

REMOVAL OF AN ANALGESIC USING ACTIVATED CARBONS PREPARED FROM URBAN AND INDUSTRIAL RESIDUES

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ABSTRACT

The removal of an analgesic drug (acetaminophen) from water was investigated using activated carbons prepared from different residues, namely urban wastes (post-consumer plastics), and agro-industrial residues (cork powder and peach stones), comparing their adsorption capacity with that of commercially available carbonaceous adsorbents. The prepared carbon samples were evaluated on the basis of their adsorption capacities and kinetic performances, which were linked with their different properties. The samples prepared from chemical activation of the biomass residues show reasonably high removal efficiencies along with fast rate of adsorption, which are in fact comparable to commercial carbons. The analysis of the carbon samples after adsorbing the analgesic showed that adsorbent-adsorbate affinity is stronger in hydrophobic carbons of basic character that contain a well developed microporosity. These characteristics are however not sufficient for an overall performance of a carbon in acetaminophen removal. The carbon must also have a well interconnected pore network (to facilitate the accessibility of acetaminophen molecules, thus speeding up adsorption kinetics) and an adequate chemical composition, which ultimately leads to a high adsorption capacity.

Keywords: Activated carbons; Residues; Analgesic; Adsorption

1. Introduction

Promoting water savings does not seem to be sufficient to meet current worldwide demands for fresh water, and therefore most countries seek new strategies to ensure water availability and a sustainable management of water resources while protecting their quality. Particularly, special attention is being paid to the reutilization of poor quality water, including treated wastewater, as a promising solution to the growing pressure on Europe's water resources [1]. However, wastewater reuse implementation in Europe faces a number of obstacles that include insufficient public acceptance, and the presence of highly toxic emergent pollutants in wastewater.

In this regard, for the last decades the scientific community is becoming increasingly concerned about the potential public health impact of new environmental contaminants originated from consumer products and by products used in industrial, agricultural, and human activities. These emergent pollutants include chemical substances such as human and veterinary pharmaceutical compounds and personal care products (PPCPs), pesticides, household-cleaning chemicals, fragrances, disinfectants, and pathogens among the most representatives. The majority of these substances is continually introduced in the environment at trace level due to their high worldwide consumption; therefore pose a high environmental hazard. Moreover, little is known about the occurrence and long-term effects of these pollutants following their end-use [2].

Pharmaceuticals are compounds with biological activity, developed to promote human health and well being. Nevertheless, since a considerable amount of the dose taken is not absorbed by the body, a variety of these chemicals -including painkillers, tranquilizers, anti-depressants, antibiotics, birth control pills, chemotherapy agents, etc.,- are finding their way into the environment via human and animal excreta from disposal into the sewage system and from landfill leachate that may impact groundwater supplies. Recent studies in Europe and North America have reported the occurrence of PPCPs in wastewater and ambient waters [3,4]. In the case of pharmaceuticals, it was demonstrated that conventional wastewater treatments are not effective to eliminate and/or degrade the majority

of these compounds and they are only partially removed; therefore residual quantities remain in treated water, and have been found to accumulate in drinking water [4,5]. The enormous diversity of chemical composition of these pollutants in waters requires special treatment technologies for water decontamination, in order to improve the quality of water and treated wastewater before promoting its reutilization.

In this sense adsorption is a well-established technique to remove pollutants, being activated carbon (AC) the preferred adsorbent for remediation of water with low pollutant concentration. Activated carbons are known to be very effective adsorbents due to their unique combination of a highly developed porous network coupled with its ability to react with other heteroatoms creating a variety of surface functionalities on its surface and within the structural framework [6,7]. Due to their versatility, ACs have been studied not only as adsorbents, but also as catalysts and catalyst supports, in many different purposes such as the removal of pollutants from gaseous or liquid phases and for the purification or recovery of chemicals [6,7]. Despite such features, the implementation of activated carbons on large scale industrial processes is limited due to a poor economic feasibility associated with its manufacture and regeneration costs [8]. Consequently, activated carbons are often replaced by costly effective adsorbents (sepiolites, diatomites) in many industrial applications, even if their removal efficiency is much lower from that of AC.

The economic cornerstone for the use of activated carbons in advanced water treatments based on adsorption processes can be overcome by exploring new synthetic routes to lower the production costs of activated carbons, or using non expensive materials (such as non valuable by-products or residues) as precursors for their preparation. In this sense, the utilization of residues as precursors of carbon adsorbents is an interesting strategy that enables to deal with the problem of waste disposal and recycling [9-16]. On the other hand, it is well known that that the chemical and textural properties of activated carbons does not depend only on the activation conditions (temperature of carbonization and activation, heating rate, nature and ratio of activating agent, etc.), but also on the

chemical composition of the raw precursor (its intrinsic reactivity), as well as on how those carbons are handled (aging effect) afterwards [7]. Thus, the use of residues for the preparation of AC seems very attractive from the point of view of obtaining low cost adsorbents, but still the choice of the precursor may define their final applicability.

In this work we have explored the synthesis of adsorbents from residues of different nature, comparing the physical and chemical features of the prepared materials upon the nature of the precursor, and assessing the potential application of these adsorbents in water remediation for the removal of an analgesic. We have used several widely produced residues for the preparation of carbon materials: cork powder, an agro-industrial residue from cork processing; peach stones, a lignocellulosic residue from fruit beverage industry; and a municipal waste, poly(ethylene terephthalate) -PET- from used plastic bottles. The objective of this study was to link the characteristics of the prepared adsorbents with the removal efficiency of the target compound. Our interest was to identify the best adsorbent, not only on the basis of the cost of the activated carbon but also on its adsorption capacity. As probe molecule, we have selected acetaminophen which is also known as paracetamol, and is one of the most worldwide consumed analgesics.

