



Adsorption of naphthalene from aqueous solution on activated carbons obtained from bean pods

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ABSTRACT

The preparation of activated carbons from bean pods waste by chemical (K₂CO₃) and physical (water vapor) activation was investigated. The carbon prepared by chemical activation presented a more developed porous structure (surface area 1580 m² g⁻¹ and pore volume 0.809 cm³ g⁻¹) than the one obtained by water vapor activation (258 m² g⁻¹ and 0.206 cm³ g⁻¹). These carbons were explored as adsorbents for the adsorption of naphthalene from water solutions at low concentration and room temperature and their properties are compared with those of commercial activated carbons. Naphthalene adsorption on the carbons obtained from agricultural waste was stronger than that of carbon adsorbents reported in the literature. This seems to be due to the presence of large amounts of basic groups on the bean-pod-based carbons. The adsorption capacity evaluated from Freundlich equation was found to depend on both the textural and chemical properties of the carbons. Naphthalene uptake on biomass-derived carbons was 300 and 85 mg g⁻¹ for the carbon prepared by chemical and physical activation, respectively. Moreover, when the uptake is normalized per unit area of adsorbent, the least porous carbon displays enhanced naphthalene removal. The results suggest an important role of the carbon composition including mineral matter in naphthalene retention. This issue remains under investigation.

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1. Introduction

Dependence and abuse of chemicals along with an uncontrolled use and exploitation of natural resources entail one of the most adverse aspects of global industrialization. A direct consequence of the fast development of industrial activities is that the amount and variety of chemical wastes thrown into water resources has rapidly increased. The occurrence of large concentrations of toxic pollutants in wastewater has become an important environmental issue, particularly in densely populated cities where the demand for water is very high. In this regard, very often drinking water has been found to contain small amounts of a large number of synthetic organic compounds including phenols, pesticides, aliphatic and aromatic hydrocarbons, dyes, surfactants, which noxious impact in the environment and human health is not well known yet [1–3].

PAH constitute an important class of highly toxic and long persistent environmental pollutants. For recognition of their toxicity

and high mobility in the environment, the World Health Organization has recommended a limit for PAH in drinking water [1], and the European Environmental Agency (EEA) has included these compounds in its list of priority pollutants to be monitored in industrial effluents [4]. Despite this, they have been identified in a variety of waters and wastewaters [5,6], since they are associated to a number of industrial sources such as incomplete fuel combustions and cokemaking.

Faced with an increasing contamination of water resources, adsorption technology has become widely used in water treatment plants [7], since it is a well established and powerful technique due to its high depuration efficiency. Activated carbons are the most effectively used adsorbents due to their adequate porous and chemical features. Notwithstanding there is large market for activated carbons, the specific mechanism of the adsorption of many compounds (i.e., aromatics) from solution remains still ambiguous [7,8]. Liquid-phase adsorption is a more complicated process than gas phase adsorption, due to competitive interactions arising inside the multi-component solution. Besides the expected and desired adsorbate–adsorbent interactions, preferential adsorption of targeted probe could be significantly suppressed by competitive retention of a second solution component (i.e., solvent) [7–11].

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This is particularly remarkable in diluted solutions where the solvent concentration is very high, as it usually occurs with high toxic compounds.

Activated carbons can be produced from a large variety of precursors, conventionally via two methods: physical (i.e., CO₂ or steam) and chemical activation (i.e., ZnCl₂, H₃PO₄, alkaline hydroxides). Commonly used precursors include bituminous coal, wood, peat, petroleum, pitch, polymers and biomass. In this connection, a number of works report the thermo-chemical conversion of agricultural by-products and other sources of biomass as alternative precursors for the preparation of carbon-based adsorbents [12–17]. Pyrolysis of agricultural wastes enables obtaining several sub-products: char, tar and gases. The carbonaceous char turns to be a good precursor for the preparation of activated carbons.

The objective of this work was to investigate the preparation of a high value carbon material from biomass waste (i.e., bean pods) as an alternative to energy conversion, and to extend the field of the potential applications to the removal of refractarious compounds. After pyrolysis, the carbonaceous solid residue was submitted to different activation procedures (physical and chemical activation), in order to synthesize the adsorbents. The capacity of these materials for the removal of naphthalene – one of the most abundant polycyclic aromatic compounds in wastewater – from diluted aqueous solutions was evaluated and compared to that reported in the literature for other adsorbents [9,11].

