Adsorption (2008) 14: 343–355
DOI 10.1007/s10450-007-9096-3

Naphthalene adsorption on activated carbons using solvents of different polarity

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Received: 30 April 2007 / Revised: 28 September 2007 / Accepted: 20 December 2007 / Published online: 11 January 2008

Abstract The hydrophobic-hydrophilic character of a series of microporous activated carbons was explored as a key factor in competitive adsorption of a non-polar compound from liquid phase. The selectivity of the carbon surface towards naphthalene was explored by performing the adsorption isotherms in water, cyclohexane and heptane. Solvent polarity and adsorbent hydrophobic character were found to strongly influence the adsorption capacity of naphthalene. In aqueous media, despite the non-polar character of the adsorbate, surface acidity lowered adsorption capacity. This is attributed to the competition of water from the adsorption sites, via H-bonding with surface functionalities and the formation of hydration clusters that reduce the accessibility and affinity of naphthalene to the inner pore structure. In organic media the uptake decreased due to competition of the hydrophobic solvent for the active sites of the carbon and to solvation effects. This competitive effect of the solvent is minimized in oxidized carbons as opposed to the trend obtained in aqueous solutions. The results confirmed that although adsorption of naphthalene strongly depends on the narrow microporosity of the adsorbent, competitive adsorption of the solvent for the active sites becomes important.

Keywords Hydrophobicity · Surface polarity · Organic solvents · Naphthalene · Adsorption

Abbreviations

S_{BET}	Apparent specific surface obtained from the nitrogen adsorption data at −196 °C by the BET model ($\mathrm{m^2\,g^{-1}}$)
p	Pressure
p_0	Saturation pressure
V_{MICRO}	Micropore volume, obtained from the nitrogen adsorption data at −196 °C, by the *t*-plot method ($\mathrm{cm^3\,g^{-1}}$)
V_{MESO}	Mesopores volume, obtained from the nitrogen adsorption data at −196 °C, by the *t*-plot method ($\mathrm{cm^3\,g^{-1}}$)
V_{TOTAL}	Total pore obtained from the nitrogen adsorption at −196 °C, and evaluated at $p/p_0 \sim 0.95$ ($\mathrm{cm^3\,g^{-1}}$)
$\mathrm{pH_{PZC}}$	pH of the point of zero charge (pH units)
q	Amount of naphthalene adsorbed ($\mathrm{mg\,g^{-1}}$)
q_e	Amount of naphthalene adsorbed at equilibrium ($\mathrm{mg\,g^{-1}}$)
C	Solution concentration ($\mathrm{mg\,L^{-1}}$)
C_0	Initial solution concentration ($\mathrm{mg\,L^{-1}}$)
DR	Dubinin-Radushkevich method
S_{EXT}	External surface area, obtained from the nitrogen adsorption data at −196 °C, by the *t*-plot method ($\mathrm{m^2\,g^{-1}}$)
S_{MICRO}	Microporous surface area, obtained from the nitrogen adsorption data at −196 °C, by the *t*-plot method ($\mathrm{m^2\,g^{-1}}$)

1 Introduction

Polycyclic aromatic hydrocarbons (PAH) constitute an important class of highly toxic environmental pollutants, which are metabolized into derivatives capable of reacting with

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DNA to promote mutagenic and carcinogenic responses (Williams 1990). In recognition of their high mobility and long persistence in the environment, the World Health Organization has recommended a limit for PAH in drinking water (WHO 2006), and the European Environmental Agency (EEA) has included these compounds in its list of priority pollutants to be monitored in industrial effluents (Directive 2000/60/EC). Despite this, they have been identified in a variety of waters and wastewaters (Douben 2003; Williams 1990) since they are associated to a number of industrial sources such as incomplete fuel combustions and cokemaking. As a consequence of their low biodegradability, adsorption on activated carbons is nowadays one of the most attractive techniques for the removal of PAH from wastewater. In this work we report the removal of naphthalene from liquid phase on activated carbon. This compound was chosen as a representative PAH in our study, given that it is one of the most frequently found in wastewater from industrial activities.

Although activated carbon has been widely used as an adsorbent in environmental remediation for a long time, investigation of the mechanisms of adsorption of aromatic compounds and the role of the characteristics of the adsorbent are still ambiguous and remain unclear (Walters and Luthy 1984; Seredych et al. 2004, 2005; Ania et al. 2007a, 2007b).

