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The influence of the textural properties of activated carbons on acetaminophen adsorption at different temperatures†

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The influence of temperature (20–40 °C) 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 distribution patterns: adsorption capacity increased for pine gasification residues (Pi-fa) derived carbons and decreased for sisal based materials. No significant variation was seen for carbon CP. The species identified by ^{1}H NMR spectroscopy on the back-extraction solution 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 ($\approx$40 kJ mol^{-1}) was enough to allow a change in the dimer, or even a larger oligomer, 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 the planar form seem to be crucial for a positive evolution of the adsorption capacity with temperature.

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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 being focused on the performance of the materials,[2–6] only in a few cases has some insight into the mechanism of the adsorption process been 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 depends on the textural characteristics of the carbon, content and type of the surface functionalities, as well as on the structure of the 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 on 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 increasing the temperature by 30 °C promoted an increase of 34 percentage points on the monolayer capacity. In the study developed

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by Al-Degs *et al.*,[31] focused on the adsorption of reactive dyes onto a commercial activated carbon, a 30 °C 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 result is the data reported by Ramos *et al.*[28] on benzene adsorption onto a carbon cloth, demonstrating that for low relative pressures, benzene uptake increased when the temperature changed from 0 to 25 °C.

To explain these thermodynamically unexpected results several hypotheses have been proposed in the literature. The most common one assumes 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 considered 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 to 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 was increased by 20 °C.[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 °C). 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 by a rope industry.

The experimental details of the material production are described in detail in ref. 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. 21 100) under N_2 flow (5 cm^3 s^{-1}), Pi-fa at 800 and 900 °C (samples Pi-fa/800 and Pi-fa/900) and sisal residues at 700 °C (sample S/700), for 1 h. The samples obtained were thoroughly washed with distilled water and dried at 100 °C.

2.2 Characterization techniques

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

For kinetic studies, *ca.* 6 mg of adsorbents, were mixed with 20 cm^3 of acetaminophen solution (120 mg dm^{-3}) prepared using 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. 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 λ_{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 ^{1}H 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 °C.

After stirring (700 rpm) for 17 h, the exhausted activated carbon was recovered by filtration under vacuum (Whatman 5) and dried overnight at 100 °C. 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 were collected in a Bruker Avance 400 spectrometer. The ^{1}H NMR spectrum was recorded at 400.13 MHz in acetone-d_6, at 20 °C. A standard pulse sequence from Bruker library was used and 64 scans were accumulated with 8278 spectral widths 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 the acetaminophen species identified in the ^{1}H NMR spectrum of the back-extracted adsorbed species was accessed using 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 6-31G(d) basis set. Geometry optimizations were performed without constraints 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 (5° step) the dihedral angle between the two monomers (Fig. S1 in the ESI†) 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 discussed in detail in previous studies,[24,32,33] but it should be noted that sample S/700 corresponds to a different batch to 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 microporous 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 the 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 (ultramicropores – 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.

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 °C.

The kinetic data displayed in Fig. 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 24 h of contact time (data not shown).

The results obtained show that, in the case of Pi-fa based carbons (Fig. 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 were the sole possible explanation for these results, then it would be expected that the increase of temperature would accelerate the adsorption process.

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})	α_s method: $V_{\alpha total}$[b] (cm^3 g^{-1})	$V_{\alpha ultra}$[c] (cm^3 g^{-1})	$V_{\alpha super}$[d] (cm^3 g^{-1})	Ref.
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 < ϕ < 2 nm).