2. Methods

2.1. Adsorbents

Several activated carbons have been prepared from various residues, namely cork powder, peach stones and PET for the adsorption of acetaminophen from aqueous phase. Further details about the experimental procedures for the preparation of the activated carbons from cork powder and PET residues have been previously reported [17,18]. Peach stones based material was obtained following the same experimental procedure used to activate cork powder. Briefly, the biomass residues (particle size fraction < 0.297 mm) were submitted to a chemical activation with K_2CO_3 (weight ratio 1:1) at 700 °C for 1 hour. After carbonization, the samples were washed up to neutral pH and

dried at 100 °C. Sample CC was prepared using cork powder waste as raw material, and the activation corresponds to 88 % of burn-off degree; sample CP was prepared from peach stones previously grounded, and the activation corresponds to a burn off degree of 85 %. The carbon derived from plastic waste, labeled as PP, was obtained from physical activation of PET waste at 925 °C under CO₂ atmosphere up to a burn-off degree of 30 %. Two commercial activated carbons commonly used in water treatment and obtained from physical activation of coal -B- and wood -NS- were selected for comparison purposes. Both materials were selected due to their differences in porosity and surface chemistry.

2.2. Nanotextural and chemical characterization of the carbon samples

Nanotexture of the carbon materials was characterized by N₂ and CO₂ adsorption at -196 and 0 °C, respectively, in conventional volumetric apparatus (ASAP 2000 and Tristar 3000, from Micromeritics). Before each experiment, the samples were outgassed under vacuum at 120 °C for overnight. The isotherms were used to calculate the specific surface area, S_{BET} , total pore volume, V_{TOTAL} , and pore size distribution. The pore size distributions (PSD) were evaluated using the density functional theory (DFT), assuming slit-shape pore geometry. Additionally, the volumes and distribution of pores smaller than 0.7 nm (ultramicropores) were assessed from CO₂ adsorption isotherms at 0 °C with DR and DRS formulisms, respectively. The samples were further characterized by the determination of the pH at the point of zero charge (pH_{PZC}) and thermal analysis. The pH_{PZC} was estimated using a modification of the mass titration procedure by Noh and Schwarz [19]. Details of the procedure have been reported elsewhere [20]. The thermal analysis (Setaram Labsys) was carried out under a flow rate of 50 cm³ min⁻¹ of nitrogen, with a heating rate of 15 °C min⁻¹ and ca. 20 mg of sample. In order to investigate the adsorption interactions between the adsorbents and adsorbate molecules, the thermal analysis was also carried out after acetaminophen exposure.

2.3. Adsorption from solution

Acetaminophen, also known as paracetamol, (N-(4-hydroxyphenyl)ethanamide, $C_8H_9NO_2$) was supplied by Aldrich (Lot. 535764-326, purity 98%). All the solutions were prepared with ultra-pure water obtained from Milli-Q water purification systems. The solutions were used as prepared, that is, without pH adjustment, presenting values around 5.8 units.

To study the adsorption kinetics, 15 cm^3 of acetaminophen solution (initial concentration 120 $mg\ dm^{-3}$) were mixed with ca. 10 mg of activated carbon in glass vials and continuously stirred (700 rpm) at a controlled temperature of 30 °C in a water bath. The time recording was started when the stirring began and several samples were collected between 5 min and 24 h. All adsorption assays were made in triplicate. After filtration, the residual concentration of acetaminophen remaining on the solution was analyzed in a UV-vis spectrophotometer (Shimadzu UV-1603) at 243 nm. The amount adsorbed was determined according to Eq. (1)

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

where q_t is the amount ($mg\ g^{-1}$) adsorbed at time t , C_0 is the initial concentration ($mg\ dm^{-3}$), C_t is the concentration at time t ($mg\ dm^{-3}$), V is the volume (dm^3) of the adsorbate solution and W is the weight (g) of dried carbon.

Equilibrium adsorption studies were made at 30 °C varying the adsorbent dose (5-10 mg), the solution volumes (15, 30 cm^3) and the acetaminophen solution concentration (20-180 $mg\ dm^{-3}$). The acetaminophen remaining in solution (C_e) was assessed as described above and the uptake (q_e) was calculated using Eq. 1. The time needed to reach equilibrium was chosen based on the kinetic studies of each material.

3. Results and Discussion

The aim of this work was to investigate the feasibility of an adsorption process using activated carbons for the removal of a common analgesic frequently found in wastewater and treated water from urban sewage facilities. For this reason, we have selected two commercially available activated carbons -prepared from different precursors and therefore exhibiting varied porous features and chemical composition- and a series of activated carbons in-house prepared from various residues. Details of the preparation of the cork and PET wastes derived activated carbons, as well as the optimization of various synthesis conditions and their effect on the properties of prepared materials have been deeply discussed in previous studies [17,18] so would remain out of the scope of this paper. Nevertheless, their characteristics are herein showed for data interpretation purposes.

