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Influence of oxidation process on the adsorption capacity of activated carbons from lignocellulosic precursors

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ABSTRACT

A set of activated carbon materials non-oxidised and oxidised, were successfully prepared from two different lignocellulosic precursors, almond shell and vine shoot, by physical activation with carbon dioxide and posterior oxidation with nitric acid. All samples were characterised in relation to their structural properties and chemical composition, by different techniques, namely nitrogen adsorption at 77 K, elemental analysis (C, H, N, O and S), point of zero charge (PZC) and FTIR. A judicious choice was made to obtain carbon materials with similar structural properties (apparent BET surface area $\sim 850\text{--}950\text{ m}^2\text{g}^{-1}$, micropore volume $\sim 0.4\text{ cm}^3\text{g}^{-1}$, mean pore width $\sim 1.2\text{ nm}$ and external surface area $\sim 14\text{--}26\text{ m}^2\text{g}^{-1}$). After their characterisation, these microporous activated carbons were also tested for the adsorption of phenolic compounds (p-nitrophenol and phenol) in the liquid phase at room temperature. The performance in liquid phase was correlated with their structural and chemical properties. The oxidation had a major impact at a chemical level but only a moderate modification of the porous structure of the samples. The Langmuir and Freundlich equations were applied to the experimental adsorption isotherms of phenolic compounds with good agreement for the different estimated parameters.

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1. Introduction

Activated carbons (AC) are porous materials prepared using specific methods in order to acquire certain specific properties. Lignocellulosic materials are one of the most used materials for the production of activated carbons with wood and coconut shell being the major precursors and which are responsible for the production of more than 300,000 tons/year of AC [1]. Other commonly used materials are agricultural by-products such as eucalyptus wood, almond shell, vetiver grass, peanut shells, coir pith, chestnut and pistachio nut shells, corncobs, palm stones, cork, coffee endocarp and vine shoots [2–13]. Activated carbons have a wide range of applications in the liquid and gaseous phases with uses at industrial and domestic level and also in an extensive number of areas, such as energy, health and environment. Because of their unique characteristics of high surface area, well developed porous structure, high adsorption capacity and rich surface chemistry, that can all be modified by controlling the production process, depending on the end use, they are ideal for adsorbing inorganic and organic pollutants. In addition, activated carbons are known to have amphoteric behaviour, which gives flexibility to the materials and can be considered an advantage. This attribute is very important when the carbons are in contact with a solution of weak electrolytes because

these are attracted or repelled by the surface of the AC, depending on the solution pH and the point of zero charge of the carbons [14]. The adsorption of aromatic compounds in solution, mainly phenols, has been extensively studied [15–27] because their presence in the environment, in particular water, is still a major concern. Phenol is an important toxic material listed as a priority pollutant by the US Environmental Protection Agency (EPA) [28], and also by the EU. The European Commission released a directive (80/778/ECC) that specified a maximum admissible concentration of $0.5\text{ }\mu\text{g L}^{-1}$ for phenol in water intended for human consumption. As already known, phenol has a high level of toxicity to human beings by oral exposure. Some symptoms are muscle weakness, tremors, loss of coordination, paralysis, convulsions, coma, liver and kidney damage, headache and other mental disturbances. Phenol is the base structure unit of a variety of synthetic organic compounds. It usually enters water sources from various chemicals, pesticides, paper and pulp and dye manufacturing industries, wastewaters from industries such as gas and coke, resin, tanning, textile, plastic, rubber, pharmaceutical and petroleum.

It is accepted that, despite all the studies already carried out on the use of activated carbons from lignocellulosic and other materials, the mechanism and influence of the various factors affecting phenol uptake is still not clear. For instance, Leng and Pinto state that the uptake of phenol is a combined effect of physisorption, caused by the interaction of phenol with the carbon basal planes, and surface polymerisation [20]. They also concluded that the AC functional groups have an important role in the electrostatic and dispersive

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interactions. Moreover, the increase of phenol uptake is directly connected to the removal of carboxylic groups from the AC surface. Radovic and co-workers have studied the effect of the surface chemistry on the adsorption of several compounds [24]. They concluded that the oxidation of the AC decreases the π -electron density in the graphene layers reducing the intensity and magnitude of the dispersive interactions between the carbon and the adsorptive. Likewise, the removal of the oxygen groups causes an increase in the π -electron density and thus an increase in the adsorption potential via the dispersive interactions.