For a given activated carbon, it is considered that the capacity and rate of adsorption depend on the nature of the adsorbed molecule. In general, non-polar compounds are retained due to dispersive forces, whereas the adsorption of polar compounds involves specific interactions via oxygen species present at the surface (Radovic et al. 2000). As the carbon surface is hydrophobic in nature, it is generally accepted that dispersive forces have a predominant effect. However, at the solid/liquid interface the mechanism of adsorption becomes quite complex. Besides the expected adsorbate-adsorbent interactions, one must consider the likely solvent-adsorbate and solvent-adsorbent interactions that arise when the liquid phase is not a pure compound but a solution.

Contrary to gas phase adsorption, investigations on the effect of water competitive adsorption on liquid phase are very scarce (Pires et al. 2003; Ahnert et al. 2003; Ania et al. 2007a, 2007b). In an aqueous medium, the presence of even relatively small amounts of oxygen groups on the carbon can affect its surface properties, in terms of polarity and/or hydrophilic character; as a result, water may be readily adsorbed on the carbon surface and non-cooperative adsorption arises due to occupancy of active sites of adsorption by water clusters (Müller and Gubbins 1998; Pan and Jaroniec 1996). Thus, the preferential adsorption of the targeted probe can be significantly suppressed by competitive retention of a second component. In other words, adsorption capacity and adsorption selectivity can be dominated by the hydrophobic character of the adsorbent and the interactions with the solvent.

The goal of this study was to understand the competitive adsorption between naphthalene and water in aqueous medium on porous carbons. Our purpose is to demonstrate that, even in the case of a non-polar adsorbate, the hydrophilic nature of the carbon surface becomes critical when adsorption is carried out from aqueous solutions, due to the specific interactions of bulk water with the carbon surface (via hydrogen-bonding). To this aim, the adsorption capacity of naphthalene was evaluated using solvents with different polarity, ranging from high (water) to low dielectric constants (cyclohexane and heptane). Using combinations of organic solvents and solutes and carbons with different amounts of surface oxygen groups, the effects of carbon surface polarity on the adsorption of a non-polar aromatic compound (naphthalene) was determined.

2 Experimental

Activated carbons A commercial activated carbon -B-, obtained from physical activation of coal was used as starting material. A series of carbons with a similar porous structure but different surface chemistry was prepared by wet oxidation with nitric acid at different concentrations (20 and 60%) and ammonium persulfate as described elsewhere (Ania et al. 2004). The samples will be referred to in the text as BN20, BN60 and BS, respectively. After oxidation, the samples were washed and dried at 110 °C overnight. Before the experiments, the samples were ground, sieved and a particle size fraction of 0.71–1.0 mm was used. The ultimate analyses of the carbons are summarized in Table 1.

Textural and chemical characterization Textural characterization was carried out by measuring the N_2 (Micromeritics ASAP 2010M) adsorption isotherms at −196 °C, respectively. Before the experiments, the samples were outgassed under vacuum at 120 °C overnight. The N_2 isotherms were used to calculate the specific surface area, S_{BET}, total pore volume, V_{TOTAL}, and micropore and mesopore volumes, which were evaluated by means of the t-plot method using a nonporous carbon-coated silica (Sooty Silica) as reference material (Carrott et al. 1987). Pore size distribution functions were also calculated using the DFT model and slit-shape pore geometry. Further characterization was performed by means of ultimate analysis and the point of zero charge ($\mathrm{pH_{PZC}}$), as indicated elsewhere (Ania et al. 2007a).

X-ray photoelectron spectroscopy (XPS) The different types of functional groups were identified by X-ray photoelectron spectroscopy (XPS) in an ESCALAB MK2 (VG-Instrument) apparatus equipped with an X-ray aluminum source (K_α radiation) operating at 6.7×10^{-7} Pa. To correct the effects of sample charging the C1s peak with a binding energy (BE) of 284.6 eV was used as reference.