3.1. Acetaminophen removal from solution

Figure 1 shows the evolution of acetaminophen (ACE) concentration with time for the studied activated carbons, and the results show large differences in the performance of the adsorbents. The removal efficiency (RE) was calculated after 6 hours according to the equation: $RE = [(C_0 - C_e)/C_0] \times 100$, where C_0 and C_e are the initial and equilibrium acetaminophen concentrations, respectively; values are quoted in Table 1. The values obtained follow the trend: $PP \ll B < CP < CC < NS$. The largest value is attained for one of the commercial carbon NS, whereas the adsorbents prepared from biomass residues (samples CP and CC) display RE values higher than those of carbon B after 6 hours. Notwithstanding for carbon B the equilibrium was attained after 24 hours (concentration decays curve slightly decreased after 6 hours), but still the calculated RE value after equilibrium was smaller than that of samples CP and CC. Large differences are also observed in the rate of adsorption of the studied carbons at short times (early adsorption stage), where the

biomass-derived activated carbons outperform the commercial B sample, although NS displays the fastest ACE uptake.

Figure 1 and Table 1

To better comprehend and analyze these differences, the kinetic data were fitted to various kinetics models. In all cases the experimental data was best fitted by a pseudo-second-order kinetics [21], with correlation coefficients higher than 0.99 with the exception of PP sample ($r^2 = 0.989$). Concerning the pseudo-second order rate constant, k_2 , the values quoted in Table 1 increase in the order: PP<B<<CP <<CC<<NS. The largest value is obtained for NS carbon, so not only the largest uptake but also the fastest adsorption rate is obtained with this material. Among other materials sample CC shows a relatively high k_2 value, twice higher than that of sample CP despite both materials have similar adsorption uptakes at equilibrium conditions. The sample obtained from physical activation of a plastic waste (carbon PP) showed the smallest rate constant and RE value. The same trends were obtained for h (initial adsorption rate) and $t_{1/2}$ (half-life time) parameters confirming the faster adsorption rate in the commercial NS carbon, followed by the carbon prepared from cork powder residues.

The experimental adsorption isotherms for ACE on the studied carbons are illustrated on Figure 2. Equilibrium was reached within 6 hours for all the carbons, with the exception of carbon B where 24 hours were needed. The shape of the ACE adsorption isotherms indicates that all of them are L type in the Giles classification [22]. The isotherms display a concavity towards the abscissa axis in all cases, indicating that as more sites in the substrate are filled, it becomes more difficult for a fresh solute molecule to find a vacant site. This implies that there is no strong competition of the solvent for the adsorption sites. At high equilibrium concentration of ACE in solution, the amount adsorbed steadily increased and the adsorption isotherms display a plateau indicating the formation of a complete monolayer.

The experimental adsorption isotherms were fitted to the classic Langmuir [23] and Freundlich models [24] (non-linear forms of the equations are displayed in Table 2). Both equations allow the adsorption capacity of the carbons to be evaluated (q_m and K_F), as well as estimating the adsorbate affinity for the adsorbent (parameters b and $1/n$). Table 2 provides a compilation of the main parameters obtained from the fittings to both equations, along with the correlation coefficients and χ^2 values [25]. The excellent goodness of the fit obtained with the Langmuir equation compared to Freundlich model indicate that the former is suitable for application for the systems studied. These results were further confirmed by the non-linear chi-square test analysis of the data, with smaller χ^2 values obtained for the fitting with the Langmuir equations (Table 2). It can be seen that the highest uptake was obtained for NS carbon (which also displayed the fastest adsorption rate); the materials prepared from lignocellulosic precursors displayed values of the monolayer adsorption capacity (q_m) larger than that of PP sample; however, at equilibrium conditions carbon B showed a slightly higher adsorption capacity than that of CC and CP samples. Since the trend observed after 6 hours of contact was just the opposite, this corroborates the slow kinetics of the commercial carbon B (Table 1). Moreover, CC sample has the highest adsorption affinity (b values) to ACE molecules, according to data quoted in Table 2. In contrast, and despite being the carbon displaying the highest adsorption capacity, NS shows much less affinity for ACE (ca. b value is twice smaller) than CC carbon.

Figure 2 and Table 2

To understand these findings, we have analyzed how the experimental adsorption conditions such as solution pH affect the nature of the activated carbon and the adsorbate. It is well-known that this parameter affects the ionization state of weak electrolyte (this is the case of acetaminophen, which $pK_a \sim 9$) and the charges that may appear on the carbon surface. In this work, all the studied carbons display a basic pH_{PZC} (Table 3); on the other hand, diluted solutions of ACE have a pH value

around 5.8 units. Under these conditions ACE is predominantly in its molecular form (the anionic form accounts for less than 0.1 mol %) whereas the carbons surface sites are either neutral or positively charged ($\text{pH}_{\text{PZC}} > \text{solution pH}$ in all the carbons). Consequently, there should be no specific repulsive or attractive electrostatic interactions between the adsorbate and the activated carbons surface that might favor/hinder the ACE uptake. On the contrary, due to their basic nature all the adsorbents should go through similar adsorption mechanisms, as a result of dispersive interactions between the carbon surfaces and ACE molecules. From these findings it is interesting to remark here that from a chemical point of view, the residue-derived carbons seem to be adequate for the uptake of acetaminophen due to their intrinsic basicity, which is linked to the nature of the carbon precursor.