The surface chemistry of activated carbons is very rich with groups that include carboxyl, carbonyl, phenol, quinone, lactone and others. The nature and prevalence of such groups may be modified by various post-activation treatment methods, of which oxidation is the most important. For gas oxidation, oxygen or air can be used while for liquid phase oxidation the most common methods use nitric acid and hydrogen peroxide. Depending on the procedure used the oxidation does not affect significantly the pore structure of the activated carbon, whereas the surface chemistry suffers great changes [29].

2. Experimental

2.1. Materials

In this study we used a set of samples prepared from two lignocellulosic precursors, namely almond shell and vine shoots. The lignocellulosic composition of these precursors was determined using Portuguese Standards NP2029 and ME-414 by the company Agroleico (Porto Salvo, Portugal). From the series of activated carbons prepared in our laboratory by physical activation with carbon dioxide, we selected two samples with similar burn-off. The activation was done in a horizontal tubular furnace with heating rate of $10\text{ }^{\circ}\text{Cmin}^{-1}$. Carbonisation was carried out for 1 h by heating to $400\text{ }^{\circ}\text{C}$ under a constant N_2 flow of $85\text{ cm}^3\text{min}^{-1}$. Activation was carried out at $800\text{ }^{\circ}\text{C}$ under a CO_2 flow of $85\text{ cm}^3\text{min}^{-1}$, in order to obtain burn-off between 35 and 40 wt.%. The gas flow was then switched back to N_2 and the sample allowed to cool to room temperature before removing the AC from the furnace. The samples were then washed with 150 mL of distilled water for 24 h with stirring at room temperature. Finally, the samples were oven dried at $110\text{ }^{\circ}\text{C}$ for 24 h and stored in sealed flasks. The designation of the samples, A835 and V840 from almond shell and vine shoots, respectively, respects the sequence PTL (P precursor, T final heat-temperature, L level of burn-off).

Subsequently, the samples were oxidised with concentrated nitric acid during 1 h on a hot plate with stirring at $80\text{--}90\text{ }^{\circ}\text{C}$. The ACs were removed and washed with distilled water until the wash water attained the same pH value as the distilled water employed in the wash. The oxidised samples were designated as A835ox and V840ox.

2.2. Materials characterisation

The activated carbons were characterised by the adsorption of nitrogen at 77 K using a Quantachrome Instruments Quadrasorb SI after outgassing the samples at $400\text{ }^{\circ}\text{C}$ for a period of 4 h in a Quantachrome MasterPrep Unit. All of the isotherms were analysed using the Brunauer-Emmett-Teller (BET), Dubinin-Radushkevich (DR) and α_s methods. Elemental analysis of carbon, hydrogen, sulfur, nitrogen and oxygen was carried out using a Eurovector EuroEA elemental analyser. The points of zero charge were determined by the mass titration method [30]. The surface functional groups were characterised by FTIR analysis. FTIR spectra were recorded with a Perkin Elmer model Paragon 1000PC spectrophotometer using the KBr disc method (1:500; AC:KBr), resolution of 4 cm^{-1} and 100 scans between 4000 and 450 cm^{-1} . The cellulose and lignin content of the precursors was carried out by Agroleico (Porto Salvo, Portugal) using Portuguese Standards NP2029 and ME-414, respectively.

