as tetramers, which have constrained access to the narrow microporosity of some activated carbons. The temperature increase (20 ºC) presented a positive effect in the adsorption amounts on some activated carbon samples (Pi-fa/800 and Pi-fa/900), which contradicts the expected behavior for a simple adsorption process. The analysis of the experimental results indicates that this increase is not due to a faster adsorption kinetics at higher temperature (kinetics effects) because these samples presented slower adsorption rates at higher temperature.

The explanation of the results was centered in the acetaminophen dimer, for which the planar conformations, estimated by electronic DFT methods, are less stable than non-planar forms (energy barrier of 70 and 23 kJ $mol^{-1}$). However, the experimental enthalpy change of the overall adsorption process presented an energy gain (endothermic) over 40 kJ $mol^{-1}$ in samples Pi-fa/800 and Pi-fa/900, which is sufficiently high to account for the change in dimer geometry to one planar form, allowing the adsorption process to occur in the narrow micropores of these sample and explaining in this way the increase in the amounts adsorbed with temperature.

The results presented in this work point out that, when the activated carbon has a continuous distribution in all of the microporosity range, the acetaminophen adsorption

follows the expected thermodinamic behaviour for a simple adsorption process.

When the micropore size distribution of the carbon is centered near the critical dimensions of the species and a continous distribution is not present, the texture becomes the key factor ruling the adsorption. In this case the effect of temperture can be contrary to the expected thermodinamic behaviour because the adsorbent-adsorbate interactions are suficiently strong to promote the change of the oligomers to a planar conformation, what could not be expected simply from the energy gain associated to the temperature increase from 20 to 40 ºC.

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**Supporting Information**

In Electronic Supporting Information (ESI) available for PCCP NMR results are presented and some theoretical calculus are detailed aiming an ease understanding of the discussion made to explain the different acetaminophen adsorption temperature dependence onto microporous activated carbons.

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## TOC Graphic

Positive effect of temperature on activated carbons' acetaminophen adsorption capacity when non-continuous micropore size distributions centered at pore widths close to the critical dimensions of acetaminophen planar form are present.