In the case of the carbon obtained from plastic waste (PP) and the commercial carbons NS and B, their low oxygen content indicates that the basicity is associated to the delocalized π electron density of the graphene layers which is in fact, capable of acting as Lewis base sites adsorbing protons [6]. The biomass-derived carbons (CC and CP carbons prepared from cork powder and peach stones, respectively) are characterized by a high amount of oxygen functionalities and most of them are of basic nature as inferred from the pH_{PZC} values. This suggests the presence of pyrone and/or chromene-like type structures as responsible for the basicity of these carbons. Such combination of unusual chemical features has already been reported in activated carbons synthesized from precursors containing ester, furanic and/or phenolic functionalities a structural units [12, 26-28], where the oxygen atoms are inserted within the carbonaceous matrix during thermochemical transformation of the precursor during the synthesis, creating ether and chromene-like structures (Lewis basic sites).

Moreover, any competitive effect due to adsorption of water molecules on the adsorbents can be disregarded [29], in the view of the hydrophobic character of the studied activated carbons. Hence the differences in ACE uptake and rate of adsorption have to be explained in terms of the variability

of the textural properties of these activated carbons, which is somehow linked to the preparation method and precursor's nature.

As abovementioned, considering the basic nature of all the adsorbents, a similar adsorption mechanism is expected for ACE retention, being dispersive forces the dominant interactions. However, the oxygen content also affects the hydrophobic/hydrophilic nature of the adsorbents. In fact, the carbons synthesized from lignocellulosic precursors have large amounts of oxygen that render them an important hydrophilic character. Thus, it seems reasonable to expect that the wettability of these carbons is favoured in aqueous solutions, compared to samples B and PP which are strongly hydrophobic (low oxygen content). This favors the adsorption rate which seems reasonable for a compound with rather high water solubility (14 mg cm^{-3}) which affinity towards the carbon phase would be determined by the accessibility of the aqueous solution to the adsorption sites (inner porosity).

3.2. Textural characterization of the activated carbons

As mentioned above, a detailed analysis about the effect of the synthesis conditions during the carbonization and activation of some studied precursors (i.e., plastic waste and cork powder) on the porosity of the corresponding activated carbons has been previously reported and remains out of the scope of this paper. Here we merely report the textural characterization of selected synthesized carbons for data interpretation [17,18]. The main textural parameters of the series of studied carbons obtained from gas adsorption, and the N_2 adsorption isotherms are shown in Table 3 and Figure 3, respectively.

Figure 3 and Table 3

The studied activated carbons present very different porous features; the nitrogen adsorption isotherm of carbon NS is characterized by a wide knee at low relative pressures, as well as a gradually upward increase at relative pressures above 0.2, as opposed to the horizontal plateau

shown by samples PP, CP and CC. This is indicative of the presence of a well-developed mesoporosity in NS carbon, along with a large microporosity. The analysis of the PSD by the DFT method is in good agreement with the experimental data. The volume of mesopores is most remarkable for the commercial carbons NS and B, whereas it only accounts for less than 7 % in the waste-derived carbons. In contrast, these adsorbents possess highly microporous structures, confirmed by the type I nitrogen adsorption isotherms. Along with its large mesopore volume, carbon NS also presents a high volume of micropores. The CO₂ adsorption isotherms were used to evaluate the so-called ultramicroporosity (pore width < 0.7 nm); the pore volumes obtained from DR formulism indicate that all studied carbons have a large contribution of micropores of small sizes, particularly the carbons obtained from chemical activation of biomass wastes (CC and CP samples) show the highest values. This contrasts with the microporosity determined by N₂ adsorption, where the sample prepared from the plastic waste (PP) showed the highest value, indicating the presence of micropores of wider sizes. This finding was further confirmed by applying the DRS method to the CO₂ adsorption isotherms to evaluate the distribution of micropore sizes (Figure 4). It can be seen that carbons CC and CP (biomass derived) display identical narrow and sharp distributions centered at 0.74 nm. Thus, the narrow microporosity of these two carbons is alike, and only minor differences are observed in the pores of wider sizes (determined by N₂ adsorption). This is in good agreement with the experimental burn-off degree obtained for both materials. At converse, PP, NS and B carbons -the last two also displaying similar profiles- show the broad micropore size distributions characteristic of most activated carbons.

Figure 4

It is interesting to remark that, regardless the carbon precursor there are close similarities in the porosity of adsorbents prepared from the same activation procedures; chemical activation leads to carbons with network of narrow micropores whereas physical activation seems to enlarge the dimensions of the micropores. Moreover, carbons CC and CP showed rather similar overall textural

properties. This observation demonstrates that for carbon precursors with close reactivities (biomass derived precursors), the porosity development is more strongly related to the activation procedure than to the chemistry of the precursor which in fact define the chemical composition of the resulting activated material.

The studied carbons are characterized by high apparent surface areas, with values between 850-1200 m² g⁻¹; however neither the ACE uptake nor the rate of adsorption show a linear correlation with the apparent surface area or micropore volume. For instance, the lowest retention was attained in PP carbon, with a S_{BET} value very close to that of NS which displayed the highest ACE adsorption capacity. Moreover, carbon PP displaying the highest micropore volume shows the lowest removal efficiency, indicating that the microporosity is not the only important parameter ruling this adsorption process: although the adsorption of ACE is expected to take place primarily in micropores, it may be limited by the accessibility to the inner porosity since the overall uptake is largely reduced in carbons that lack from an adequate network of mesopores connecting the micropores.

