

Aplicaciones de adsorbentes y catalizadores en procesos medioambientales y energéticos

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CAPÍTULO VII

Adsorption of organic compounds in aqueous solution with activated carbons

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1. Introduction

None of us can imagine how our daily life would be without a great number of personal care products or living without medicines that, fortunately nowadays can help to overcome from a simple headache to most severe diseases. Despite the unquestionable benefits of all of these products to the human health and wellbeing, in other situations, their ubiquitous use leads to undesirable problems, as for example, those related with water pollution.

Since the pioneer study of Stummm-Zollinger & Fair (1965) reporting the presence of steroids hormones in effluents of wastewater treatment plants, and especially after the detection of clofibric acid (metabolite of clorofibrate, the active ingredient of blood lipid regulators) in 64 drinking water samples collected in Berlin, in 1994 (Stan et al., 1994), the scientific community and the governmental entities started to consider this type of compounds as a threat for the environment and public health.

At present, pharmaceutical compounds are considered emergent pollutants and a great number of monitoring studies have been performed to assess their presence in the aquatic environment (Rivera-Utrilla et al., 2013; Rodriguez-

Mozaz et al., 2015). Although being detected at trace level (e.g. in the order of ng L^{-1} - mg L^{-1}) the potential noxious effect of these compounds have been demonstrated, drawing the attention of the authorities for this issue. In this sense, the report of the European Parliament and the Council for the Review of Annex X of the Directive 2000/60/EC on priority substances in the field of water policy (2012) included three pharmaceutical compounds (diclofenac, 17-beta-estradiol, 17-alfa-ethinylestradiol) in the watching list, being this a first step for a future regulation. The European Medicine Agency also expressed its concern about this problematic, recommending a 100 ng L^{-1} limit for all types of pharmaceuticals in surface water (Ternes & Joss, 2006).

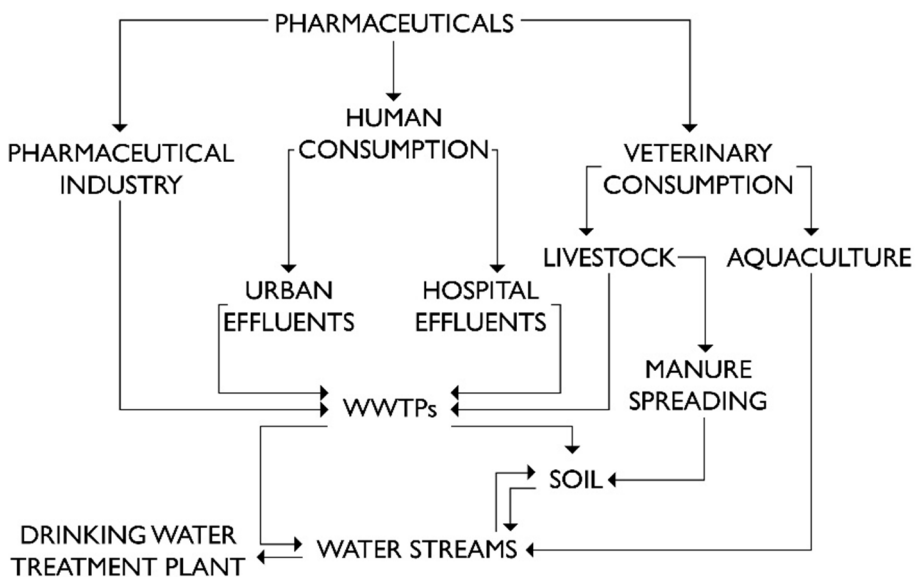


Fig. 1. Main routes of water streams pollution by pharmaceutical compounds and their metabolites.

The simplified scheme reproduced in Fig. 1 presents the main pathways by which pharmaceuticals enter in the aquatic environment due to the lack of effectiveness of the current wastewater treatment plants (WWTPs) to degrade these compounds.

Unlike PPCPs, pesticides have long been recognized as environmental and public health problems, being their limits and uses strictly regulated (Council Directive 80/68/EEC, 1979; European Parliament and the Council Directive 2000/60/EC, 2000). However despite all the efforts to control the amount of pesticides that are used for the continuous increase of crops yields, the fact is that these nasty compounds leach out from the soil reaching the surface and groundwater bodies. The recently published work by the group of Damià Barceló (Alonso et al., 2015) is an illustrative example of how pesticides are, as the authors mention, a "toxic heritage". The study was focused on pyrethroids, a class of insecticides for which carcinogenic, neurotoxic, immunosuppressive, and allergenic effects, as well as reproductive potential toxicity in mammals, were already suggested from the results of various studies (Jin et al., 2012; Scollon et al., 2011; Shafer et al., 2008). This particular class of insecticides are worldwide detected in surface water in concentrations in the order of ng L^{-1} (Amweg et al., 2006; Feo et al., 2010), and due to their hydrophobicity they can be easily absorbed and accumulated in animal tissues. The aim of the study developed by Alonso et al. (2015) was to go a step further, proving that mother dolphins transferred pyrethroids to their fetus through placenta. The analysis of the tissue samples of mother-fetus pair from wild dolphins from the Brazilian coast revealed that higher concentrations of pyrethroids were detected in the fetuses than in their respective mothers.

The effective removal of a large number of compounds with very different chemical nature is actually a great challenge to

water treatment plants (either wastewater or drinking water facilities), that can only be overcome through finding new solutions, which ideally must be easily implemented in the existing facilities. To fulfil this goal, the contribution of the scientific community is of paramount importance in various levels, namely in developing new materials or elucidating the mechanism of the process occurring in different stages of the WWTPs, thus allowing its further optimization.

WWTPs can involve up to three consecutive steps, as listed in Table 1. Unlike primary and secondary stages, tertiary treatment is not universally implemented although it would allow a more efficient degradation of recalcitrant pollutants, that is, compounds that fail to be degraded by the biological process. The effectiveness of some of the advanced processes to be implemented as a tertiary step are well documented in the literature, as is the case of photocatalysis using semiconductors like TiO_2 (Miranda-García et al., 2011, Wang et al., 2012). However, there are also studies pointing out that some of the processes occurring in the tertiary treatment can lead to the formation of even more noxious compounds than the pristine molecule. For example, chlorination with ClO_2 is effective to oxidize sulphonamides, macrolide-derived antibiotics, and estrogens (Huber et al., 2005), but in the case of functionalized drugs (e.g. acetaminophen), undesirable oxidation products might be obtained (Pinkston & Sedlak., 2004).

As specified in Table 1, adsorption onto activated carbons is one of the end-of-pipe technologies, and has the advantage of being easily implemented, allowing the removal of a great number of micropollutants (Li et al., 2011). When highly polluted influents arrive at WWTPs activated carbons are also employed in early steps of the wastewater treatment process, aiming the preservation of the microorganisms operating in the secondary treatment.

	Process	Effluent quality
Primary or pre-treatment	Sedimentation and primary clarifiers Screening out coarse solids and other floating materials Skim off oil, grease and fat	Not applied
Secondary or biological	Microorganisms remove biodegradable soluble organic substances Clarification	Suitable for discharge into surface waters, restricted irrigation and some industrial applications
Tertiary	Disinfection with UV radiation, ozone or chloride and/or advanced water treatment technologies (i.e. activated carbons adsorption and advanced oxidation processes)	May be sufficiently clean to become a reclaimed water source which may be reused as groundwater for irrigation purposes (i.e. agricultural, golf course, green way or park)

Table 1. Treatment processes made in each step of municipal wastewater treatment plants.

Among the available technologies, the use of granular activated carbon columns is one of the most used in the tertiary treatment. Furthermore, the application of activated carbons in hybrid technologies is becoming increasingly explored. Actually, it was already demonstrated that the addition of powdered activated carbon to the ultrafiltration membrane module of a membrane bioreactor allowed to achieve high removal percentages of erythromycin and carbamazepine, both hydrophilic and resistant to biological degradation medicines (Nguyen et al., 2012)

In drinking water treatment plants, the technologies based on adsorption onto activated carbons are present in

various stages of the process, allowing the adsorption of unwanted compounds onto the carbons and consequently decrease their concentration to values below the analytical quantification limits. An illustrative example of the advantage of the use of activated carbon filtration is the study developed by Kim et al. (2007) in a drinking water plant of Seoul, where the drastic reduction of ibuprofen concentrations of the 15 ng L⁻¹ concentration detected in the influent to quantification limits has proved to be linked to the use of granular activated carbon filtration.