2. Experimental

2.1. Material and methods

2.1.1. Preparation of the activated carbons

2.1.1.1. Activation with water vapor. Bean pods were used as carbonaceous precursor for the preparation of activated carbons. Around 50 g of the raw material (fraction of 1–5 mm) was heated in a laboratory installation at atmospheric pressure and heating rate of 60 °C min⁻¹ up to a carbonization temperature of 600 °C. The sample was maintained at the final temperature for 10 min, and then cooled down to ambient temperature. After that the solid product was activated at 700 °C with water vapor for 1 h time of activation (carbon A).

2.1.1.2. Chemical activation with K₂CO₃. The initial material of bean pods was ground to 0.5 mm particle size. The activation process involved mixing of the initial material and the activating agent in water, in a ratio reagent to bean pods material of 4:6. The mixing was performed at room temperature under stirring for 12 h. After mixing, the slurry was subjected to drying at 110 °C overnight. The chemical-loaded sample was then carbonized in a N₂ atmosphere. Carbonization was carried out by heating the sample at 10 °C min⁻¹ from room temperature up to 950 °C, and then heated at this temperature for 10 min. After cooling under N₂, the carbonized product was washed to remove the residual chemical. The final product was then dried at 110 °C (activated carbon B).

For comparison purposes, a sample (carbon PC47) obtained from physical activation of plastic residues up to a burn-off degree of 47% was prepared, following the procedure described elsewhere [18,19].

2.2. Characterization of porous texture

Textural characterization was carried out by measuring the N₂ adsorption isotherms at –196 °C in an automatic apparatus (Micrometrics ASAP 2010 M). Before the experiments, the samples were outgassed under vacuum at 300 °C overnight. The isotherms were used to calculate specific surface area S_{BET}, total pore volume V_T, and micropore volume W₀ using the DR equation [20]. The mean pore

size *L* was evaluated from the Stoeckli–Ballerini equation [21], as $L = 10.8/(E_0 - 11.4)$. The micropore surface area S_{mic}, was evaluated according to the equation $S_{mic} = 2W_0/L$ [22].

2.3. Oxygen functional group

The content of oxygen-containing functional groups with acidic character on the carbon surface was determined applying the Boehm method by neutralization with bases of increasing strength: NaHCO₃, Na₂CO₃, NaOH and sodium ethoxide [23]. About 0.5 g (±0.0001 g) of the carbon was put in contact with 100 ml of 0.05 N base solution in sealed flasks. The suspensions were shaken at least 16 h, and then filtered. The excess of base remaining in the solution was determined from back titration after adding an excess of standard HCl solution. It was assumed that sodium NaHCO₃ was capable of neutralizing all carboxylic groups, Na₂CO₃ – carboxylic and lactonic groups, NaOH – carboxylic, lactonic and phenolic groups, and sodium ethoxide was assumed to neutralize all acidic groups. The total number of basic sites was determined with 0.05 N HCl [24]. The procedure is the same as above mentioned, as back-titration of the excess of HCl was performed using titration with 0.05 N NaOH solution.

2.4. pH measurements

The pH of the carbons was measured according to the following procedure: exactly 4.0 g of carbon was weighed into a 250-ml beaker, and 100 ml of water was added. The beaker was covered with a watch glass, and the mixture was boiled for 5 min. The suspension was set aside, and the supernatant liquid was poured off as hot as possible but not below 60 °C. The decanted portion was cooled to ambient temperature and its pH was measured to the nearest 0.1 pH unit.

2.5. Point of zero charge (PZC)

The nature of the carbon surface was determined from the pH value corresponding to the point of zero charge (PZC). This was measured by the mass titration method as described by Noh and Schwarz [25], employing the following procedure. Briefly, the activated carbon was dispersed in a suitable volume of distilled water and stored with constant stirring under a nitrogen atmosphere at room temperature until equilibrium was attained (ca. 48 h). Typical activated carbon/water ratios employed were 1, 2, 4, 6, 8, 10, 12, 14 and 16. Once equilibrium had been reached, the pH value was measured via a glass electrode. Newly portion of distilled water was then added in order to obtain the next solid/weight fraction. The plateau in the plot of equilibrium pH versus solid weight fraction corresponded to the PZC value of the activated carbon.