To further understand the differences in the retention of the studied carbons, a thermal analysis was also carried out before and after exposure of the carbons to the ACE solution (Figure 5). The peak around 100 °C is due to the moisture of the carbons; in the case of as-received CP and CC carbons, the profiles both before and after adsorption show two humps -centered at about 300 °C and 600 °C-, which are attributed to their surface functionalities. This is in good agreement with their large oxygen content (Table 3). The profiles of the carbons after ACE exposure show one peak centered at about 400°C attributed to the desorption of the analgesic. What is interestingly observed is that all the profiles display similar shapes regardless the chemical nature of the activated carbons. There is only a small difference (a few tens of degrees) concerning the maximum of ACE desorption peak; it is located at 380 °C for CC and CP carbons, and above 400 °C for NS, B and PP carbons (i.e., 400, 402 and 415 °C, respectively). The lower temperature of the peak in the biomass derived carbons

suggests slightly weaker interactions between the ACE molecules and the adsorbents, which could be due to either their chemical nature or porous features. It should also be pointed out that the highest desorption temperature is attained in PP carbon, with the lowest ACE removal efficiency (Table 1).

Figure 5

A close look to the distribution of micropore sizes in Figure 4 throws some light to this issue. As opposed to expectations, the lowest temperatures of the ACE desorption peak are attained in the carbons with the largest volumes of ultramicropores, where the microporosity is composed of pores of narrower dimensions (i.e., CC and CP). According to its molecular formula acetaminophen is not expected to have large dimensions, so it would be reasonable to expect stronger interactions in the carbon exhibiting pores of smaller dimensions. Based on this, the highest desorption temperatures obtained in the TG profiles of the samples after ACE exposure should correspond to CC and CP carbons, which does not match with the experimental observations. Again, it appears that microporosity is not the only factor to be considered, but chemical features (composition and hydrophobicity) must also be taken into consideration. In fact, all the studied carbons present a basic character, but the highest desorption temperature is obtained in the material with lowest oxygen content (i.e., PP carbon). Thus, it seems that the presence of oxygen decreases the strength of the ACE adsorption, regardless the overall basicity of the activated carbons.

4. Conclusions

The potentialities of activated carbons obtained from various wastes for the removal of acetaminophen were investigated and compared with commercial carbons. The characterization of the materials revealed that the adsorption of ACE is a complex process that depends strongly on the

characteristics of the adsorbent (in terms of porosity and chemical composition). Indeed, even when dispersive interactions between the adsorbate and the adsorbent are dominant, a large micropore volume -traditionally regarded as a key factor for optimum removal efficiencies in activated carbons- does not guarantee a good performance of the adsorbent. This is the case of PP sample, that despite displaying the most adequate microporous structure and the highest affinity towards the ACE molecules -revealed by the TG desorption profiles-, possesses the lowest removal efficiency as well as a slow adsorption kinetic. In contrast, chemical activation of biomass residues produced adsorbents that couple a large micro and mesoporosity development and an adequate chemical composition (large amounts of oxygen rendering a hydrophilic carbon of basic nature). These characteristics render adsorbents combining fast ACE removal and large adsorption capacities. For instance, the adsorbent prepared from chemical activation of cork residues presented a large ACE uptake and relatively fast adsorption kinetics, comparable to performance of commercial adsorbents.

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Figure 1. Kinetic results of acetaminophen adsorption at 30 °C. ($[ACE] = 120 \text{ mg dm}^{-3}$, activated carbon dose $10 \text{ mg} / 15 \text{ cm}^3$ of solution). Dotted lines are a guide to the eye for clarity.