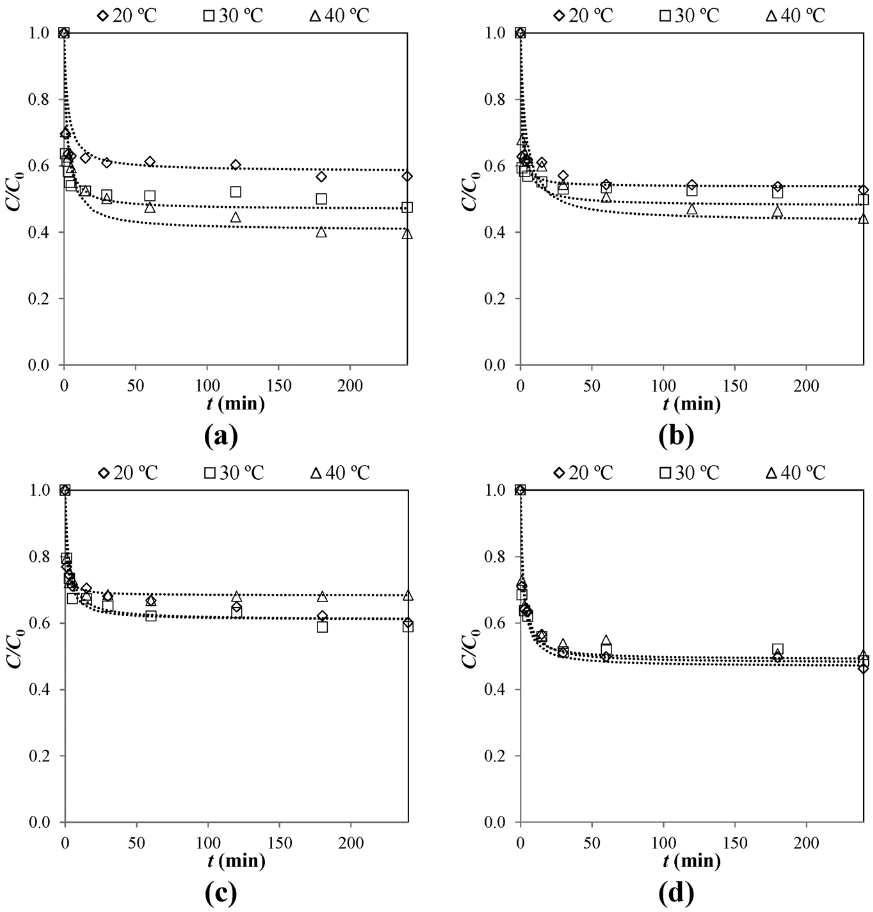

Fig. 1 Kinetic results of acetaminophen obtained at 20, 30 and 40 °C for (a) Pi-fa/800, (b) Pi-fa/900, (c) S/700 and (d) CP (C_0 = 120 mg dm^{-3}, 6 mg of carbon, and 20 cm^3 of solution). Symbols correspond to the experimental data, whereas lines represent the fitting to the pseudo-second order kinetic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

However, the kinetic parameters obtained from the fitting of the kinetic data to the pseudo-second order model[43] (Table 2), particularly the initial adsorption rates (h) evaluated by the product of $k_2q_e^2$, show exactly the opposite trend. This behavior is specially marked in the case of the sample Pi-fa/900, where the initial adsorption rate decreased one order of magnitude when the temperature increased from 20 up to 40 °C.

In contrast 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, either in the uptake, or 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 only an adsorption process, but other simultaneous chemical and physical process also occur, as we will discuss below.

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.

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

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

The acetaminophen adsorption isotherms presented in Fig. 2 show a completely different behavior of the samples assayed when the temperature increases from 20 up to 40 °C. In fact, all the possible dependences of the adsorption capacity with