2. Activated carbons

Activated carbons are the preferred adsorbents for the adsorption processes implemented in WWTPs since these materials combine a highly developed porous network (specific surface areas and pore volumes) with the presence of surface functionalities resulting from the presence of heteroatoms, i.e., atoms other than carbon (Bandosz & Ania, 2006; Marsh & Rodríguez-Reinoso, 2006). The pore network of these materials is, in general, constituted by a large percentage of micropores ($\phi < 2$ nm (Thommes et al., 2015)) that are known to be active sites for the adsorption of most organic pollutants. The presence of a mesopore network is important to allow the diffusion of the organic molecules towards the inner structure of the adsorbents. For this reason, mesopores ($2 \text{ nm} < \phi < 50 \text{ nm}$) are also known as transport pores.

Another advantage of activated carbons is their versatility of forms, shapes and structures. In the case of water remediation technologies the most used forms are powder (PAC) and granular (GAC) activated carbons, but monoliths, fibers and cloths are also important forms to be applied, namely, in gas adsorption processes.

Activated carbons can be prepared from a large number of precursors that must present several characteristics. First of all, they must have a high carbon content and low amount of inorganic matter. Simultaneously the precursor must be available in large quantities and be the cheapest possible due to the low yield of the activation procedure, that is why commercial activated carbons are produced mainly from coal (see for example the website of Cabot-Norit: <http://www.cabotcorp.com/solutions/products-plus/activated-carbon>). The other widely used precursor is coconut husk, since it allows the preparation of high density carbons, as it is for example the case of the granular carbon GCN 830 commercialized by Cabot-Norit. According to the datasheet available on <http://www.cabotcorp.com/solutions/products-plus/activated-carbon/granulated>, this material has an apparent density of 510 kg m^{-3} . Along with the specific surface area, density must also to be considered when selecting a carbon to be applied in a large scale process.

Besides the two raw materials mentioned above, a considerable number of studies in the literature report the use of industrial and agricultural biomass residues as precursors of activated carbons. The main goal of these studies is to transform a renewable biomass, which in most of the cases is an industrial waste problem, into a product that can be applied, for example, in environmental remediation processes. Some of the wastes that have been transformed into activated carbons with similar, or even better, properties and performances for liquid phase adsorption that those obtained with commercial carbons are: olive stones (Rodríguez-Valero et al., 2001; Ubago-Pérez et al., 2006), peach stones (Cabrita et al., 2010); orange peel (Foo & Hameed, 2012); sisal (Mestre et al., 2011), coffee grounds (Kante et al., 2012; Reffas et al., 2010), and cork (Mestre et al., 2007; 2014b).

The conventional preparation procedures for the manufacturing of activated carbons are the physical (thermal) and chemical activation. Details concerning this subject can be found in various reviews and in the textbook of Marsh & Rodríguez-Reinoso (2006). The most commonly reported activating/oxidizing agents for physical activation are steam (Budinova et al., 2006; Mestre et al., 2014b) and CO₂ (Veksha et al., 2016). Regarding chemical activation, several compounds can be employed, being H₃PO₄, (Reffas et al., 2010; Romero-Anaya et al., 2012; Veksha et al., 2016), ZnCl₂ (Kante et al., 2012), KOH, (Mestre et al., 2014b, 2015; Wang & Kaskel, 2012) and K₂CO₃ (Mestre et al., 2007, 2011, 2014b, 2015) those more extensively explored in the studies reported in the literature.

The characteristics of the materials, namely texture, surface chemistry and density can be controlled by the precursor, the activation methodology and through the variation of a great number of experimental parameters. This is an enormous advantage of these materials that allows to customize the carbon to obtain a high performance for a specific process.

More recently, less conventional preparation methodologies have been explored. Fechler et al. (2013) prepared aerogel-like carbons with high apparent surface area (up to 673 m² g⁻¹), allied with a developed mesopore network, by hydrothermal carbonization of glucose in the presence of eutectic salt mixtures. The best results were obtained for the system lithium chloride/zinc chloride. The hydrothermal treatment was made at 180 °C overnight.

A different approach was followed in the study developed by Wang et al., 2010, in which the lignocellulosic raw material (rice husk) was treated with concentrated sulfuric acid to extract the saccharic units. The hydrochar obtained after polymerization of the sugars in acid media was chemically activated with H₃PO₄ or KOH, leading to materials exhibiting

specific surface areas of, 2700 m² g⁻¹ and 2488 m² g⁻¹, respectively.

The activation of sucrose derived hydrochars with spherical morphology allowed Mestre et al. (2015) to prepare materials with different textural and morphologic properties, depending on the activation agent used. KOH lead to sponge-like materials with specific surface areas reaching ~2500 m² g⁻¹ but with very low density. When K₂CO₃ was used the porosity development was not so high (~1400 m² g⁻¹) but the spherical morphology was retained, leading to porous materials with very high density (Mestre et al., 2014c).

In the particular case of carbon materials prepared at low to moderate temperatures (< 600 °C) or derived from precursors with high percentage of inorganic matter, before assessing their potentialities as adsorbents for water remediation purposes, it is important to assure that there is no leaching of undesirable contaminants for the media. In this sense, metals mobility through leaching tests must be made to evaluate the possible toxicity that could arise from the use of the materials. According to standard procedures (European Standard EN 12457-2) the sample must be mixed with ultrapure water for 24 h using a liquid to solid ratio of 10 dm³ kg⁻¹. The leached must be analyzed by atomic absorption spectrophotometry to evaluate the amount of several elements, such as Hg, Mn or Pb. To draw conclusions about a potential toxicity of the carbon material the results must be compared with the values reported on the European Council Decision 2003/33/EC.

The leaching of noxious organic compounds that can occur when carbons have high volatiles amounts must also be considered. In the study developed by Galhetas et al. (2015) the authors address this issue evaluating the total organic carbon (TOC) of the leachates obtained as described above for the metals mobility assays. Since the TOC values measured were below the quantification limit of the method used (1.0 mg

dm⁻³), the authors considered the use of the tested samples for liquid phase assays. Even though this was a simple approach to assess the possible contamination with organic compounds due to the use of carbon materials, it is not a common practice.

3. Adsorption from solution - batch assays

Studies of adsorption from aqueous solutions in batch reactors are relatively easy to be implemented and, as schematized in Fig. 2, comprise four major steps.

Even though the first step is obvious, it was introduced in the scheme to highlight the importance of some preliminary tests that have to be done in most of the cases. Before start any study it is mandatory to perform blank experiments to rule out the possibility of the pollutant being adsorbed in the walls of the vial, or, if magnetic stirring is to be used, in the magnetic stirrer. The first test is especially important in the case of dyes and metals adsorption assays since in relatively low concentration these species can be effectively adsorbed by the glass surface of the vials.

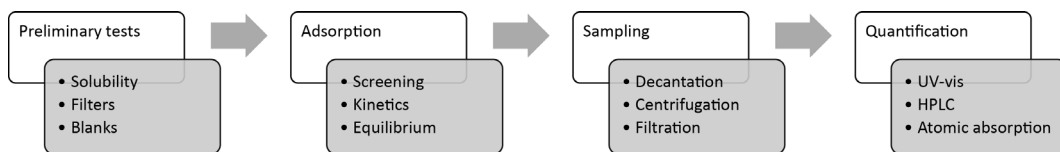


Fig. 2. Scheme of the major steps of batch adsorption studies.