2.6. IR spectroscopy

The carbon samples were analyzed using FTIR spectroscopy (using Bruker IFS 113V). The samples were mixed with potassium bromide and the mixture was pressed into pellets to be used in the analysis. The raw precursor and the as-prepared samples were further characterized by ultimate and proximate analyses (Table 1).

2.7. Adsorption measurements

Adsorption measurements of naphthalene from aqueous solutions on carbon adsorbents were performed at room temperature in a stirred batch system, thermostatically controlled with an external circulating bath. Kinetic studies revealed that the adsorption

Table 1

Proximate and ultimate analysis (wt.%) of the raw precursor (bean pods) and the activated carbons obtained by different activation procedures

	Proximate analysis		Ultimate analysis				
	Ash	Volatiles	C	H	N	S	O
Raw material	6.09	80.07	43.25	5.98	0.92	0.11	49.74
Carbon A	22.8	30.26	60.25	3.90	0.73	0.16	34.96
Carbon B	10.8	BDL	83.74	1.51	0.52	0.10	14.13

BDL: below detection limit.

equilibrium was established after 3 days. Details of the procedure followed for the measurement of the adsorption isotherms are described elsewhere [9]. Briefly, different amounts of carbons (from 3 mg to 40 mg) were weighed and added to flasks containing 100 ml of a naphthalene solution with concentration 30 mg l^{-1} (solution pH ~ 5.5). The covered flasks were shaken for 72 h at a constant temperature. Initial and equilibrium concentrations of the aqueous solutions were measured using a UV spectrometer at a wavelength of 275.5 nm. In addition, a blank was checked for every experiment to verify that there was no adsorbate volatilization or adsorption on the walls. The amount of solute adsorbed per unit gram of adsorbent q_e , was evaluated from the equation:

$$q_e = \frac{V(C_0 - C_e)}{M} \quad (1)$$

where V is the volume of the solution, C_0 is the initial concentration of the adsorbate solution, C_e is the concentration of the solute in the bulk phase at equilibrium and M is the mass of the adsorbent.

The equilibrium data were fitted to the Freundlich isotherm [26]. This is an empirical model based on the assumption that the surface is energetically heterogeneous and therefore not all the adsorption sites are equally active. It also considers a likelihood of appearing of intermolecular interactions between the adsorbate molecules. This equation was used in the form:

$$q_e = K_f C_e^{1/n} \quad (2)$$

where q is the amount adsorbed per gram of adsorbent, C is the adsorbate concentration in the liquid phase, n is an empirical parameter representing the heterogeneity of site energies and K_f is the unit capacity factor related to the adsorbent capacity.

3. Results and discussion

3.1. Chemical composition

Analysis of the chemical composition of the initial waste showed that the bean pods used as carbon source are mainly composed of cellulose and hemi-cellulose (33.03 and 45.46 wt.%, respectively), lignin (17.24 wt.%), and a small amount of lipids (4.47 wt.%). From ultimate and proximate analyses (Table 1) it was observed that agricultural waste bean pods contain relatively high volatile matter, along with a large oxygen content (almost 50 wt.%).

Previous studies carried out in our research group have shown that the composition of agricultural by-products has a strong influence on the final porous and chemical features of the solid products obtained from pyrolysis and activation [17]. It was found that high contents of lignin favor the development of a macroporous structure, whereas cellulose yields predominantly microporous materials. Bean pods exhibit a combination of large quantities of cellulose and lignin, which makes this material an excellent candidate for preparation of carbons, probably with well-developed micro- and macroporosity.

Details from chemical composition data of the raw precursor and the prepared carbons are compiled in Table 1. Activated car-

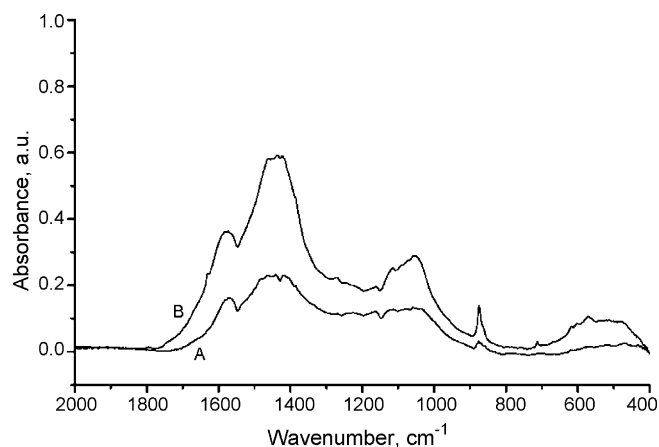


Fig. 1. IR spectra of different modifications of carbons, obtained from bean pods.