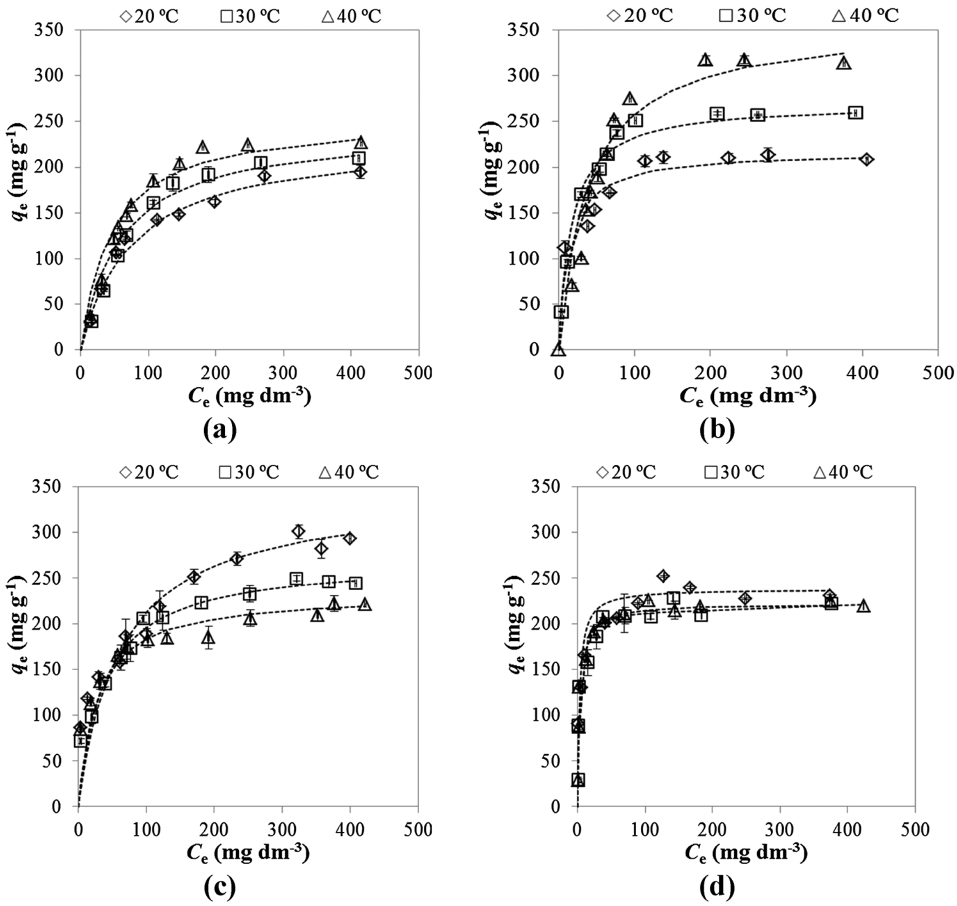

Fig. 2 Acetaminophen adsorption isotherms at 20, 30 and 40 °C on (a) Pi-fa/800, (b) Pi-fa/900, (c) S/700 and (d) CP. Symbols correspond to the experimental data, and dotted lines to the fitting to the Langmuir equation. Error bars are included.

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, for carbon S/700 the increase of the temperature led to a continuous decrease of the adsorption capacity, and no significant dependence was observed in the results obtained for the commercial carbon CP.

From the analysis of the isotherm configuration it is also possible to conclude that the highest adsorption capacity was achieved for the sample Pi-fa/900 when the adsorption process was carried out at 40 °C. On the other hand, the steeper 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, eqn (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 χ^2 values, evaluated following the method used by Ho,[46] both proving a better fitting of the experimental values to the Langmuir model.

The values of the monolayer capacities allow to quantify the influence of the temperature on acetaminophen adsorption onto 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 ($\approx$120 mg g^{-1}) is detected. In other words, for each sample, the percentage difference between its higher and lower q_m values is 60% of the lower q_m value.

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 isotherm configuration, is demonstrated by the K_L values which are one order of magnitude higher

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

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

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

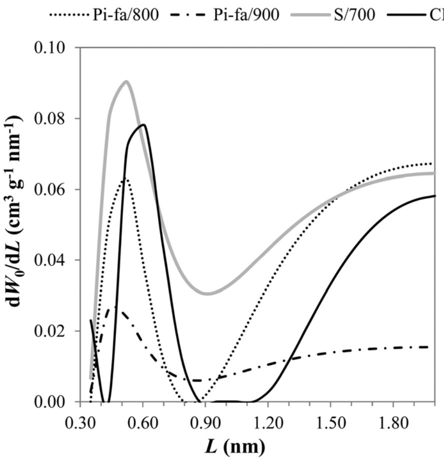

Fig. 3 Micropore size distribution of mentioned samples.