During the adsorption step it is essential to guarantee that the assays are made under constant temperature and continuous stirring. When a magnetic stirrer is used, the temperature is normally controlled with a thermostatic bath; while when an orbital shaking apparatus is the option to stir

the mixtures the control of the temperature is made, in most of the cases, controlling the laboratory ambient temperature.

The third step requires different approaches, depending on whether granular or powder carbons samples are being used. For granular samples, a simple decantation is normally adequate to recover the liquid phase and to further quantify the solute remaining in the solution. However if the assay is focused on a powdered carbon, the separation methodology is a centrifugation or a filtration, usually with syringe filters. This last option is always preferable, especially in the case of kinetic assays, but to be applied it must be previously optimized, i.e. it has to be proved that the filter does not retain the pollutant to be quantified.

The final step is the quantification of the pollutant remaining in solution after the contact with the adsorbent. Several analytical techniques can be used, being UV-vis spectrophotometry, HPLC and atomic absorption the most reported ones, which obviously have to be optimized before starting the experiments. Once the equilibrium concentration is known, the uptake is calculated using eq. 1

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

where q_t is the amount (mg g^{-1}) of compound adsorbed at time t , C_0 is the initial concentration (mg dm^{-3}) and C_t 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.

Regarding the planning of the assays, it is usual that, as schematized in Fig. 3, the study starts with screening assays to establish the experimental conditions (mass of carbon, and concentration and volume of pollutant solution) that allow an incomplete removal of the pollutant, which is mandatory

to correctly perform the kinetic assays. In fact, if the solute is completely removed from the solution, the equilibrium $specie_{\text{solution}} \leftrightarrow specie_{\text{adsorbed}}$ is no longer present. For these screening assays it is common to use a 24 h contact time, or higher if using GAC, and/or in the case of slow adsorption processes.

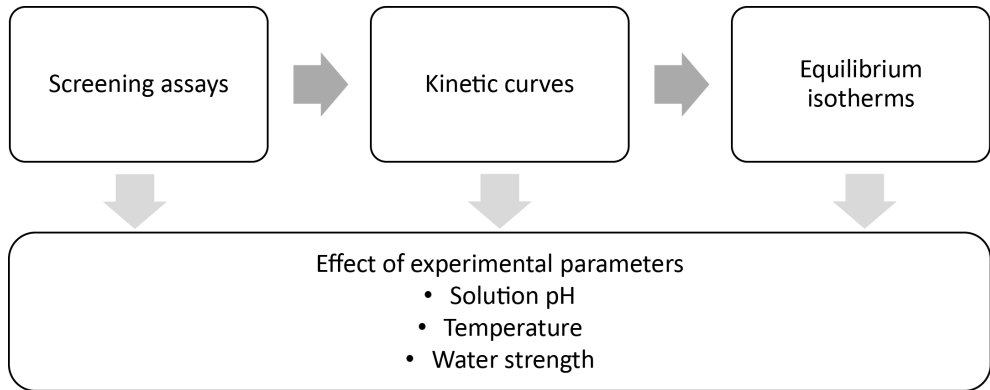


Fig. 3. Common working plan for batch adsorption studies in solution.

Kinetic results give important information to an eventual application of the system in a larger scale and, for academic studies, allow to determine the time that a given system needs to reach equilibrium and gives insights into the mechanism of the adsorption process. The equilibrium experiments are usually the last step of the process, i.e., the assays that allow to obtain the adsorption isotherms and consequently the adsorption capacity.

From the analysis of kinetic and equilibrium results using several theoretical models (see the most relevant ones in Table 2), important information concerning the mechanism of the adsorption process can be obtained. However, deeper insights can only be achieved when the results are analyzed along with the properties of the carbon and the

physico-chemical properties of the target compound. The adsorption from solution is, in fact, a complex process that is strongly dependent on many factors including texture (specific surface area and pore size distribution) and surface chemistry (functional groups) of the carbon, properties of the target molecule (e.g. solubility, speciation, molecular dimensions), and the operating conditions (e.g. solution pH and temperature), including the properties of the solvent used, as it will be illustrated in the case studies presented in the following paragraphs.

Model	Non-linear form	Linear form	Reference
Kinetic			
Pseudo-first order	$\frac{dq_t}{dt} = k_1 (q_e - q_t)$	$\log(q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2.303}\right) t$	Ho, 2006
Pseudo-second order	$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t$	Ho, 2006
<i>Parameters: k_1 - pseudo-first order rate constant (h^{-1}), k_2 - pseudo-second order rate constant ($\text{g mg}^{-1} \text{h}^{-1}$), q_e and q_t - adsorbate uptake (mg g^{-1}) at equilibrium and at time t (h).</i>			
Isotherm			
Langmuir	$q_e = \frac{b q_m C_e}{1 + b C_e}$	$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{1}{q_m} C_e$	Langmuir, 1918
Freundlich	$q_e = K_F (C_e)^{1/n}$	$\ln(q_e) = \ln(K_F) + \frac{1}{n} \ln(C_e)$	Freundlich, 1906
<i>Parameters: q_e – uptake at equilibrium (mg g^{-1}), b – Langmuir constant ($\text{dm}^3 \text{mg}^{-1}$), K_F – Freundlich constant ($\text{mg}^{1-1/n} (\text{dm}^3)^{1/n} \text{g}^{-1}$), n – Freundlich exponent, q_m - monolayer adsorption capacity (mg g^{-1}), C_e – solution concentration at equilibrium (mg g^{-1}).</i>			

Table 2. Most commonly used kinetic and isotherm models in their non-linear and linear forms.

3. 1st case study – Effect of texture: iopamidol adsorption

This study was developed by Mestre et al. (2014a) and illustrates the importance of a deep textural characterization of the carbons, namely concerning the microporosity, to understand the mechanism of the adsorption from solution. At the same time, it is also an example of the interdisciplinary character needed in most cases to elucidate the complexity of the phenomenon.

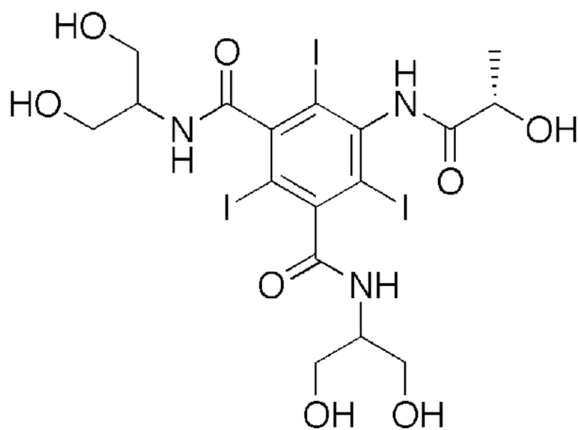


Fig. 4. Molecular structure of iopamidol.

The work was focused on the adsorption of iopamidol (Fig. 4), an iodinated contrast media (ICM) that allows blood vessels and other non-bony tissues to be more clearly seen in X-ray examination. This type of compounds has special importance in the diagnosis of certain disorders as, for example, heart or brain diseases.

The annual consumption of ICM reaches very high values since for a clinical exam intravenous doses up to 200 mg are used, and according to Christiansen (2005) it is estimated that approximately 75 million doses of ICM are given worldwide each year. Having this information in mind, and also the fact that ICM are highly water soluble compounds (in the particular case of iopamidol water solubility is $> 200,000 \text{ mg dm}^{-3}$ (Mestre et al., 2014a) designed to have high biochemical stability, they are excreted mainly in non-metabolized form, one could anticipate that the common water treatment technologies would fail to

degrade this class of medicines. In fact, ICM have been detected worldwide in sewage and wastewater effluents in concentrations in the order of mg dm^{-3} (Kormos et al., 2011) and even in potable water concentrations of 0.244 mg dm^{-3} were detected (Kormos et al., 2009).

Regarding the efficiency of activated carbons to eliminate iopamidol from aqueous media available literature does not allow to draw consistent conclusions, since in three WWTPs located in Germany, registered iopamidol elimination in GAC filtration facilities ranged from 8% up to 78% (Kormos et al., 2011).