bons from bean pods have relatively high ash content, and relatively high amount of oxygen. Comparatively, carbon B obtained by chemical activation presents a lower amount of oxygen than the carbon obtained by pyrolysis in the presence of water vapor. Also, the ash content in B sample is 2 times lower than typical values reported in the literature [12–16,27]. Probably this trend may be due to partial removal of mineral matter by reaction with the potassium carbonate, used as activating agent. It should be noted that in general the activated carbons studied here have lower ash contents than others when biomass waste is used as carbon source (up to 50%) [27].

3.2. Oxygen functional groups content

The identification and quantification of the oxygen groups present in the prepared carbons is shown in Table 2. Despite the large amount of oxygen, the values of PZC revealed that the surface groups are predominantly of basic nature. Acidic groups (carboxylic or lactone-like binding structures) were not detected by Boehm titration, whereas phenolic hydroxyl and carbonyl groups were present in both carbons. The amount of basic groups is nearly six times higher for carbon A, which is in good agreement with the PZC values. Such basic functionalities could be due to the presence of oxygen containing groups of basic nature or related to species in the inorganic matter of this carbon sample (which accounts for more than 30 wt.%).

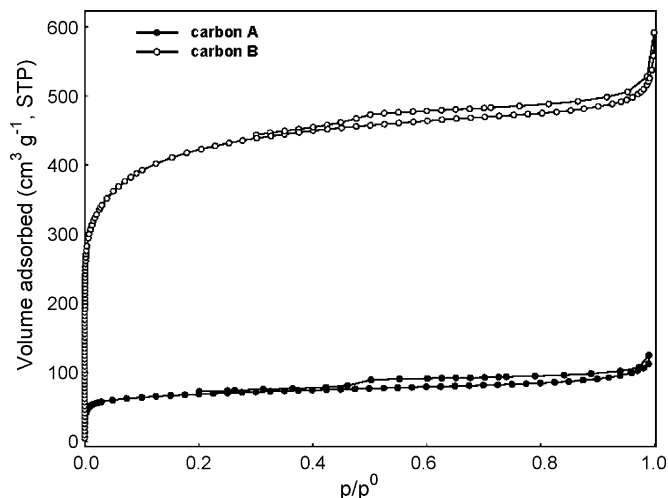


Fig. 2. Nitrogen adsorption-desorption isotherms of the studied carbons.