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. Under 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 isotherm data with the methodology adopted by Pinto *et al.*[47] The results presented in Fig. 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 ranges of pore widths, while carbons Pi-fa/800 and CP do not present pores in the range of 0.8–0.9 nm and 0.9–1.1 nm, respectively. The maximum observed at small pore widths 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.

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 phenomena may occur in the reaction media that result in the opposite behaviors observed.

Searching for an explanation, we considered the study developed by Nematollahi *et al.*,[48] in which it was shown that at pH $\approx$ 5 and under oxidative conditions acetaminophen forms a dimer. This species and 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 present visible-light photochemical activity for example in the case of phenol photooxidation. Merging the information obtained we can assume that at the 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 Fig. S1 of the ESI.† As discussed in detail in the ESI,† 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 Fig. S2 in the ESI†).

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 critical dimension of the dimer in the lowest energy conformation 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 species 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.

In contrast to 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. A possible reasoning is to consider the presence of species with conformations having smaller critical dimensions than the lowest energy conformation, which are 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 a smaller critical dimension 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. The calculus were made using electronic DFT computational methods (see Section 2.4 for details, and Fig. S3 (ESI†) that show the atoms chosen to define the dihedral angle), and the results are displayed in Fig. 4. The conformations computed for each dihedral angle between the two monomers correspond to the energy minima of the molecule with that given dihedral angle, and the energy profile shown in Fig. 4 can thus be regarded as the minimum energy necessary to rotate the two monomers.

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 of around 0.46 nm, and under 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 with an increase of the temperature from 20 up to 40 °C was determined, using the C_v estimated from DFT calculations. Considering an increase of 20 °C and the estimated C_v value, the internal energy associated is only 7 kJ mol^{-1} (see ESI† for details). This energy gain is, however, much lower than the energy barrier corresponding to the formation of the species A ($\approx$70 kJ mol^{-1}), and B ($\approx$ 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 °C in the population distribution of the species presenting different dihedral angles (see details in the ESI,† and results in Fig. S4). The higher increase was observed in the species that correspond to the conformations associated with 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 Fig. 4) have critical

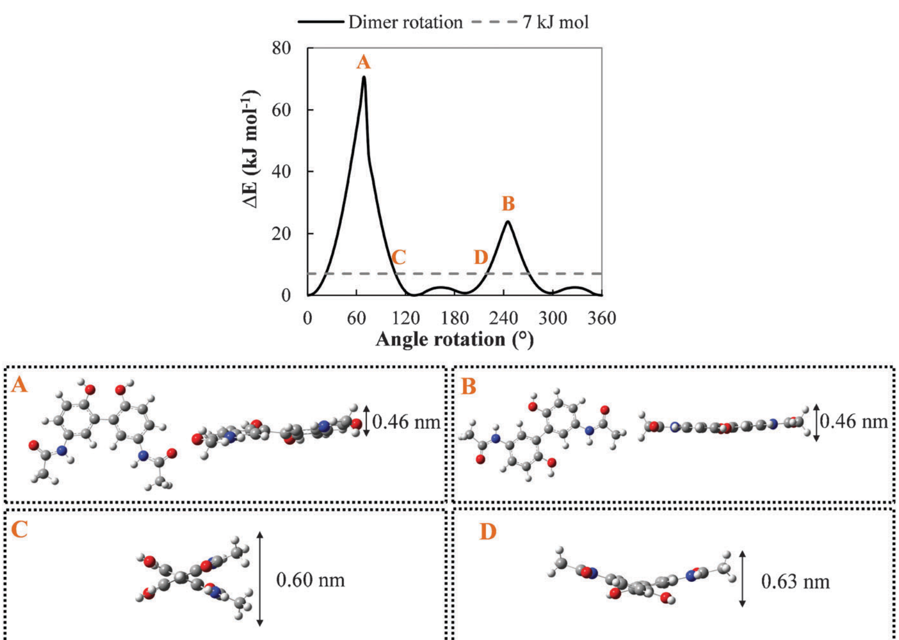

Fig. 4 Energy profile of the different dimer conformation considering the rotation between two monomers, and conformations of the dimer associated to the energy states A, B, C and D (oxygen in red, nitrogen in blue, carbon in gray, and hydrogen in white).

dimensions of 0.60 and 0.63 nm, respectively. These dimensions are still significantly above the maxima of the pore size distributions of the 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 the theoretical results pointing out that no significant decrease of the average critical dimension of dimer is associated with the energy gain resulting from the temperature increase from 20 to 40 °C; the experimental data indicate that a significant number of species with a near planar conformation 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 for the conformational change of the molecules.