In this context, the objective of the study carried out by Mestre et al. (2014a) was to evaluate the influence of the textural characteristics of activated carbons on the iopamidol adsorption mechanism. To achieve this goal the authors used two commercial carbons (NS and VP) and three lab-made carbons, prepared from chemical activation of sisal with KOH (samples S1, S2 and S3). The textural properties of the materials are summarized in Table 3. The possible influence of the surface chemistry was discarded since, although the lab-made carbons are slightly acid carbons ($\text{pH}_{\text{PZC}} \sim 6.5$) and commercial samples have basic surface properties ($\text{pH}_{\text{PZC}} \sim 10$), at the iopamidol dissolution pH (~ 5) all the samples have identical surface net charge and the compound is in its neutral form ($\text{pK}_a 10.7$).

Sample	A_{BET} ($\text{m}^2 \text{g}^{-1}$)	α_s Method			V_{meso}^4 ($\text{cm}^3 \text{g}^{-1}$)
		V_{micro}^1 ($\text{cm}^3 \text{g}^{-1}$)	V_{ultra}^2 ($\text{cm}^3 \text{g}^{-1}$)	V_{super}^3 ($\text{cm}^3 \text{g}^{-1}$)	
CP	907	0.40	0.16	0.24	0.03
VP	758	0.30	0.15	0.15	0.13
S1	564	0.22	0.17	0.05	0.01
S2	752	0.31	0.15	0.16	0.02
S3	615	0.23	0.10	0.13	0.08

$^1V_{\text{micro}}$ – total micropore volume ($\phi < 2 \text{ nm}$); $^2V_{\text{ultra}}$ – ultramicropore volume ($\phi < 0.7 \text{ nm}$).

$^3V_{\text{super}}$ – supermicropore volume ($0.7 < \phi < 2 \text{ nm}$); $^4V_{\text{meso}}$ – mesopore volume ($2 < \phi < 50 \text{ nm}$): difference between the volume adsorbed at $p/p^0 = 0.975$ and V_{micro} .

Table 3. Textural properties of the commercial and sisal-derived carbons. The microporosity was analyzed applying the α_s method using the reference isotherm reported by Rodríguez-Reinoso et al. (1987). (Adapted from Mestre et al., 2014a).

The adsorption kinetic results (Table 4) reveal that the textural properties of the carbons do play a determinant role in the adsorption of iopamidol. In one hand, the results of the two commercial carbons pointed out that, in the experimental conditions used, the presence of a developed mesopore network allows a quicker adsorption process, since the time needed for the essentially microporous sample (CP) to reach equilibrium was four times longer than that of carbon VP. On the other hand, regarding the removal efficiency, the performance of the samples were quite distinct, with the commercial carbons showing considerable higher iopamidol uptakes than any of the lab-made carbons. The almost negligible uptake of sample S1 revealed that a micropore network composed only by narrow micropores (ultramicropores) does not promote the adsorption of this

compound, which is achieved only when wider micropores (supermicropores) are present.

Sample	Pore network	Micropore network	Time to reach equilibrium (h)	q_e (mg g ⁻¹)
CP	micro	ultra+super	17	122.9
VP	micro+meso	ultra+super	4	115.5
S1	micro	ultra	n.a.	6.4
S2	micro	ultra+super	n.a.	37.5
S3	micro+meso	ultra+super	n.a.	40.1

n.a.- not available; to determine contact time to reach equilibrium the authors obtained limited iopamidol uptake values between 1 h and 4 days; Experimental conditions: 120 mg dm⁻³; 6 mg of carbon; 9 cm³ of solution; 30 °C.

Table 4. Summary of the textural characteristics of the samples, and some data from kinetic adsorption assays: time to reach equilibrium and iopamidol uptake at equilibrium (q_e) calculated by the pseudo-second order kinetic model in the case of commercial carbons and after 4 days of contact time for sisal derived carbons.

To interpret these data the authors used DFT calculations to assess the molecular dimensions of iopamidol. The values corresponding to the lowest energy conformation are presented in Table 5, showing that the critical dimension for iopamidol diffusion is 0.6 nm. This value is in fact, quite close to the maximum width considered in the literature for narrow micropores (ultramicropores: $\phi < 0.7$ nm (Thommes et al., 2015)), what indicates that the access of iopamidol to the ultramicropores must have considerable steric limitations. In other words, the result explained the negligible removal of iopamidol attained with sample S1.

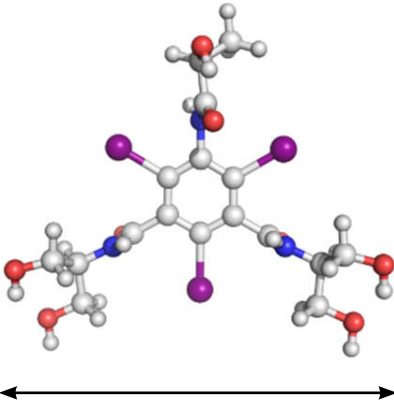
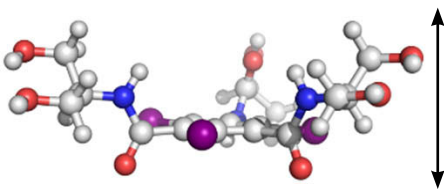
Lateral distance	Height
	
1.5 nm	0.6 nm (critical dimension)

Table 5. Dimensions of the lowest energy conformation of iopamidol molecule (Mestre et al., 2014a).

At this point the authors made a first attempt to correlate the iopamidol uptake and the textural parameters considering the volume of mesopores and wider micropores (supermicropores). As displayed in Fig. 5, it seems that, in the experimental conditions used in the kinetic assays, the iopamidol uptake at equilibrium is linearly correlated with the values of $V_{\text{super}} + V_{\text{meso}}$, although a higher uptake would be expected in the case of sample S3.

The equilibrium results reported in this study revealed very different behaviors for the commercial and the two sisal-derived samples assayed (S2 and S3). Actually, while the isotherms obtained with carbons CP and VP are typically L curves according to the Gilles classification (Giles et al., 1960), the results obtained with the lab-made carbon are two-step isotherms, as schematized in Fig. 6.

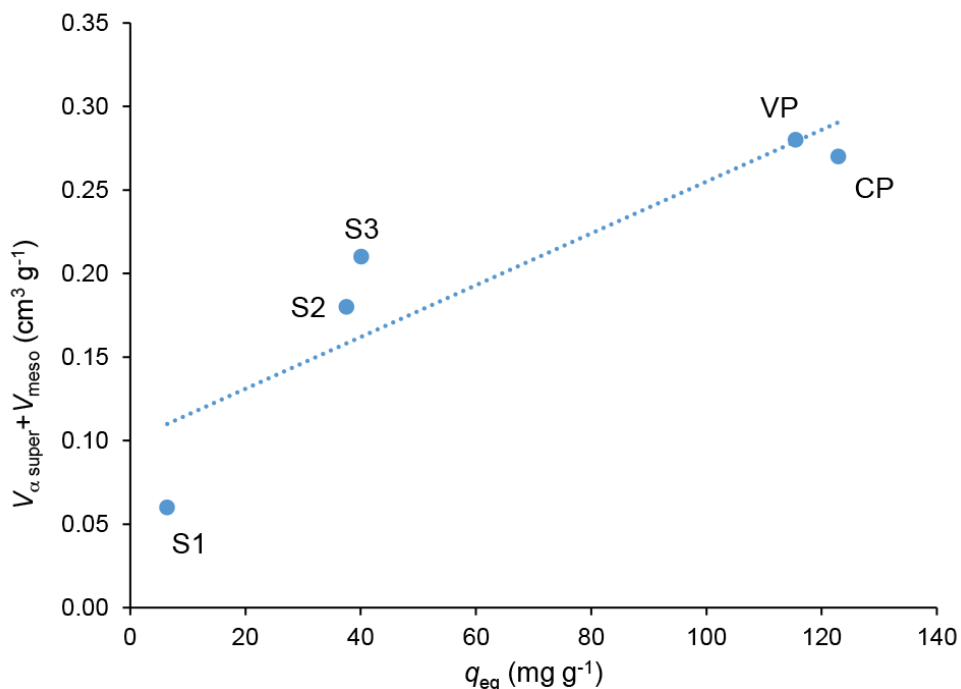


Fig. 5. $V_{\alpha\ super} + V_{meso}$ values of the activated carbon samples versus iopamidol uptake at equilibrium (120 mg dm^{-3} ; 6 mg of carbon; 9 cm^3 of solution; $30\text{ }^{\circ}\text{C}$).