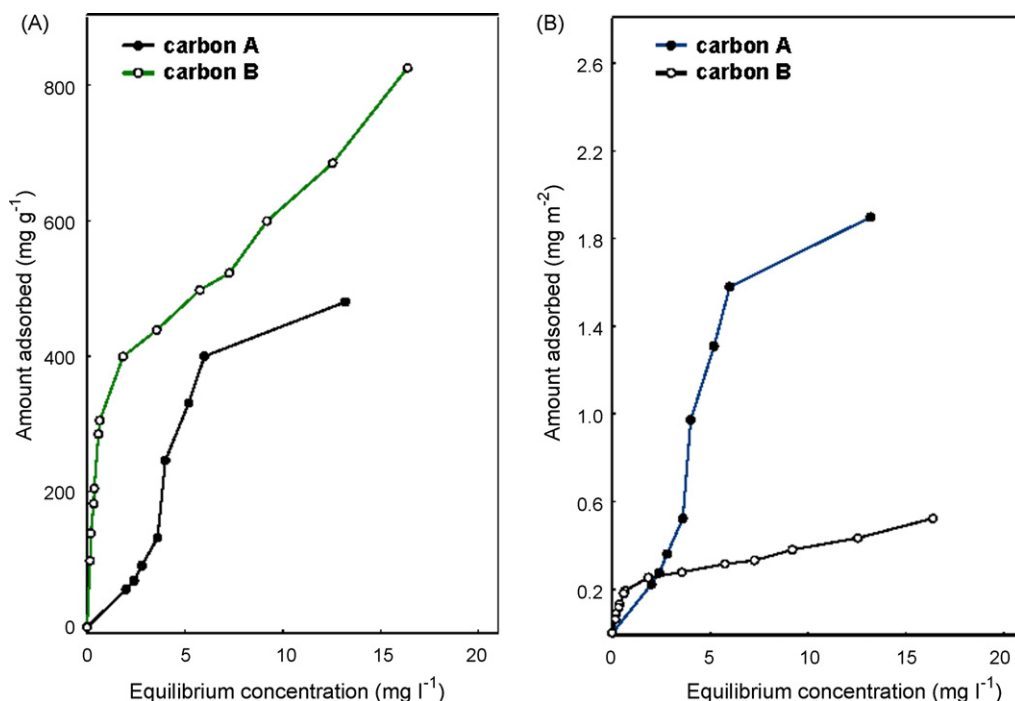


Fig. 3. Adsorption isotherms of naphthalene on the series of carbons obtained from activation of bean pods. (A) Absolute adsorption isotherms in terms of mg g^{-1} and (B) normalized adsorption isotherms per unit area of adsorbent.

IR spectra of the samples are depicted in Fig. 1. It is worth to notice that all the bands are more intense for the carbon obtained by chemical activation than for this, prepared by steam activation. The band detected at 1574 cm^{-1} in the carbon obtained by K_2CO_3 activation is shifted to 1567 cm^{-1} in the carbon obtained by pyrolysis in steam. Assignments of the bands to different surface functionalities were made according to the literature

[28–30]. This band is assigned to ring vibrations in large condensed aromatic skeletons. The band with maximum at 1460 cm^{-1} is attributed to C–H stretching modes. The bands in the region $1400\text{--}1380\text{ cm}^{-1}$, that also appear, can be ascribed to aromatic C=C bond and various substitution modes of the aromatic ring. The bands in the region $1200\text{--}1000\text{ cm}^{-1}$ have been assigned to C–O stretching modes in alcohols, phenols, ethers and esters.

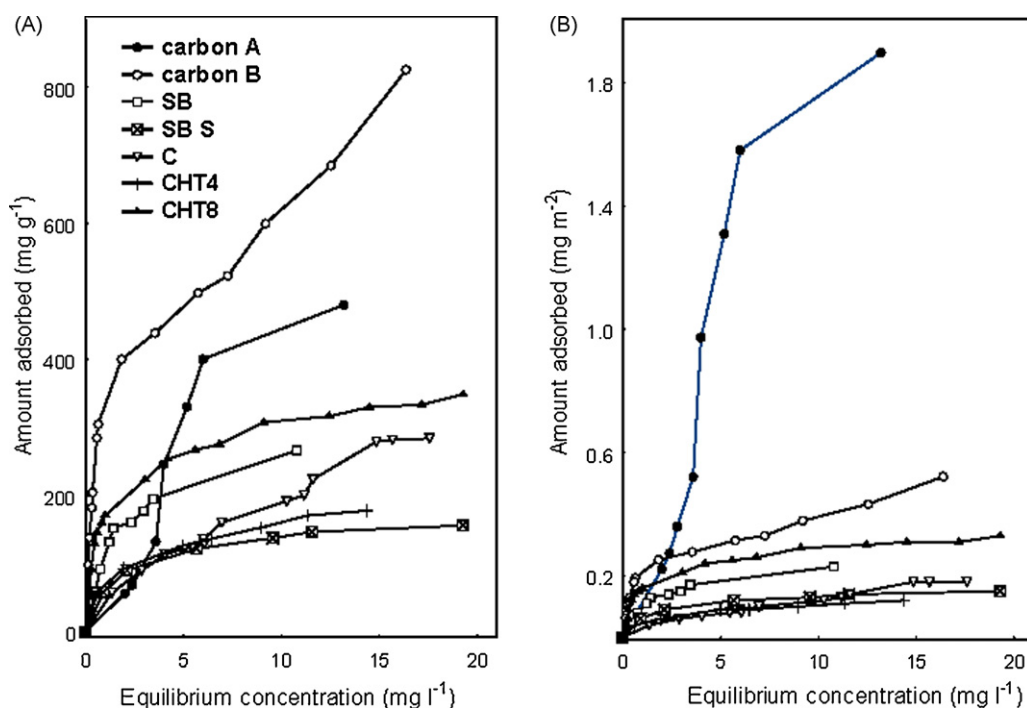


Fig. 4. Comparison of naphthalene retention using commercial carbons with different porous and chemical features [9,11]. (A) Absolute adsorption isotherms in terms of mg g^{-1} and (B) normalized adsorption isotherms per unit area of adsorbent.