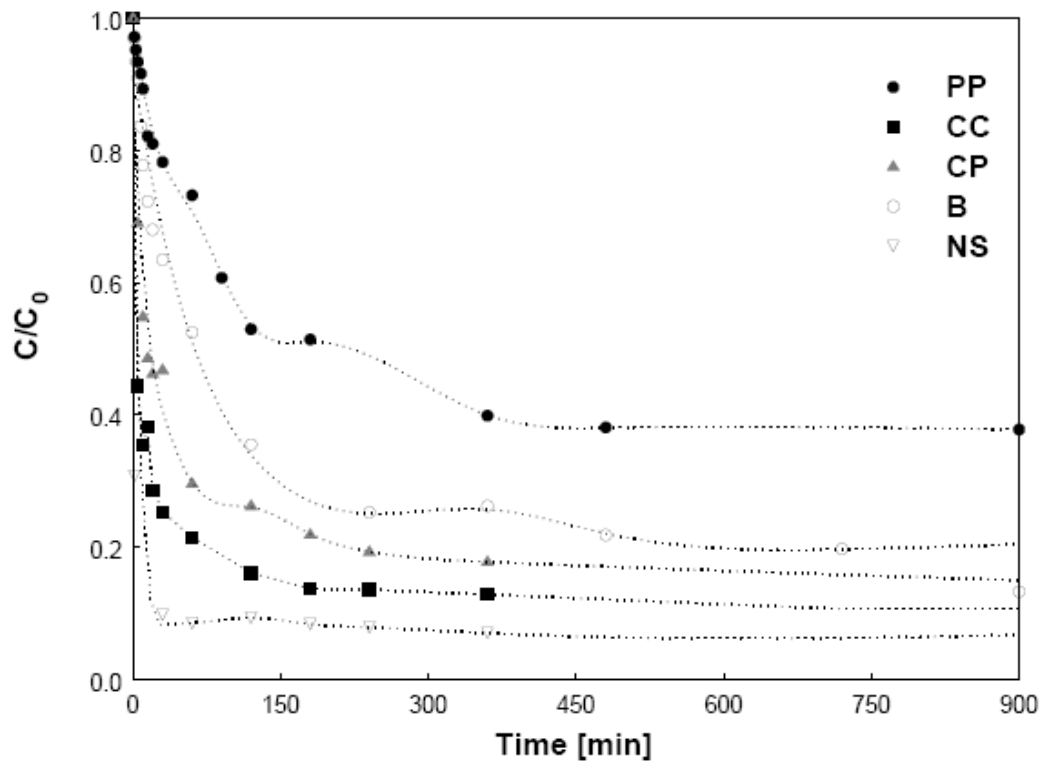


Figure 2. Equilibrium adsorption isotherms of acetaminophen on the investigated carbons at 30 °C. Symbols correspond to experimental data, and dotted lines to the fitting to the Langmuir equation.

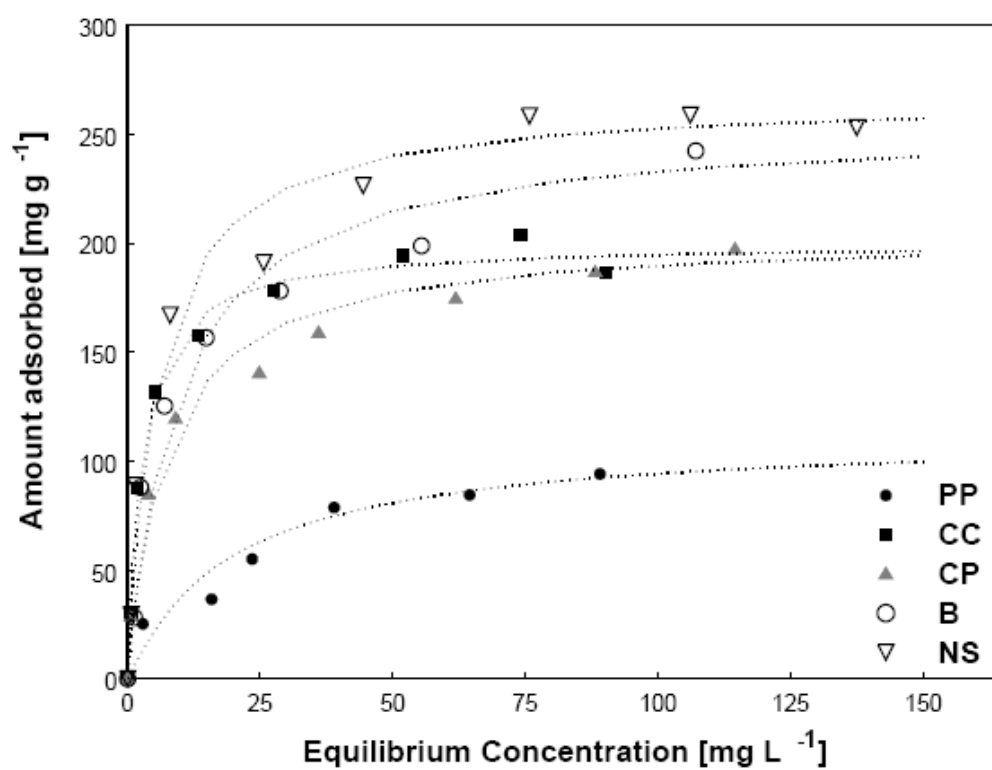


Figure 3. Nitrogen adsorption isotherms at -196 °C of the studied activated carbons.

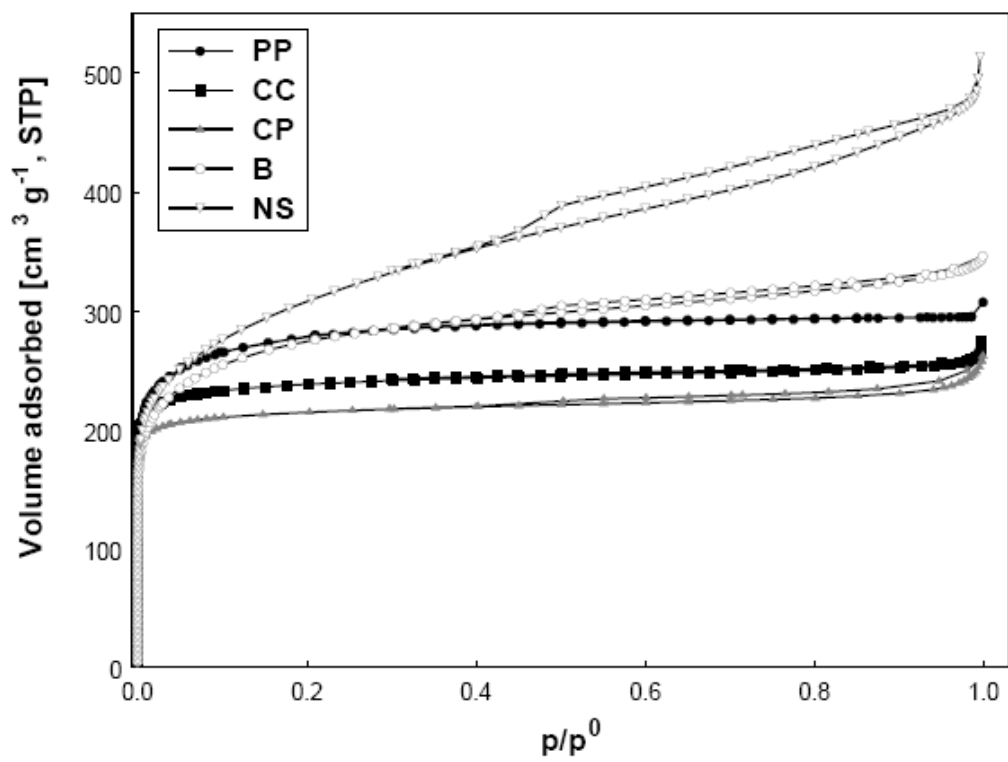


Figure 4. Micropore size distribution of studied carbons, obtained by the DRS method applied to the CO₂ adsorption isotherms at 0 °C.