Two-step isotherms are not frequently reported in the literature, being usually associated to the adsorption of surfactants in solids (Jonsson et al., 1998) or pesticides in soils (Czinkota, et al., 2002). This type of isotherm was also reported by Blázquez, et al. (2010) for the adsorption of metal ions in biosorbents, and to analyze the data the authors considered a two-step Langmuir type isotherm, that is, the Langmuir equation in its linear form (see Table 2) was fitted independently to the data of each step.

The same approach was considered to analyze the iopamidol results, allowing the assessment of the iopamidol monolayer capacity in each of the carbons tested. The values

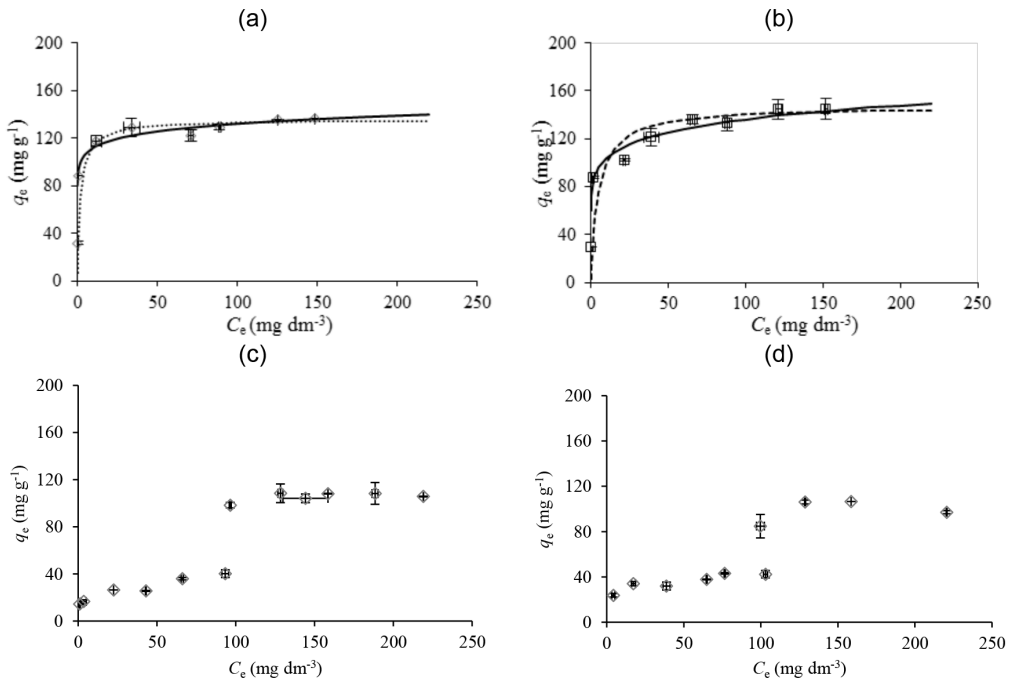


Fig. 6 . Iopamidol adsorption isotherms on the samples CP (a), VP (b), S2 (c) and S3 (d). Reprinted from reference Mestre et al. (2014a) with permission from Elsevier.

reported are reproduced in Table 6. Assuming the q_m values obtained for the second step as characteristic of the iopamidol adsorption capacity of the sisal-based carbons, it can be concluded that the results compare favorably with those of the commercial carbons.

Sample	Data	q_m (mg g^{-1})
CP	All	135.5
VP	All	147.0
S2	1 st step	40.7
	2 nd step	112.4
S3	1 st step	44.6
	2 nd step	105.3

Table 6. Monolayer adsorption capacity of iopamidol for commercial carbons (CP and VP) and sisal-derived materials (S2 and S3).

The two-steps isotherms obtained with the lab-made samples allowed the authors to explain the difference in iopamidol uptake observed in the kinetic assays. The lower value presented by the sisal-derived samples is due to fact that the experimental conditions of the kinetic assays corresponds to the last point of the first step of the isotherm.

To explain the different isotherms configurations was more complex because, the two-step isotherm an unusual result for the adsorption of pharmaceuticals in activated carbons, was more complex.

Since these type of isotherms have been reported for the adsorption of surfactants, and above a certain concentration these species tend to form aggregates, the authors carried out conductivity measurements of iopamidol solutions in the concentration range used to define the isotherms (0 – 250 mg dm^{-3}). The results showed an accentuated decrease of the molar conductivity of the solution up to 50 mg dm^{-3} , after what an almost undetectable decay of the conductivity values was observed, suggesting molecular aggregation for higher iopamidol concentrations ($\geq 100 \text{ mg dm}^{-3}$).

Considering that the results of the conductivity assays pointed out that at least two iopamidol molecular species could

be present in the working concentration range, and the fact that in both isotherms, q_m (2nd step) $\sim 3 x_m$ (1st step), the authors extended the molecular dimension calculations to iopamidol aggregates, namely, dimers and trimers. The results reported are presented in Table 7. The results also proved that dimers and trimers are linked with lower Gibbs energies indicating that the molecule tends to forms aggregates, thus the higher concentrations of monomer occur only in diluted solutions.

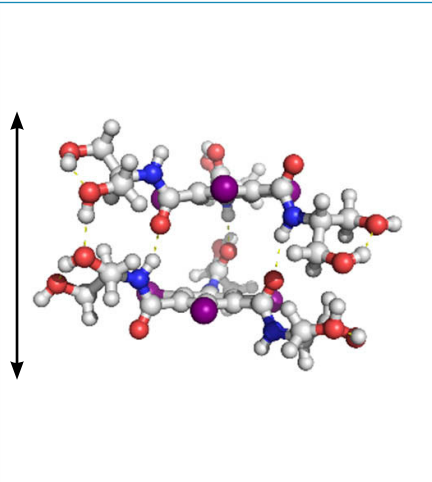
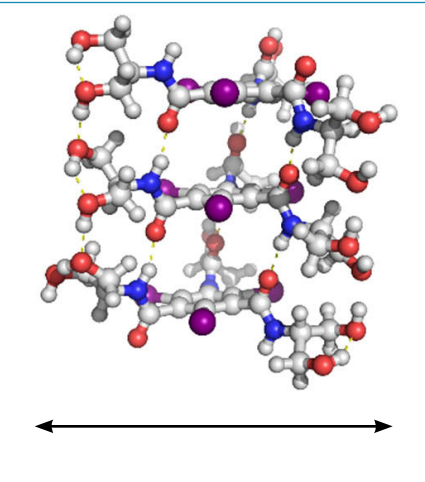
Aggregate	
Dimer	Trimer
	
1.2 nm	nm

Table 7. Critical dimension of the lowest energy conformation of iopamidol dimer and trimer (Mestre et al., 2014a).

Considering that all the three iopamidol species are present in solution, it became evident that the carbons textural characteristics must play an important role in the adsorption process of this compound. To verify this hypothesis the authors performed a detailed characterization of the microporosity through CO₂ adsorption isotherms at 0 °C. To

obtain the micropore size distributions the authors followed the methodology proposed by Pinto et al. (2010). The results are reproduced in Fig. 7 along with the critical dimensions of the iopamidol species and the micropore volume accessible to each specie. This combination of results revealed that in the case of carbons CP and VP, the three iopamidol species have no steric hindrances to access their micropore network. However, in the case of sisal-derived carbons only the monomer can diffuse into the micropore system of the samples, which will correspond to the first step of the isotherm. The second step of the isotherms corresponds to the adsorption of dimer and trimer species in larger porosity, in line with the relation between the q_m values of the first and second step of the isotherms mentioned before.