2.3. Adsorption of phenolic compounds

$2 \times 10^{-2}\text{ M}$ p-nitrophenol and phenol stock solutions were prepared from p-nitrophenol and phenol, both from Aldrich and with purity greater than 99%. Batch and kinetics adsorption experiments were carried out in test tubes of 50 mL covered with rubber stoppers placed into a shaking thermostat bath for 7 days. A fixed amount ($\sim 0.01\text{ g}$) of each carbon and 10 mL of aqueous solution of the phenolic compound of desired concentration were placed into the test tubes. The optimum pH for the adsorption medium was also determined for these carbon materials. The quantification of the phenolic compounds in the liquid phase was carried out using a Thermo UV/visible spectrophotometer at 399 and 269 nm for p-nitrophenol and phenol, respectively. The determination of the amount of the phenolic compounds was made at pH values that assured only one of the forms of the phenolic compound (basic and acid for p-nitrophenol and phenol, respectively).

3. Results and discussion

3.1. Materials characterisation

The lignocellulosic precursors have slightly different compositions, but in essential they have a major quantity of cellulose ($\sim 33\%$), followed by different amounts of hemicellulose (~ 26 and 22%) and lignin (~ 25 and 15%), respectively for almond shell and vine shoots. The higher content in lignin and hemicellulose is responsible for the hard nature of the almond shell when compared with the soft vine shoots [7,31].

All of the nitrogen adsorption isotherms, presented in Fig. 1, are predominantly type I in shape according to the IUPAC classification, with some variation in terms of pore volume, external surface area and micropore size [32]. These variations reflect the different nature of the precursors and the effects of the oxidation process.

From the isotherms in Fig. 1 it is possible to observe that the activated carbon samples are composed essentially of micropores and with low external surface area. Besides this, a small type H4 hysteresis loop is visible, more clearly in the case of the oxidised samples, synonymous of the presence of a small quantity of mesopores or larger micropores. The oxidation process with nitric acid lead to a reduction of the pore volume especially with the soft precursor vine shoots. This fact is also reflected in the reduction of the apparent surface area obtained by the BET method. On the other hand, the mean pore width remained constant during the oxidation. From this data, we can suggest that the oxidation with nitric acid leads to the destruction of some of the original porous structure of the activated carbon. Also, as usually observed, a slightly increase in the external surface area is obtained in this process.

The elemental analysis and point of zero charge also reflect differences between the activated carbons, namely the oxidised and non-oxidised samples. The non-oxidised activated carbons show a high value of PZC (~ 10), characteristic of carbon materials prepared by activation with CO_2 , in particular from lignocellulosic materials [7,12,13]. As expected, the oxidation lead to a reduction of the PZC to low values, between 2 and 3. The decrease is greater in the case of the soft lignocellulosic precursor (V840ox). The elemental analysis confirms this transformation in terms of an increase of the content in oxygen for the oxidised samples.

A summary of the chemical and textural characteristics for the different activated carbons are presented in Table 1.

The FTIR spectra, shown in Fig. 2, permit evaluation of the extent of the activation process with CO_2 as well as of the intensity of the oxidation procedure. In the first case, because it is well know that the reaction with the activating agent leads to the development of new functional groups that explain the basic properties of the activated carbons. The surface chemistry of the non-oxidised carbons, jointly