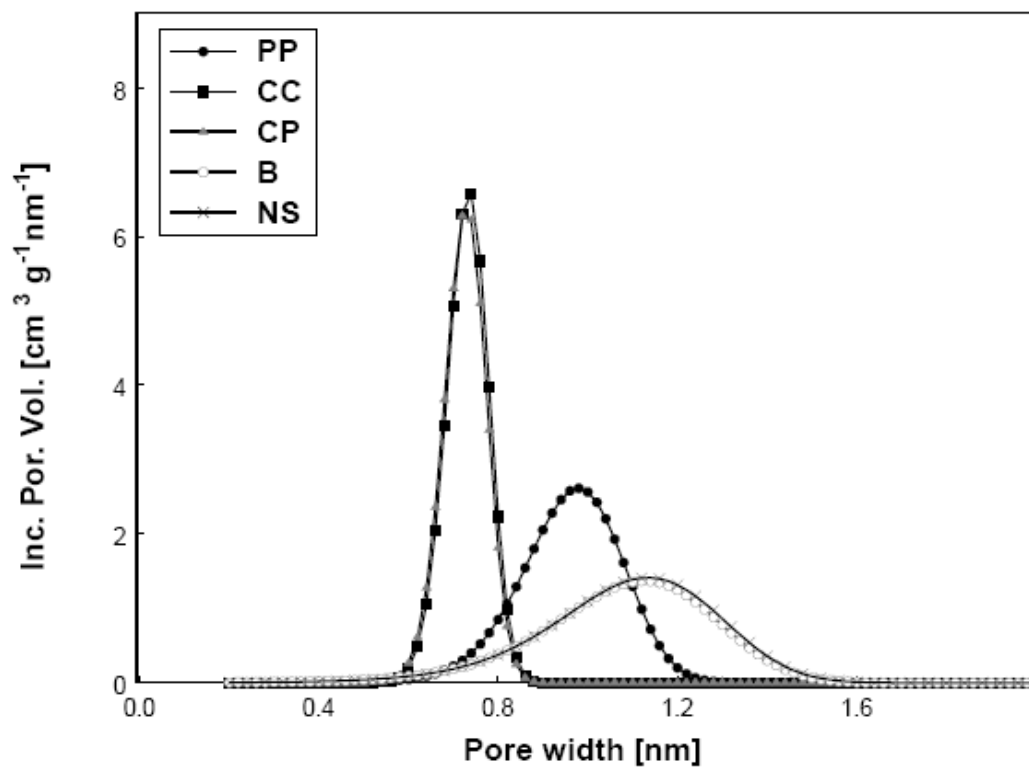
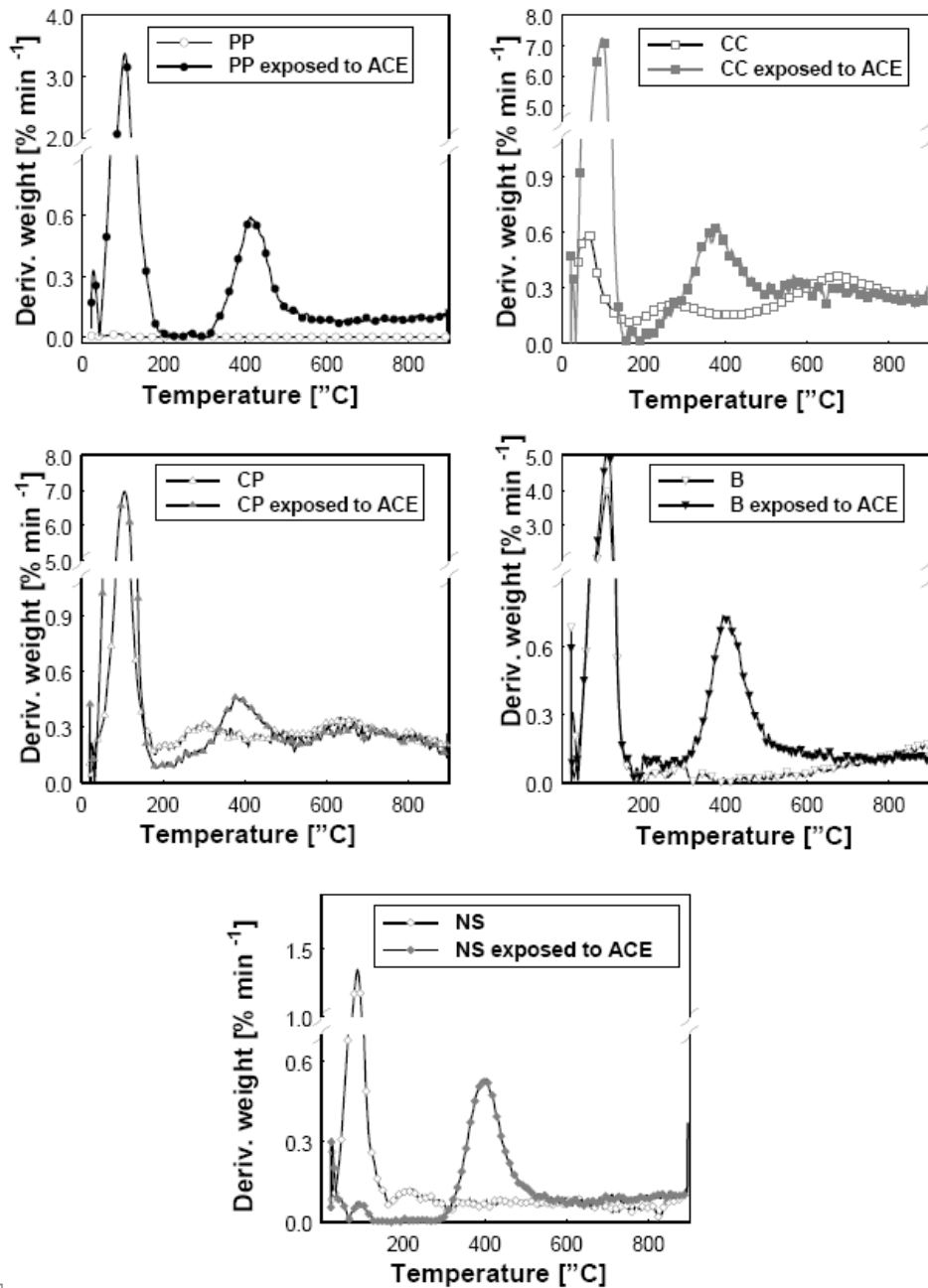