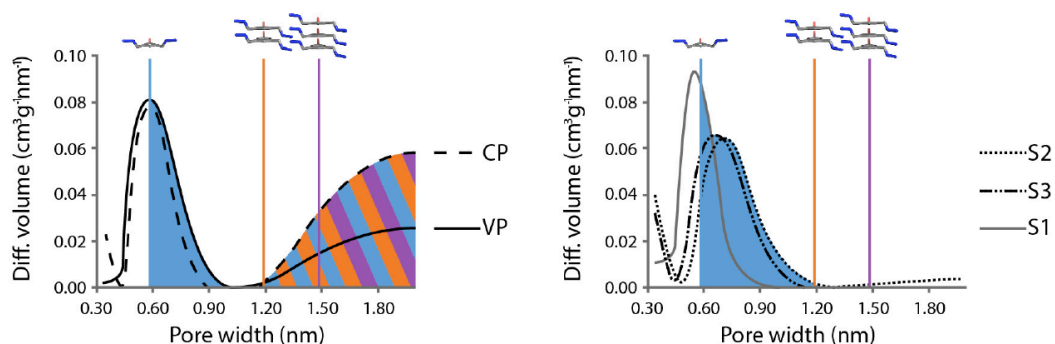


Fig. 7. Micropore size distributions obtained from the CO₂ isotherms on commercial carbons (CP and VP) and sisal-derived carbons (S1, S2 and S3), following the method described in (Pinto et al., 2010). Critical dimensions and micropore volume accessible to iopamidol species are also presented. (Adapted from Mestre et al., 2014a).

As a final conclusion, the authors pointed out the importance of combining different approaches to explain an uncommon two-step isotherm configuration that seems to be related with the lack of micropores wider than 1.2 nm.

A detailed characterization of the micropore structure has also proved to be important to rationalize the results of other

compounds adsorption. This approach was followed by the same group of authors to rationalize the ibuprofen adsorption data onto cork-derived carbons (Mestre et al., 2006, 2014b) and of acetaminophen and iopamidol adsorption onto sucrose derived carbons (Mestre et al., 2015)

4. 2nd case study – Effect of pH, solubility and temperature: fluroxypyr and acetamoniphen adsorption

This case study demonstrates the influence of pH, solubility, and temperature in the mechanism of adsorption from solution processes. The study was developed by Pastrana-Martínez et al. (2009) and was focused on the adsorption of an herbicide (fluroxypyr) onto carbons with different morphologies (activated carbon fiber and cloth).

The use of herbicides and pesticides is of fundamental importance to achieve large crop yields, needed to feed the continuously growing world population. Due to its extensive use, and to leaching effects, this type of compounds is detected in the aquatic environment and since they can pose

risks to the environment and humans, in most of the cases, the maximum amount allowed in different media is regulated. Regarding herbicides, according to the European Directive 98/83/EC the maximum concentration allowed for drinking water is 0.1 mg dm⁻³. (EU, Concil Directive 98/83/EC, 1998).

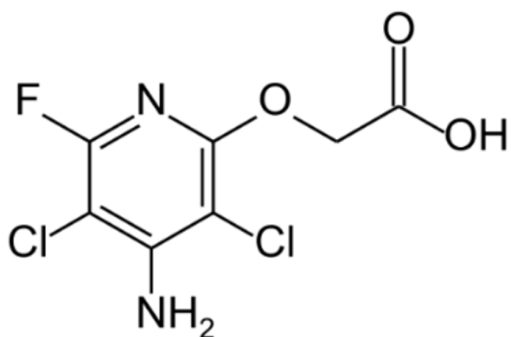


Fig. 8. Molecular structure of fluroxypyr.

Fluroxypyr (Fig. 8) is an extensively used herbicide in

the control of the proliferation of broadleaf weeds in, for example, olive trees fields. Its toxicity was assessed by the Environmental Protection Agency of USA (EPA, 1998), and although it is classified as “not likely” to be human carcinogen, toxic assays in rats proved its nephrotoxicity.

The results of the fluroxypyr adsorption equilibrium assays at 25 °C on the two carbons tested (ACF-activated carbon fiber; ACC-activated carbon cloth) are presented in Fig. 9(a) revealing that the adsorption capacity values, q_m , assessed by the fitting of the Langmuir equation to the experimental data are consistently higher in the case of sample ACC, in line with the higher micropore volume of this material ($0.913 \text{ cm}^3 \text{ g}^{-1}$), in comparison with that of ACF ($0.734 \text{ cm}^3 \text{ g}^{-1}$). From this graphic it is also clear that the solution pH increase has a marked effect on the monolayer capacity values which significantly decrease, especially between pH 2 and 7.

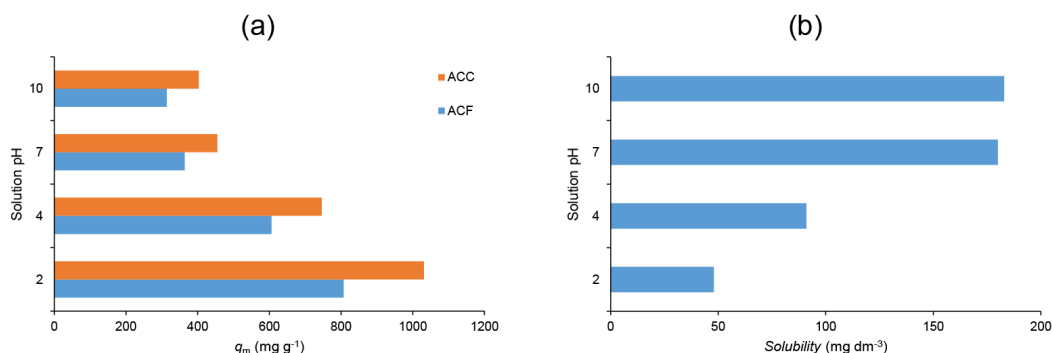


Fig. 9. Fluoroxypyr (a) monolayer adsorption capacities of ACF and ACC and (b) solubility, at 25 °C for different pH values. Data from Pastrana-Martínez et al. (2009).

The authors explained these results demonstrating that fluroxypyr solubility (Fig. 9(b)) significantly increases as pH increases. Solubility is, in fact, a major parameter that controls the adsorption mechanism, since higher solubility results from

strong interactions between the adsorbate and the solvent (normally water) molecules that hinder the interactions of the specie with the carbon's surface functionalities or, in other words, disfavors adsorption.

Besides the particular case of this study, there are several works in the literature reporting the dependence of the adsorption process with the pollutant solubility (Galhetas et al., 2014; Mestre et al., 2014b). For example, in the study developed by Gallhetas et al. (2014), slower adsorption rates were observed for caffeine removal when compared with those obtained for the adsorption of acetaminophen, in line with the much higher solubility of caffeine (30 g dm^{-3} , Mestre et al., 2012) compared to that of acetaminophen (17.39 mg dm^{-3} (Granberg & Rasmuson, 1999)). Regarding the adsorption capacity, in almost all the cases a higher monolayer capacity was also achieved with caffeine. To interpret the results the authors also took into account the relationship between the microporosity characteristics of the carbons and the molecular dimensions of both compounds, being the smaller critical dimension of caffeine (0.45 nm) an additional factor that favors molecules packing inside the pore network.

To understand the accentuated difference of the solubility with the pH Pastrana-Martínez et al. considered the speciation diagram of the fluroxyppy, which demonstrates that the compound remains undissociated only up to pH 2. As the pH reaches higher values, the deprotonation of the carboxylic group occurs, followed by the amino group, leading to the formation of mono and di-negatively charged species, that obviously can establish progressively stronger interaction with the water molecules, thus explaining the increase of the solubility.