Table 1 Chemical and textural parameters of the series of activated carbons, evaluated from the t-plot method applied to the N_2 adsorption isotherms at −196 °C

	S_{BET} [$m^2\,g^{-1}$]	S_{MICRO} [$m^2\,g^{-1}$]	S_{EXT} [$m^2\,g^{-1}$]	V_{TOTAL} [$cm^3\,g^{-1}$]	V_{MICRO} [$cm^3\,g^{-1}$]	V_{MESO} [$cm^3\,g^{-1}$]	pH_{PZC}	O [wt. %]
B	1156	934	73	0.646	0.433	0.186	9.0	2.0
BS	1048	790	53	0.559	0.403	0.133	2.4	12.5
BN20	1003	737	49	0.532	0.377	0.129	3.5	11.3
BN60	843	645	40	0.447	0.325	0.106	2.4	18.6

Thermal analysis Thermal analysis was carried out using a TGA92 thermogravimetric analyzer from Setaram (TG). Temperature programmed desorption (TPD) experiments were carried out under a nitrogen flow rate of 50 $cm^3\,min^{-1}$, at a heating rate of 15 °C min^{-1}, up to a final temperature of 1000 °C. For each experiment, about 35 mg of a carbon sample was used.

Adsorption from solution Equilibrium adsorption isotherms for the retention of naphthalene were obtained from close batch experiments using the bottle-point technique (Leng and Pinto 1997). Adsorption isotherms were generated at 30 °C using water, cyclohexane or heptane as the solvents. Previously, kinetics measurements had been performed to determine to time need to reach equilibrium in each case (ca. 10, 7 and 3 days for cyclohexane, heptane and water, respectively). Different amounts of activated carbon were accurately weighed and placed in dark glass flasks containing a constant volume of a solution of the organic compound of initial concentration 30 ppm w/v. The flasks were covered with caps and shaken at 100 rpm until equilibrium was reached. Afterwards, the adsorbate concentration in the supernatant liquid was measured on a Shimadzu 2501 UV-Vis spectrophotometer at the corresponding wavelength. The amount adsorbed, q_e, was calculated from the equation $q_e = (C_0 - C_e) \cdot V/m$, where C_0 is the initial concentration, C_e the remaining concentration after equilibrium, V is the volume of the solution and m the mass of the adsorbent.

3 Results and discussion

Textural properties and chemical composition of the modified samples Detailed characteristics of the pore structure of the series of modified carbons are presented in Table 1. A deep discussion about the effect of the oxidation treatment on the textural properties of the activated carbons has been previously reported (Ania et al. 2007b). Briefly, oxidation in mild conditions (i.e., persulfate -BS- and 20% nitric acid -BN20-) showed a slight decrease in nitrogen uptake, as compared to the initial counterpart, indicating minor modification in the pore volume and pore sizes. The apparent surface areas of these samples decreased by 9 and 13%, respectively, whereas the volume of total micropores accessible to the nitrogen probe decreased by 13 and 18%, respectively. By contrast, this decrease reached 27% in the sample treated under the most aggressive conditions of concentrated nitric acid (BN60). The changes are more remarkable in the microporosity, suggesting the creation of new porosity upon oxidation.

A detailed analysis of the textural features was performed by calculating the pore size distribution functions from the N_2 adsorption isotherms (Fig. 1). It can be observed that the changes induced in the samples affected both the micro and mesoporosity. Oxidation brought about a widening of the microporosity whereas mesoporosity remaining somewhat constant. These results suggest an effect of open porosity with oxidation in the micropore range. This issue has been deeply discussed in a previous work (Ania et al. 2007b).

The changes in surface chemistry after oxidation and the nature of the functionalities created were studied by different techniques (i.e., point of zero charge -pH_{PZC}- and chemical analysis) and the results are summarized in Table 1. As expected, the oxidized samples become more acidic (lower pH_{PZC} values) indicating that the majority of the functionalities created are of an acidic nature. It should be underlined that BS presented an almost 1.5 times smaller oxygen content than BN60, despite their similar pH_{PZC} values. This is indicative of differences between the nature of the surface oxygen groups created in samples BS and BN60. That is, oxidation in mild conditions (i.e., ammonium persulphate) created groups of a stronger acidic character in the carbon (i.e, carboxylic acids) whereas the use of concentrated nitric acid gave rise to larger amounts of functionalities (possible phenolic groups) of a weaker acidic nature.