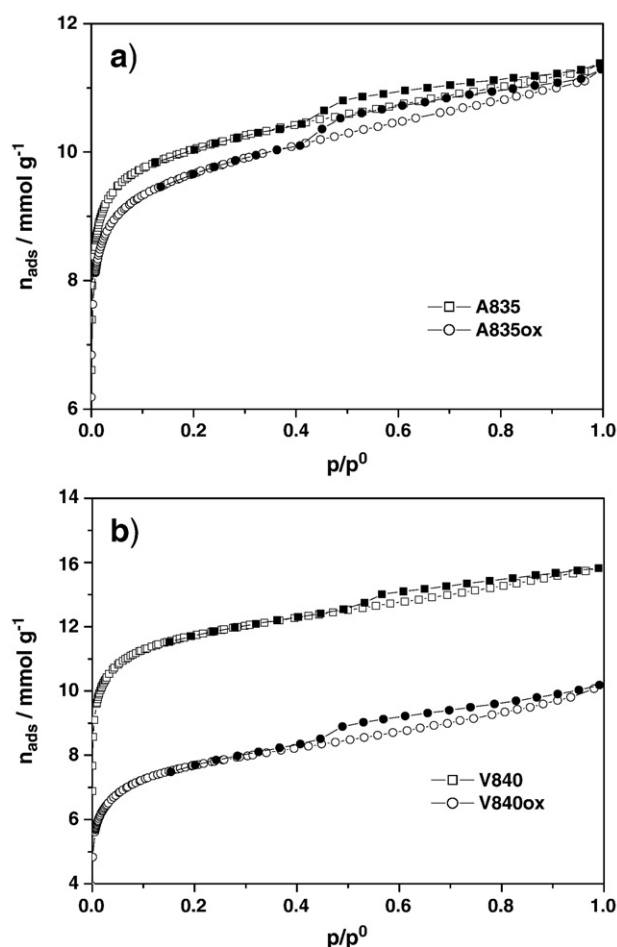


Fig. 1. Nitrogen adsorption isotherms at 77 K determined on samples prepared by physical activation and after oxidation from almond shell (a) and vine shoots (b) precursors (Open symbols represent adsorption, closed symbols represent desorption).

with the presence of delocalised π electrons in the basal planes, acting as Lewis bases, enabled us to produce carbon materials with good performance for adsorbing substances with net negative charge from the liquid phase at low pH.

In the analysis of the FTIR spectral data the usual terminology was used: *stretching* – ν ; *deformation* – δ ; *rocking* – ρ_r ; *wagging* – ρ_w ; *in plane bending* – π ; *out of plane bending* – γ . From Fig. 2 we can see that in general the non-oxidised samples show as principal functional groups: the hydroxyl group ($\nu(\text{O-H})$); bands situated at wavenumbers higher than 3500 cm^{-1} , the carbonyl bonds clearly visible in all spectra by the presence of several bands, namely quinones and lactones ($\nu(\text{C=O})$, in the characteristic range of $1700\text{--}1900\text{ cm}^{-1}$), the absorption bands at 1565 and 1556 cm^{-1} ($\nu(\text{C=C})$ vibrations in aromatic rings, bands related to the presence of pyrone groups (at $1450\text{--}1420\text{ cm}^{-1}$), bands between 990 and 1060 cm^{-1} ($\nu(\text{C-O})$ vibrations in hydroxyl groups and/or ether-type structures). In the

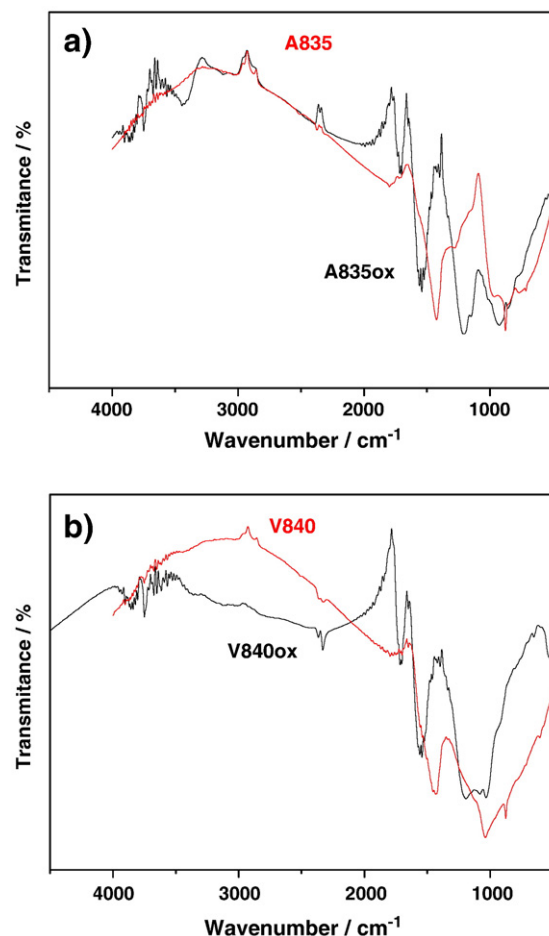


Fig. 2. FTIR spectra of samples prepared by physical activation and after oxidation from almond shell (a) and vine shoot (b) precursors.

same range other bands indicate the presence of different groups and structures containing C–O bonds, such as pyrones, bands at $\sim 874\text{ cm}^{-1}$ attributed to ρ_w (Si–H) and finally the band at $\sim 603\text{ cm}^{-1}$ assigned to γ (O–H).