The importance of the speciation diagram goes far beyond the interpretation of solubility values. In fact, this is an essential information to understand the mechanism of adsorption from solution, especially when weak electrolytes

(e.g. most pharmaceutical compounds) are considered. The pH is actually, a critical factor of the process because it controls not only the nature of the specie present in solution, but also the surface chemistry of the carbon due to the dissociation of the surface functionalities. The carbon surface can be either positively ($\text{pH} > \text{pH}_{\text{PZC}}$ ($\text{pH}_{\text{PZC}} - \text{pH}$ at the point of zero charge) or negatively ($\text{pH} < \text{pH}_{\text{PZC}}$) charged, thus at a given pH, the carbon surface and the adsorbate species can present similar or opposite charges.

With this information in mind, and knowing that the pH_{PZC} of the carbons ACF and ACC tested by Pastrana-Martínez et al. present values of, respectively, 7 and 8, it becomes evident that depending on the solution pH, dispersive interaction between the graphene layers and nondissociated specie or electrostatic attractions/repulsions can occur, as systematized in Table 7.

	pH			
	2	4	7	10
Fluoroxypyr specie	HFlu	Flu^-	Flu^-	$\text{Flu}^- \rightleftharpoons \text{Flu}^{2-}$
ACF surface charge	++	++	+/-	- -
ACC surface charge	++	++	+ (low)	- -
Interaction	Dispersive	Electrostatic attraction	Electrostatic repulsion	Electrostatic repulsion
Adsorption	high	high	low	low

Table 7. Charges of the fluoroxypyr specie and carbons ACF and ACC at different pH, predominate interaction present in the system and how it affects the adsorption process.

The observed monotonous decrease of fluoroxypyr adsorption onto ACF and ACC, as the pH turned progressively more basic, can then only be explained considering the combined effect of the solubility and the different interactions

that arise from the various possible combinations of charges present in each of the solution pH assayed, pointing out the complexity of the adsorption process. In the literature there are many more examples of studies evidencing the influence of the solution pH on the adsorption process of organic compounds onto carbons (Ji et al., 2009; Mestre et al., 2007, 2009; Zhang et al., 2014).

Pastrana-Martínez et al. also evaluated the influence of the temperature on the adsorption capacity of ACF and ACC for fluoxypyr. The authors carried out assays at 25 °C and at 40 °C, at the different pHs previously mentioned. The results obtained showed that the increase of the temperature was consistently related with a decrease of the adsorption capacity. This is the expected result since adsorption, being a spontaneous phenomenon, which results in an entropy decrease, according to thermodynamic principles must be an exothermic process, thus disfavored as the temperature increases ($\Delta G = \Delta H - T\Delta S$). However, regarding adsorption from solution, there are numerous examples in the literature that, in contrast with the results reported in the study herein described, demonstrate that the increase of temperature leads to higher adsorption capacity (Acemioğlu, 2004; Aksakal & Uçun, 2010; Galhetas et al., 2014, 2015; Guedidi et al., 2013; Kyzas et al., 2012; Mestre et al. 2007; Yu & Luo, 2014).

To explain these thermodynamically unexpected results two hypothesis have been proposed. Some authors consider that the increase of temperature results in a higher mobility of the molecules, favoring the diffusion of the species towards the narrowest porosity of the solid (Kyzas et al., 2012; Terzyk, et al., 2003; Ramos et al., 2010), while others consider the occurrence of some interactions of chemical nature in the adsorption process (Aksakal & Uçun, 2010; Galhetas et al., 2014; Mestre et al, 2007).

A study recently developed by Galhetas et al. (2015) on the adsorption of acetaminophen on four activated carbons with different surface chemistry and micropore size distribution brought a new proposal to explain the dependence of the adsorption capacity with the temperature. In the set of carbons tested, the authors found all the possible dependences, i.e., increase, decrease or no change of the acetaminophen adsorption capacity when the temperature was raised from 20 °C up to 40 °C. As the critical dimension of acetaminophen is 0.44 nm, from the micropore size distributions it was not expected that the samples would present different behaviors, since no hindrance to the diffusion towards the adsorption sites was expected.

However, the micropore network characteristics of the carbons must be related with the phenomenon; in fact, the thermodynamic behavior was observed when a continuous micropore size distribution was present, but not when the carbon present a micropore size distribution covering a restricted range of the microporosity or when the maximum was centered at pores with width of 0.44 nm and 0.52 nm.

To support their hypothesis, the authors needed to prove that in the adsorption phase, besides de acetaminophen monomer, other species were also present. The ^1H NMR spectroscopy data of the back-extraction solution proved the existence of acetaminophen aggregates, namely dimers, which in the low energy configuration have a critical dimension of 0.66 nm. These findings did not match with the increasing adsorption capacity observed for the samples with mainly narrow micropores, because due to its dimensions, the dimer would have constrained access to this type of microporosity.

Assuming that the texture was a key factor ruling the adsorption, the authors explained that the unexpected effect of temperature resulted of adsorbent–adsorbate interactions sufficiently strong to overcome the energetic barrier and

promote the change of the acetaminophen oligomers to a planar conformation which has a critical dimension of 0.44 nm. Therefore, when the maximum of the micropore size distributions of the samples were near this value, a great number of species can access the microporosity, thus increasing the adsorption capacity of the samples.

5. 3th case study – Effect of pH and solvation energy: clofibric acid adsorption

As it was mentioned in the introduction section, clofibric acid (Fig. 10) detection on Berlin tap water samples (Stan et al., 1994) is one of the most important facts regarding the presence of pharmaceutical compounds on the aquatic media. This compound has been consistently detected in water bodies worldwide (Heberer, 2002; Zuccato et al., 2000)

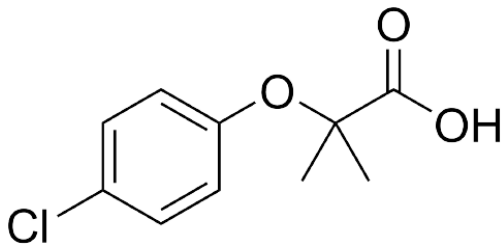


Fig. 10. Molecular structure of clofibric acid.

due to its recalcitrant behavior in conventional water treatments technologies (Matamoros et al., 2008; Onesios et al., 2009; Ternes et al., 2002).

The work described in this case study was focused on the adsorption of this pollutant, addressing the importance of the solution pH in the adsorption

mechanism from a distinct point of view than those presented in the 2nd case study. The study was developed by Mestre et al. (2010) using two cork-derived activated carbons and two commercial samples, all with different textural characteristics and presenting pH_{PZC} values ranging from 7.7 to 10.3

The first indication that the solution pH has a paramount importance on the removal of clofibric acid was obtained

through results of the kinetic assays. A drastic decrease of clofibric acid removal was observed when the solution pH increased from 2 up to 5. This was the opposite of what could be expected, since in the range of pH considered the carbons present positive surface charge ($\text{pH} < \text{pH}_{\text{pZC}}$) and, if at pH 2 almost all the clofibric acid species are undissociated (HClf). At pH 5 the dissociated species (Clf^-) are predominant ($\text{pK}_a \sim 3.6$, Hilal et al. (1995)), so, if only surface chemistry was ruling the process, strong attractive electrostatic interactions would enhance the adsorption.

Unexpected results were also obtained on the equilibrium assays with S-type isotherms (sigmoidal configuration) being obtained for all the carbons, as reproduced in Fig. 11. To obtain the maximum amount adsorbed (in this case designated as w_0) the curves were fitted to the Dubinin-Astakohv equation (Dubinin, 1979):

$$w^{\text{ads}} = w^0 \exp [-(A/E)^n] \quad (\text{eq. 2})$$

where w^{ads} is the adsorbed volume at temperature T and "reduced" equilibrium concentration (C_e/C_s) (concentration at equilibrium divided by adsorbate solubility), w^0 is the maximum adsorption volume, A is the adsorption affinity ($A = -RT \ln(C_e/C_s)$), and n and E (characteristic adsorption energy) are temperature independent parameters.

As in the 1st case study, to rationalize the trend of w^0 values the authors needed to consider the micropore network characteristics, namely micropore size distribution obtained from the CO_2 adsorption isotherms and the molecular dimensions of the adsorbate specie. The conclusion was that the presence of larger micropores is determinant for the adsorption of clofibric acid, particularly considering that the species are strongly solvated.