The nature of the surface functionalities (type and density) was evaluated from XPS. The deconvolution of the C1s spectra enabled the identification of several C-O bonds in different environments, which can be assigned to the various oxygen-containing functionalities according to the literature (Moulder et al. 1992; Terzyk 2001). The results are compiled in Table 2. The raw carbon B presented a low density and variety of oxygenated groups, which is in good agreement with its basic nature, also confirmed by ultimate analysis and the high value of pH_{PZC}. As expected, the oxidation of the carbon generated a series of adsorbents

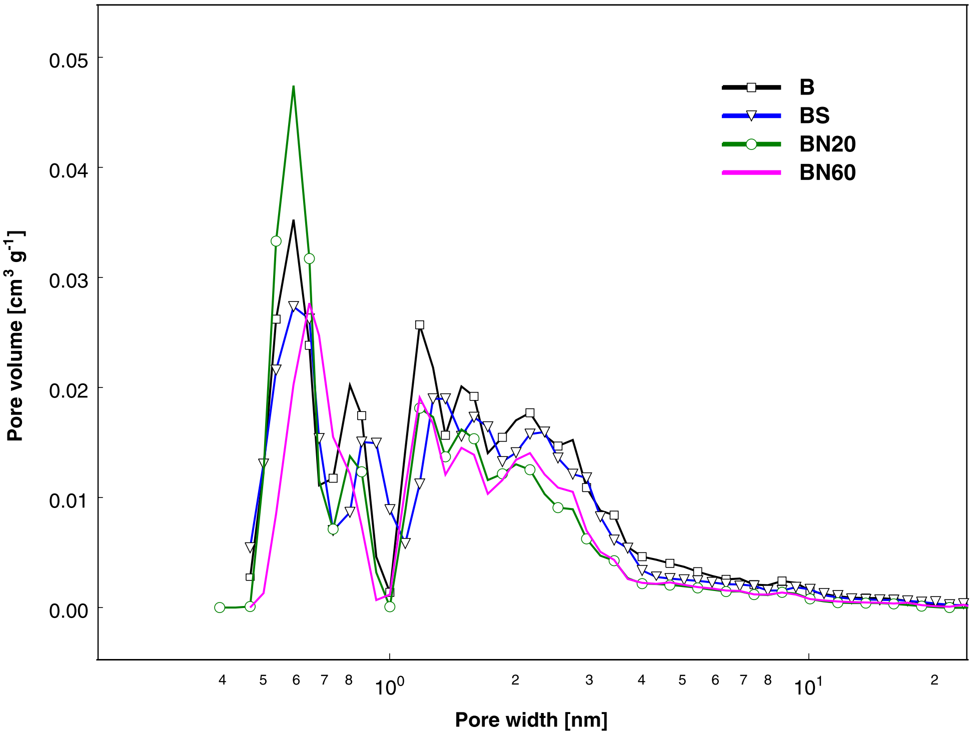


Fig. 1 Pore size distribution functions of the modified carbons, obtained from the DFT method applied to the N_2 adsorption isotherms at −196 °C

Table 2 Data obtained by fitting the C1s core level spectra of the series of modified carbons

Surface groups Assignment	BE position [eV]	B [% wt.]	BS [% wt.]	BN20 [% wt.]	BN60 [% wt.]
Phenolic, etheric (C-O-)	285.5–285.9	3.6	5.3	5.3	4.3
Carbonyl, quinone (C=O)	287.0–287.3	–	2.1	2.0	1.7
Carboxyl, ester (COO)	288.7–289.5	–	3.2	1.5	3.2
Amount O_{XPS}	–	3.6	12.4	10.2	13.8

with a wide variety of functionalities, including quinones, phenolic-type and carboxylic groups. The data indicate that acidic nature of the carbons (i.e, BS and BN60) after oxidation is attributable to large amounts of carboxylic groups. Phenol-like functionalities are also increased upon oxidation to a large extent. These results are in good agreement with those obtained from complementary techniques, previously reported (Ania et al. 2007b).

In sum, we have successfully modified the surface chemistry of an activated carbon by using different oxidizing agents, obtaining a series of adsorbents with a similar porous structure but different surface chemistry.

Adsorption of naphthalene from solutions The adsorption capacity of naphthalene was evaluated using solvents with different polarity, ranging from high (water) to low dielectric constants (cyclohexane, heptane). Using combinations of organic solvents and carbons with different surface heterogeneities allows to investigate the effect of carbon surface polarity on the competitive adsorption of a non-polar aromatic compound (naphthalene).