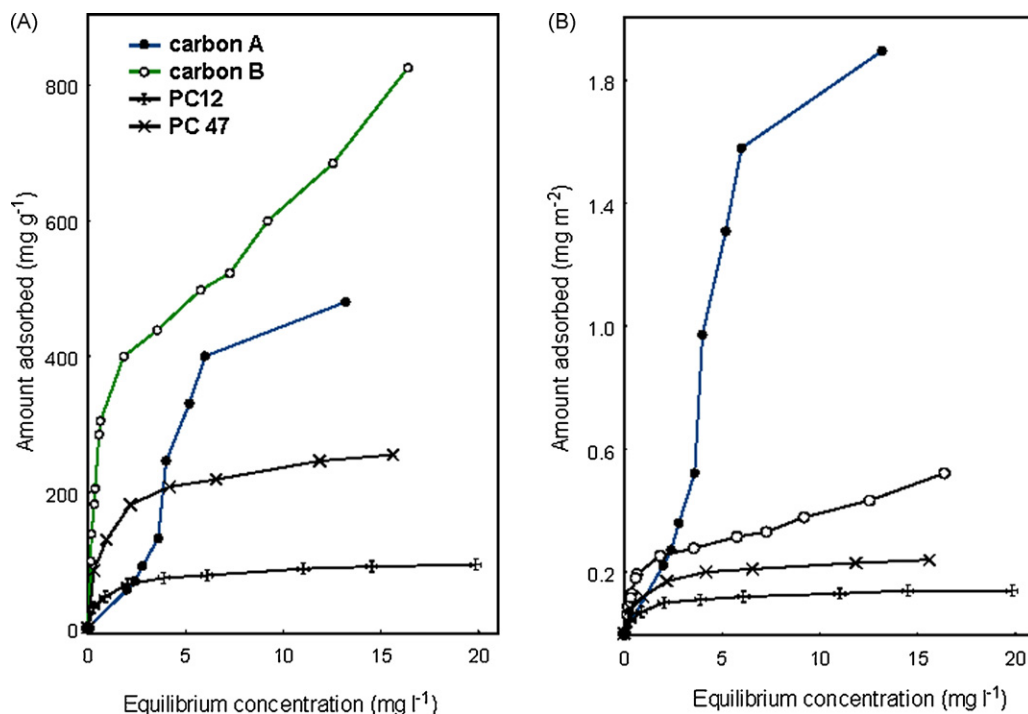


Fig. 5. Comparison of naphthalene retention using activated carbons from plastic waste [18,19]. (A) Absolute adsorption isotherms in terms of mg g^{-1} and (B) normalized adsorption isotherms per unit area of adsorbent.

The peak at 880 cm^{-1} is assigned to polycyclic aromatic skeleton structures.

3.3. Textural properties

Detailed characteristics of the pore structure of the prepared carbons are summarized in Table 3. The nitrogen adsorption isotherms are shown in Fig. 2.

Table 2

pH, point of zero charge and quantification of the oxygenated surface groups evaluated by the Boehm method and expressed in terms of mequiv. g^{-1}

	pH	PZC	Acidic groups				Total basic
			Carboxyl	Lactonic	Hydroxyl	Carbonyl	
Carbon A	10.7	11.90	BDL	BDL	0.21	1.52	7.40
Carbon B	8.2	9.21	BDL	BDL	0.53	2.37	1.38

BDL: below detection limit.

Table 3

Textural parameters of the series of activated carbons, evaluated from the DR method applied to the N_2 adsorption isotherms at -196°C

	Reference	S_{BET} ($\text{m}^2\text{ g}^{-1}$)	C_{BET}	V_{T} ($\text{cm}^3\text{ g}^{-1}$)	DR method			
					W_0 ($\text{cm}^3\text{ g}^{-1}$)	E_0 (kJ mol^{-1})	L (nm)	S_{mic} ($\text{m}^2\text{ g}^{-1}$)
Carbon A	This work	258	637	0.206	0.107	16.84	1.99	100
Carbon B	This work	1580	341	0.809	0.649	18.75	1.47	830
Modified commercial activated carbons								
SB	[9]	1156	249	0.646	0.429	18.64	1.49	576
SB S	[9]	1048	256	0.559	0.388	19.28	1.37	566
C	[11]	1548	182	0.963	0.493	16.84	1.99	497
CHT4	[11]	1489	172	0.906	0.491	17.33	1.82	539
CHT8	[11]	1063	266	0.630	0.373	20.35	1.21	618
Activated carbons obtained from plastic wastes								
PC12	[26,27]	668	1976	0.265	0.250	27.80	0.66	629
PC47	This work	1049	823	0.472	0.426	21.41	1.08	759

For comparison purposes, data of several activated carbons from literature have also been compiled.