In respect to the oxidised carbon samples, an increase of the functional groups that justified the change of PZC from high to lower values was observed. The oxidation leads to the formation of new functional groups such as lactones, carboxylic acid and anhydride, phenol and carbonyl groups [33,34]. Following this line, we can see in the FTIR spectra of the oxidised samples, Fig. 2, the presence of bands characteristic of lactones (1795 , $1675\text{--}1790\text{ cm}^{-1}$), carboxylic acid (1651 , 1697 cm^{-1}) and anhydride ($1740\text{--}1880\text{ cm}^{-1}$), phenol (1040 , 1165 cm^{-1}), quinone (1558 cm^{-1}) and others. In the case of V840ox some of the bands increased their intensity, which is in agreement with the low value of PZC of this sample. This is in total accordance with other lignocellulosic materials prepared in the same way.

Table 1

Structural and chemical parameters of carbon samples obtained by different techniques (A_{BET} – apparent surface area, A_s – external surface area, V_s – total pore volume and V_0 – micropore volume, L_0 – mean pore width; BET, S and O subscripts correspond to BET, α_s and DR methods, respectively).

Activated Carbon	N ₂ Adsorption						Elemental	Analysis		PZC
	A _{BET} [m ² g ^{−1}]	A _S [m ² g ^{−1}]	V _S [cm ³ g ^{−1}]	V ₀ [cm ³ g ^{−1}]	L ₀ [nm]	N [%]	C [%]	H [%]	O [%]	pH
A835	851	14	0.37	0.35	1.2	0.2	81.3	0.1	5.9	10.4
A835ox	817	18	0.36	0.33	1.1	0.9	83.1	1.5	14.1	3.0
V840	956	26	0.44	0.40	1.2	0.2	86.3	0.2	6.3	9.7
V840ox	646	41	0.29	0.25	1.2	1.1	75.3	2.2	21.2	2.3

3.2. Adsorption of phenolic compounds from the liquid phase

The adsorption of aromatic compounds by carbon materials is a complex process, namely because of the large number of variables involved, namely the characteristics of the solute, adsorbent, medium of adsorption and its temperature [35]. In particular aspects such as solubility, pKa, PZC, pore size and pH play a fundamental role in the adsorption mechanism.

The results obtained for the activated carbons tested are presented in Fig. 3, grouped by the phenolic compound. The isotherms express the mass of adsorptive adsorbed per unit mass of carbon material (mg g^{-1}) as a function of the equilibrium concentration (mmol dm^{-3}). In general, all isotherms have similar shape and can be characterised by a rapid increase in the amount adsorbed at low concentrations, and a decreasing slope for higher solute concentrations. Comparing the adsorption capacity of each sample for the two phenolic compounds it is clearly seen that the highest amount adsorbed is achieved with p-nitrophenol for all samples. Another difference is the more curved shape of the isotherms obtained with phenol when compared with p-nitrophenol. These facts can be explained by a stronger interaction of p-nitrophenol when compared with phenol [35–37].