The octanol-water distribution coefficient K_{ow} was used as a comparative quantitative measure of the hydrophobicity of the solute and solvents. According to tabulated data from the literature (Grasselli 1991) values for cyclohexane and heptane are 2200 and 31,623, respectively, whereas the K_{ow} for naphthalene is about 2200–2800.

The free energy of solvation (ΔG_{solv}) was also used as an index for analyzing the solvent-adsorbate interactions. According to literature, the values of ΔG_{solv} are −10.04, −30.01 and −31.84 kJ/mol for water, cyclohexane and heptane, respectively (Kravtsov et al. 2007; Delgado et al. 2006; Mcdonald et al. 1997).

Figure 2 illustrates the experimental naphthalene adsorption isotherms on the series of modified carbons in the different solvents studied. As stated elsewhere (Pires et al. 2003) the shape of the adsorption isotherms is one of the most direct manifestation of the hydrophobic-hydrophilic properties of a given material. Bearing in mind this statement, first

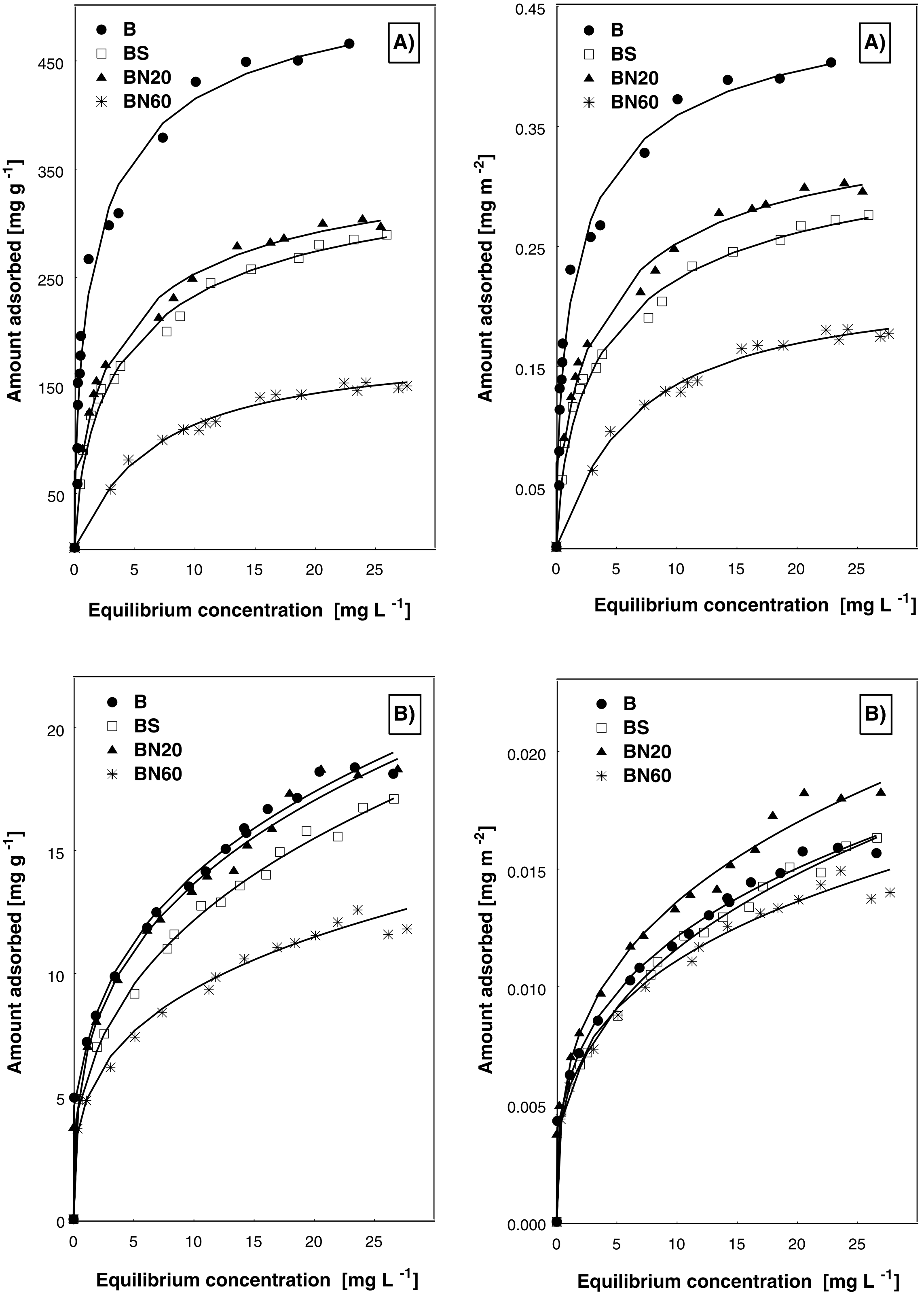


Fig. 2 ŞAdsorption isotherms of naphthalene from (**A**) water, (**B**) cyclohexane and (**C**) heptane on the series of activated carbon studied. For clarity, naphthalene uptake is expressed both in terms of mg adsorbed per gram of adsorbent [mg g^{-1}] and normalized versus the surface area of the carbons [mg m^{-2}]

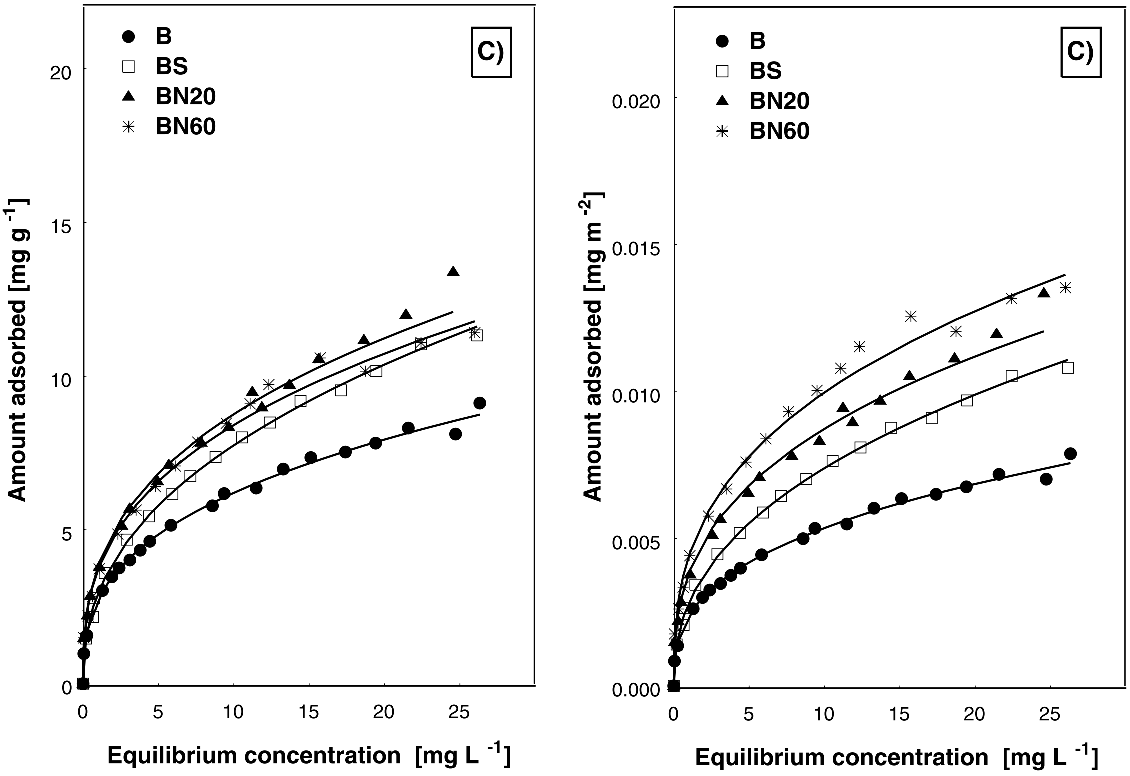


Fig. 2 (*Continued*)

useful information inferred from direct observation of the experimental isotherms, revealed that they present different shapes, suggesting different regimes of adsorption with the solvents.