It is observed that the isotherm of carbon A presents a type I–IV hybrid shape, according to the BDDT classification [31], with a hysteresis loop (H4 types) in the desorption branch at relative pressures above 0.5, which is associated with capillary condensation in slit-shaped mesopores [22]. On the contrary, carbon B gives type I isotherm, characterized by a large plateau (corresponding to the filling of the monolayer), indicating that the sample is mainly microporous and that the pores are rather of uniform sizes. The amount of nitrogen adsorbed on carbon B gradually increases in the whole relative pressure range, implying that this carbon also contains a small amount of mesopores. Comparatively, carbon B presents a much higher N_2 adsorption, indicating better development of the porosity after chemical activation.

Analysis of the nitrogen adsorption data using several equations indicates, that chemical activation brings about a large apparent surface area (S_{BET}) and micropore volume, as opposed to steam pyrolysis (carbon A). Moreover, the average pore width (L), evaluated from the Stoeckli–Ballerini equation [21], confirms that carbon

A possesses larger pores. This is in good agreement with earlier results on the development of macroporosity from lignin-enriched biomass precursors [17].

Detailed analysis of the obtained data allow us to suggest the possibility of pore opening during chemical activation, attributed to the gasification of the samples; as a consequence of the chemical reactions between the carbon matrix, the gases desorbed upon heating (i.e. volatile matter and other gases arising from the decomposition of the surface functionalities) and the activating agent. On the contrary, during steam pyrolysis the amount of gases evolved is lower, as corroborated by the chemical composition of the carbon (Table 1); therefore the degree of activation and the porosity developed are lower.

It may be inferred that the final porous features of activated carbons, obtained from agricultural by-products depend not only on the composition of the precursors, but on the activation procedure also. In this sense, chemical activation favors the development of microporosity, whereas steam activation brings about pores of larger size.

3.4. Adsorption from solution

The adsorption isotherms of naphthalene from water solution of the prepared activated carbons are depicted in Fig. 3. For comparison purposes, naphthalene adsorption isotherms of commercial carbons with different porous and chemical features and of a series of lab-made carbons obtained from plastic wastes [9,11,18,19], have also been included (Figs. 4 and 5).

The different initial shapes of the isotherms for naphthalene adsorption on both activated carbons suggest that adsorption occurred via different pathways. Naphthalene retention on the carbon B sample belongs to the L type according to the Giles classification [32]. At converse, carbon A displays a sigmoid-shaped isotherm (S-type in the Giles classification), with a concave shape at low concentrations (lower than 4 ppm), which increases with the rise in the concentration of adsorbate in solution. It seems that when sufficient concentration of naphthalene molecules is present, the rate and amount of adsorption is accelerated.

Earlier investigations have suggested that according to the non-polar character of naphthalene, retention is favored in carbons of a hydrophobic nature [9,11], where dispersive interactions with the graphene layers of the carbons are enhanced. Nevertheless, when the carbons possess high content of mineral matter, even though they may exhibit hydrophobic character, competitive effects may appear.

It is known that water molecules can effectively compete with aromatics for the adsorption sites, this effect being more remarkable in hydrophilic adsorbents [9,33]. In this case, taking into account the high oxygen content (although of a basic nature) of our adsorbents, the interactions due to the formation of water clusters via H-bonding with oxygen groups are plausible. Moreover, proton binding may also occur between water molecules and oxides on the carbon surface, particularly in carbons with high content of mineral matter, as those reported in this work. Such interactions would largely suppress the retention of the targeted probe (i.e., naphthalene) at low concentrations, leading to the S-class isotherm [34,35].

Table 4
Freundlich adsorption parameters and correlation coefficient for naphthalene removal

	K_f (mg g ⁻¹)	n	R^2	K'_f (mg m ⁻²)
Carbon A	85	1.40	0.9080	0.336
Carbon B	300	3.07	0.9794	0.190

Adsorption capacity normalized per unit surface area (K'_f) has also been included.