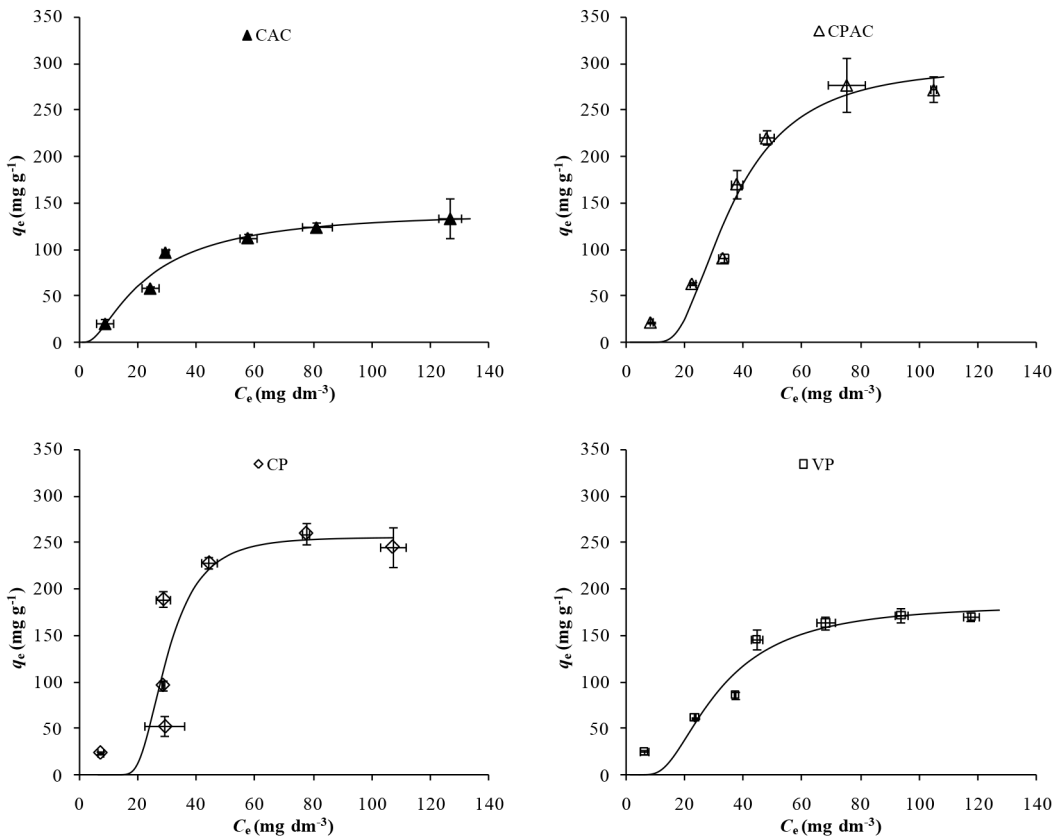


Fig. 11. Clofibric acid isotherms on commercial carbons CP and VP, and cork derived carbons CAC and CPAC at 30 °C and solution pH 3.6. Reprinted from reference Mestre et al. (2010) with permission from Elsevier.

Solvation was in fact crucial for the explanation presented by the authors to interpret the isotherms configuration which is characteristic of cooperative adsorption phenomenon. In fact, after ruling out possible explanations based on the molecular dimensions and on the possible interactions between the HOMO of the solute and the LUMO of the adsorbent (Radovic, et al., 2001), the authors considered the solvation energies of both HCl_of and Cl_of⁻ species, computed using Gaussian 03 software

and Polarised Continuum Model. The results obtained ($-18.9 \text{ kcal mol}^{-1}$ and $-74.1 \text{ kcal mol}^{-1}$, for HClf and Clf species, respectively) showed that a strong interaction with the water molecules is established in any case.

Therefore, in the initial part of the isotherms, which corresponds to lower concentrations, the adsorption is disfavored due to the fact that interactions of the clofibric acid species with the carbon surface are shielded by the strong interaction with the solvent.

As the concentration increases, the number of solute molecules increases, so it is reasonable to admit that adsorption of, mainly HClf species starts to occur. In fact, since the assays were carried out at $\text{pH} = \text{p}K_a$, equal amounts of HClf and Clf species are present in solution, but as HClf species began to be adsorbed, the dissociation equilibrium progressively changes towards the HClf specie (see reaction 1). In this conditions, in the reaction media the HClf specie prevails, enhancing the adsorption since it has the lower solvation energy.



The influence of the solvation energy on the clofibric acid adsorption mechanism proposed also allowed the interpretation of the kinetic results. The almost complete removal observed at pH 2 is linked with the almost exclusively presence of HClf specie (lower solvation energy), while the negligible removal at pH 5 results from the presence of a large percentage of Clf species (higher solvation energy).

6. 4th case study – Effect of water hardness: clofibric acid adsorption

The last case study illustrates the influence of water hardness on the adsorption process of a pharmaceutical compound, being an issue only addressed in very few studies (Couto et al., 2015; Pastrana-Martínez et al., 2010). However, as it is clearly demonstrated by the study recently developed by Mestre et al. (2016), the inorganic ions present in the reaction media play an important role in mechanism of clofibric acid adsorption.

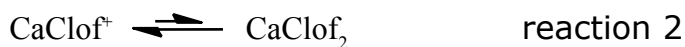
Based on the kinetic and equilibrium adsorption data, the authors evaluated the combined effect of pH and water hardness in the clofibric acid mechanism onto two commercial carbons. The samples present textural characteristics that differ mainly in the mesopore volume and similar surface chemistry properties ($\text{pH}_{\text{pZC}} \sim 10$). Experimentally, batch assays were performed using deionized water and water with hardness of 80 and 200 $\text{mg dm}^{-3} \text{CaCO}_3$, to simulate moderately hard and hard waters, respectively. The experiments were carried out at pH 3 and 8.

Regarding the effect of the solution pH, in alkaline media a decrease of the clofibric acid adsorption was observed in both activated carbons. To interpret these results, the authors determined the solubility of clofibric acid in the different experimental conditions used, and concluded that for the same hardness value a significant increase of the solubility is observed when the pH increases from 3 to 8. Thus, similarly of what was discussed in the 2nd case study, the stronger interaction with water molecules hinders the adsorption of the target compound. On the other hand, the higher solubility observed at pH 8 is an expected result, since in these conditions the anionic specie Clf^- is predominant in solution, leading to the establishment of ion-dipole interactions.

In what concerns the effect of the water hardness, the kinetic results revealed that water hardness has a strong impact when the assays are carried out at pH 8. In one of the cases the removal increases from 34 % in pure water solution to 80 % when hard water (200 mg dm⁻³ CaCO₃) was used as solvent. At pH 3 only a slight increase of the removal was observed with increasing hardness. Equilibrium data at pH 8 showed that in fact, water hardness has a strong repercussion on the adsorption capacity, which is not so important when the solution pH is 3.

To rationalize these results the authors investigated which forms of the clofibric acid-Ca²⁺ species will be likely formed in solution. From DFT computational method it was found that the formation of CaCl_of⁺ and CaCl_of₂ are associated to an energy decrease of -82 and -159 kJ mol⁻¹, respectively. Thus, whenever clofibrate (Cl_of⁻) and Ca²⁺ are present in solution, either of these complexes are liked to be formed, being pH 8 (Cl_of⁻ predominant in solution) and high hardness value (high Ca²⁺ concentration) the most favorable conditions.

The presence of these complexes in solution was demonstrated through titration assays followed by conductivity measurements, allowing the authors to rationalize the results observed considering that the increase of clofibric acid adsorption observed with increasing hardness for assays made at pH 8 is, as the consequence of the presence of CaCl_of₂ species (reaction 2):



In these conditions, the establishment of dispersive interactions with the carbons overcomes the strong interaction

with the water molecules that, as discussed above, are established in the assays that are made at this pH value.

Acknowledgments

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