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

$$\frac{\mathrm{d}\ln C_e}{\mathrm{d}T} = -\frac{\Delta H_{st,a}}{RT^2} \tag{3}$$

or

$$\Delta H_{st,a} = R\frac{\mathrm{d}\ln C_e}{\mathrm{d}(1/T)}\bigg|_{q_e} \tag{4}$$

For Pi-fa and S based carbons, the equilibrium concentration (C_e, mmol dm^{-3}) at a 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 (Fig. 5) and are presented in Table 4. For the sample CP, $\Delta H_{st,a}$ was not calculated since no temperature dependence was observed.

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.

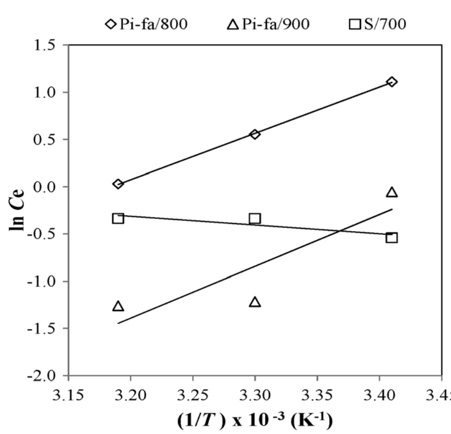

Fig. 5 Adsorption isosters for determining the apparent isosteric heat of acetaminophen adsorption onto the mentioned samples, for surface coverage of 1.32 mmol g^{-1}.

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

Considering the relatively 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 Fig. 4). 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 there is sufficient energy in the system to overcome the energy barrier associated with 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 contradictory to the expected exothermic behavior of adsorption, but in fact indicate that a very complex mechanism is taking place besides the simple adsorption.

It must be noted that the complexity of the overall process 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 enthalpy" and not simply "isosteric enthalpy" that would be associated with a sole 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 Fig. 3). Thus, a very strong interaction between the species in the planar form and the micropore network of sample Pi-fa/900 will be established, 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 a larger volume of narrow micropores, contributing to the increase of the adsorption capacity with temperature. This occurs in the case of the 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 that are identical to that of conformers C and D of the dimer, the tetramer has a critical dimension of 0.66 nm (see Fig. S5 of the ESI†). 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 access narrow micropores in a similar way to that discussed 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 the Pi-fa/800 sample was used. This is most likely due to the fact that the maximum of the micropore size distribution of the 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 the sample Pi-fa/800 is centered at the 0.52 nm, which curiously is the same as the value of the sample S/700. However, the influence of temperature in the acetaminophen adsorption onto these samples follows opposite trends. This result must be related to the fact that, in contrast to the 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 and 0.9 nm, which seems to be the reason for the overall 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 the sample CP show no dependence on 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 the 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 °C) presented a positive effect on 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 kinetic at higher temperature (kinetic effects) because these samples presented slower adsorption rates at higher temperature.

The explanation for the results was centered in the acetaminophen dimer, for which the planar conformations, estimated by electronic DFT methods, are less stable than the 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 the dimer geometry to one planar form, allowing the adsorption process to occur in the narrow micropores of these samples, 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 thermodynamic 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 continuous distribution is not present, the texture becomes the key factor ruling the adsorption. In this case the effect of temperature can be contrary to the expected thermodynamic behaviour because the adsorbent–adsorbate interactions are sufficiently strong to promote the change of the oligomers to a planar conformation, which could not be expected simply from the energy gain associated with the temperature increase from 20 to 40 °C.

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