On the other hand, comparing the different activated carbon materials the higher adsorbed quantity is obtained with the samples with better structural properties, namely higher pore volume and surface area. However, it is notable that the adsorption on the oxidised samples A835ox and V840ox is much lower, even though the difference in structural properties, especially between A835 and A835ox, is

comparatively small. Despite the good structural characteristics of the activated carbons, the changes in the surface chemistry of the oxidised samples have a negative and superior impact on the adsorption potential of A835ox and V840ox. The decrease in the PZC values and the formation of more functional groups with oxygen, such as carboxylic acid and anhydrides as determined by FTIR, reflects the intensity of the oxidation process and consequently the high facility of the water molecules to stay attached to the surface of the carbon material (via hydrogen bonds) and thereby inhibit the adsorption of the phenolic compounds. Another contribution for the lower adsorbed amount by these samples is the lower electronic density of the basal planes, due to the higher concentration of oxygen containing acidic surface groups, and which results in increased localisation of the π electrons in the graphene layers of the carbon materials. The conjugation of this fact with the experimental conditions, namely the solution pH (~ 3), which indicates that phenolic compounds are predominantly in the molecular form, leads to an impediment of a favourable π – π dispersion interaction between the aromatic ring of the adsorptives and π delocalised electrons of the adsorbent.

Another step in this work was the fitting of the most used theoretical or empirical adsorption isotherm equations to the experimental isotherms. Various kinetic models have been reported in the literature to describe and understand the adsorption process. Each model has its own limitations and is derived according to certain conditions. For convenience, explicit simple models are preferred and commonly used, and in this field, the Langmuir and Freundlich models are the most frequently employed. The Langmuir Equation, Eq. (1), is obtained under the ideal assumption of a totally homogenous adsorption surface:

$$n_{\text{ads}} = \frac{n_{\text{mL}} C_{\text{eq}} K_L}{1 + C_{\text{eq}} K_L} \quad (1)$$

where n_{ads} is the measured adsorption at a solute equilibrium concentration C_{eq} , n_{mL} is the monolayer capacity and K_L the Langmuir constant. Plotting $(C_{\text{eq}}/n_{\text{ads}})$ against C_{eq} , the parameters n_{mL} and K_L are obtained.

The Freundlich isotherm, Eq. (2), is more suitable for a highly heterogeneous surface and consequently provides a good description of non-linear adsorption isotherms:

$$n_{\text{ads}} = K_F (C_{\text{eq}})^{1/n_F} \quad (2)$$

A plot of $\ln(n_{\text{ads}})$ versus $\ln(C_{\text{eq}})$ gives the values of K_F and n_F , which are adjustable parameters whose values depend on the system.

The values obtained by the application of the equations are presented in Table 2. The calculated parameters show good agreement with the experimental results, namely the maximum amount adsorbed and also the different constants. In particular when we analyse the values of n_{mL} and K_F , measures of the amount adsorbed, the first is in general inferior to the second. Furthermore, the K_F values, which according to Eq. (2) are the adsorptions at $C_{\text{eq}} = 1 \text{ mmol dm}^{-3}$, give better agreement with the experimental isotherms. From these data we can tell that the Freundlich equation allows a better description of the experimental data than the Langmuir model. This conclusion is also in conformity with the structural and chemical properties of the activated carbons, which are materials with a high heterogeneity.

When the comparison is made for each system adsorptive-adsorbent, a larger variation for the oxidised samples (~ 11 to 38%) than for the non-oxidised samples (~ 1 to 4%) is observed. This confirms the change to greater surface heterogeneity induced by the oxidation in the liquid phase with nitric acid. It can also be seen from Table 2, that the low values of n_F and K_F are consistent with the greater curvature of the isotherms, in particular with phenol, and is one more indication of a more heterogeneous distribution of adsorption energies.