The adsorptive capacity of the carbons was obtained by fitting the experimental data to the Freundlich approach, in terms of the amount of naphthalene adsorbed per unit mass of adsorbent. Due to the extremely large difference in porosity of all samples, the adsorptive capacities were normalized by the surface area. They are also listed in Table 4 as K'_f .

Although the absolute capacities for naphthalene adsorption differ significantly and a high uptake is obtained for carbon B, which has more developed porous texture, when the capacities are normalized per unit surface area (K'_f), the importance of the chemical composition and of the acidic/basic nature of the adsorbent for naphthalene removal is clearly visible (Fig. 3B). It should be bare in mind that the overall amount of basic groups is nearly 6 times higher in carbon A than this in carbon B.

While the isotherm on carbon B shows the limiting effect of the pore sizes/pore volume for the physical adsorption process (type-L isotherm in the Giles classification), the S-shape of the isotherm in carbon A after area normalization confirms, that either cooperative adsorption of naphthalene molecules is involved in the retention, or that some kind of competing reaction within the solution is occurring for this carbon. Although, as mentioned above, A carbon possesses a poor porous texture, it does contain a large proportion of basic sites (Table 2). We would expect the vast majority of those groups to be accessible to naphthalene molecule, as the porous network of the carbon is composed of large pores according to the L parameter. As seen from Table 3, the surface of carbon A represents about 16% of the surface area of carbon B. Nevertheless, when the adsorption capacity is normalized to the available surface area, the carbon obtained from steam pyrolysis outperforms the carbon B by almost 2 times (Fig. 3A).

According to literature, the magnitude of n exponent in the Freundlich model is an indication of the favorability of the adsorbent/adsorbate system, with values of $n < 1$ representing low affinity of the adsorbate for the adsorbent [35,36]. Likewise, $n > 1$ is an indication of favorable adsorption. For the series of carbons obtained from bean-pods, it is noticed that n value is higher than 1. For both carbons obtained from bean-pods, it should be noticed that the n value is higher than 1. The n value of the sample obtained from steam pyrolysis (Table 4) is lower. The value of this parameter for the high concentration range in the isotherm of A carbon indicates a good adsorption affinity of naphthalene.

The outstanding properties of the bean pods-based carbons for the retention of naphthalene can be inferred when comparing experimental data with the performance of series of commercial activated carbons (Fig. 4), and data for home-made carbons obtained from plastic wastes (Fig. 5). Details on the preparation and characterization of these carbons have been reported elsewhere [9,11,18,19]. It is remarkable that the carbons, obtained from activation of bean-pods, present higher naphthalene adsorption capacities than commercial carbons possessing larger porous features and varied surface chemistry. Uptake is even better than the capacity of carbons obtained from plastic wastes with similar areas, therefore putting forward the benefits of an adequate surface chemistry and composition. These results show the adequateness of the adsorbents to be used for the purification of wastewater polluted with PAH, such as water discharge from coke-making industry. Moreover, the role of the hydrophobic nature of the carbons, along with an enhanced basicity, coming from the high oxygen and mineral matter contents, contribute to enhanced removal of naphthalene.

4. Conclusions

Activated carbons, obtained from activation of agricultural sub-products, have resulted to be very good adsorbent for naphthalene

removal from diluted aqueous solution. Experimental data have confirmed the importance of both porous structure and basic nature of the activated carbons in the process of adsorption of the naphthalene.

At low naphthalene concentrations, the surface chemistry of the carbon, obtained by pyrolysis in the presence of water vapor, is important and it affects the adsorption behavior. Absolute adsorption capacities increase with an increase in the surface area and micropore volume of the carbons, being the adsorption greater for the carbon prepared by chemical activation with K_2CO_3 . However, when the maximum uptake is normalized versus the surface area, the outstanding role of the surface chemistry of the carbon is clearly shown. Hence, the carbon with lower porous features, obtained by pyrolysis under steam, presented enhanced values of adsorption per unit surface area. Moreover, when compared to commercial activated carbons and adsorbents, prepared from plastic wastes, the samples obtained from bean-pods activation presented larger adsorption capacities for naphthalene uptake. These results suggest that the basic character of our adsorbents – provided by the 2-fold effect of oxygen and mineral matter – is key factor for understanding the adsorption behavior.

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