Figure 5. Thermal analysis of A) as-received carbons and B) after acetaminophen exposure from aqueous solutions.



□

Table 1. Pseudo-second order acetaminophen adsorption parameters for the studied carbons: k_2 is the pseudo-second order rate constant; h is the initial adsorption rate; $t_{1/2}$ is the half-life time; $q_{e,calc}$ and $C_{e,calc}$, are respectively, the acetaminophen uptake and that remaining in solution at equilibrium both calculated by the pseudo-second order kinetic model, and RE is the removal efficiency.

Pseudo-second order model						
	$k_2 \times 10^4$ ($\text{g mg}^{-1} \text{min}^{-1}$)	r^2	h ($\text{mg g}^{-1} \text{min}^{-1}$)	$t_{1/2}$ (min)	$q_{e, calc}$ (mg g^{-1})	RE (%)
B	2.7	0.997	5.1	27	137	74
NS	17.6	0.998	52.7	3.3	173	97
PP	1.9	0.989	2.5	46	117	60
CC	14.7	0.999	36.9	4	159	87
CP	6.7	0.999	15.2	10	150	82

$$RE = \frac{(C_0 - C_e)}{C_0} \times 100$$

Table 2. Fitting parameters of the equilibrium adsorption isotherms to the Langmuir and Freundlich models and chi-square test analysis, χ^2 .

	Langmuir equation				Freundlich equation			
	q_m (mg g ⁻¹)	b (dm ³ mg ⁻¹)	r^2	χ^{2*}	$1/n$	K_F (mg ^{1-1/n} (dm ³) ^{1/n} g ⁻¹)	r^2	χ^{2*}
B	255	0.108	0.990	5.76	0.408	43.3	0.823	34.30
NS	267	0.181	0.997	5.30	0.350	56.4	0.862	46.97
CC	200	0.360	0.996	2.14	0.325	55.7	0.830	41.65
CP	204	0.136	0.995	6.02	0.345	43.9	0.934	16.44
PP	113	0.050	0.949	3.76	0.408	15.4	0.929	4.43

* $\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}}$ where q_e is the experimental equilibrium uptake and $q_{e,m}$ is the equilibrium uptake

calculated from the model [25].

Langmuir equation: $q_e = \frac{q_m b C_e}{1 + b C_e}$

Freundlich equation: $q_e = k_F C_e^{1/n}$

Table 3. Nanotextural and chemical characteristics of the waste-derived carbons and selected commercial adsorbents.

	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	$V_{\text{TOTAL}}^{\text{a}}$ ($\text{cm}^3 \text{g}^{-1}$)	$V_{\text{micro}}^{\text{b}}$ ($\text{cm}^3 \text{g}^{-1}$)	$V_{\text{meso}}^{\text{b}}$ ($\text{cm}^3 \text{g}^{-1}$)	$W_{\text{CO}_2}^{\text{c}}$ ($\text{cm}^3 \text{g}^{-1}$)	Ash (wt. %)	O (wt. %)	pH _{pzc}
B	1033	0.524	0.316	0.089	0.190	11.4	2.0	9.2
NS	1120	0.742	0.301	0.265	0.205	13	3.6	9.0
PP	1071	0.463	0.350	0.032	0.310	<1	<1	10.7
CC	891	0.420	0.308	0.007	0.381	4.1	9.8	7.5
CP	866	0.385	0.279	0.010	0.371	13	9.8	9.0

^a evaluated at relative pressure = 0.95 in the N₂ adsorption isotherms at -196 °C.

^b evaluated from the DFT method applied to the N₂ adsorption isotherms at -196 °C.

^c evaluated from the DR method applied to the CO₂ adsorption isotherms at 0 °C.