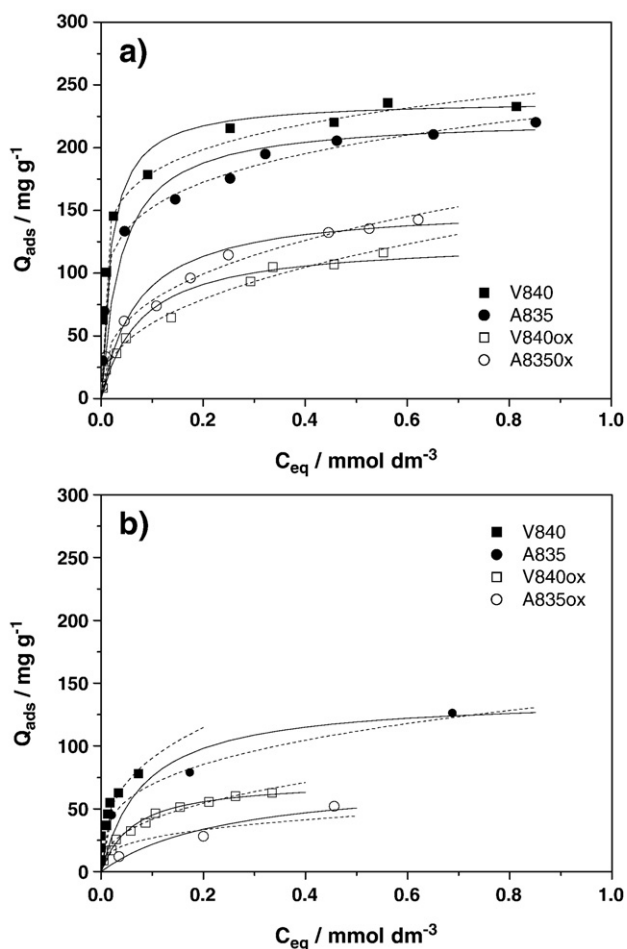


Fig. 3. Experimental adsorption isotherms of p-nitrophenol (a) and phenol (b) on V840, V840ox, A835 and A835ox activated carbons at 25 °C (solid and dashed lines represent the theoretical curves calculated by Langmuir and Freundlich equations respectively).

Table 2

Results from fitting the Langmuir and Freundlich equations to experimental isotherms on activated carbon materials (n_{ml} monolayer capacity, K_L Langmuir constant; K_F Freundlich constant, n_F Freundlich exponent).

System	Langmuir		Freundlich	
	$n_{ml}/[\text{mg g}^{-1}]$	$K_L/[\text{dm}^3 \text{mg}^{-1}]$	$K_F/[\text{units } \S]$	n_F
A835				
PNF	224	26	230	5.6
F	139	12	137	3.4
A835ox				
PNF	154	14	173	2.9
F	76	4	55	3.2
V840				
PNF	238	53	249	7.1
F	– *	– *	200	2.9
V840ox				
PNF	126	13	151	2.5
F	73	16	101	2.6

* Values not presented because the C_{eq} range is not adequate for the estimation.

§ units are $\text{mg g}^{-1}(\text{mmol dm}^{-3})^{1/n_F}$.

4. Conclusions

In this work we confirm the possibility of producing microporous activated carbon materials with good structural and chemical properties by physical activation with carbon dioxide from lignocellulosic precursors. Although a judicious choice to obtain carbon materials with similar burn-off and similar structural properties was made, it was found that the adsorbents presented different behaviour not only in the adsorption from the gas phase, namely nitrogen at 77 K, but also and mainly in the adsorption of phenolic compounds from the liquid phase.

The adsorption at 25 °C of the probe molecules phenol and p-nitrophenol is essentially controlled by the chemical properties of the adsorbent and then by their structural characteristics. Hence, we observed a favourable mechanism of adsorption when the carbon materials presented basic characteristics and the pH of the adsorptive-adsorbent system is lower than the point of zero charge (PZC). The post oxidation of the activated carbon materials did not improve the capability of adsorption in the range of equilibrium concentration studied. Comparing the two adsorptives tested, p-nitrophenol shows a better affinity for all the samples, including the oxidised materials.

Another conclusion from the treatment of activated carbon with nitric acid, was the distinct behaviour in terms of structural properties, namely the good resistance of the almond shell precursor when compared with vine shoots material, almost certainly justified by the lignocellulosic composition of the precursor materials. In this case the treatment resulted in a more extensive depletion of the materials external area without having a significant impact on the pore volume.

This work is also one more contribution to the exploitation and valorisation of solid wastes produced in different phases of cultivation practices leading to a more sustainable agriculture.

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