For instance, isotherms in water showed the typical L-type shape (concave curvature at low equilibrium concentrations) according to the Giles classification (Giles et al. 1960), characteristic of systems where the adsorbate presents a high affinity towards the adsorbent. It should be pointed out that the curvature (i.e., L-type character) becomes less pronounced with increasing the carbon polarity. This indicates that as the hydrophilic nature of the carbon increases, the affinity of naphthalene for the adsorbent decreases. At converse, the isotherms in organic solvents media showed somewhat less L-type character regardless the carbon, suggesting a strong competition of the solvent for the active sites of adsorption. This is in good agreement with initial expectations for adsorption from strong hydrophobic organic solutions.

In order to obtain the maximum adsorption capacity at equilibrium, experimental isotherms in the three solvents were fitted to classical Freundlich (F) and Langmuir (L) models. The results are compiled in Table 3, along with the fitting parameters and correlation coefficients. Adsorption from aqueous phase showed a rather good agreement with both models, although a different behaviour was obtained for the more hydrophobic cyclohexane and heptane. In both cases, good correlation coefficients were obtained when data was fitted to the Freundlich model, whereas the Langmuir theory did not fit adequately the experimental data, as revealed by the poor correlation coefficients. These results must be explained in terms of the different assumptions of both models.

Langmuir theory (1918) is based on the assumption that all adsorption sites are equally "active", the surface is energetically homogenous and that a monolayer surface coverage is formed with no interactions between molecules adsorbed. On the other hand, the Freundlich model (1926) is an empirical equation that was originally developed to overcome some limitations of the Langmuir theory, by taking into account the surface heterogeneity and that there might exist intermolecular interactions between the adsorbate molecules. Hence, in aqueous media, good agreement with Langmuir equation indicates that the saturation limit is attained, which is also supported by the shape of the isotherms. In organic media, the adsorption capacity is long too far from the saturation limit, therefore the Langmuir model cannot explain the trend observed.

This is attributed to the large adsorbate-solvent affinity in the organic solvents, as confirmed from the ΔG_{solv} values. For instance, the free energy of solvation for naphthalene in cyclohexane and heptane is three times lower than in wa-

Table 3 Fitting parameters of the experimental naphthalene isotherms to the Freundlich and Langmuir approaches

	B			BS			BN20			BN60		
	W	Cy	hp	W	Cy	hp	W	Cy	hp	W	Cy	hp
Freundlich (F) approach												
K_F [mg g^{-1}]	221	7	3	100	6	3	119	7	4	41	5	4
n	0.26	0.31	0..36	0.35	0.34	0.42	0.31	0.31	0.36	0.42	0.29	0.38
R^2	0.976	0.994	0.997	0.963	0.994	0.995	0.979	0.994	0.991	0.934	0.992	0.994
Langmuir (L) approach												
Q_m [mg g^{-1}]	405	17	5	267	17	7	291	18	7	198	10	9
b	1.83	0.57	4.5	0.628	0.33	1.16	0.66	0.53	5.4	0.13	1.6	0.88
R^2	0.935	0.913	0.843	0.978	0.938	0.880	0.977	0.916	0.754	0.978	0.835	0.936

ter; in other words, the more negative the value is, the more stable (i.e., less reactive) is the naphthalene solution. Therefore naphthalene adsorption is energetically more favoured from aqueous phase than from organic media. This is in good agreement with the experimental adsorption isotherms (Fig. 2).

Regarding the role of surface properties of the carbons, two different trends were observed for aqueous and organic solutions. This observation is more remarkable when the isotherms are normalized vs the surface area of the carbons (where the amount adsorbed is expressed in terms of mg m^{-2}), in order to underline the effect of the surface chemistry.

One may assume that simultaneous adsorption of the solvent and hydrophobic naphthalene on the carbon surface leads to preferential adsorption of polar and non-polar species on the different carbon surface patches, hydrophilic and hydrophobic, respectively.

In general, the presence of hydrophilic centers renders the carbon surface polar, enhancing the interaction with polar liquids (i.e., water). Hence the decrease in naphthalene adsorption capacity upon oxidation of the carbon is attributed to increasing water anchoring to hydrophilic centers. The uptake follows the trend: B>BS>BN20>BN60. Furthermore, an inverse linear correlation (Fig. 3) was found between the total number of acidic groups and the amount of naphthalene adsorbed per unit area from aqueous solutions; this is, with adsorbent polarity ($R^2 = 0.998$). In contrast, when organic solvents are used, a different behaviour was observed.

When heptane is used as solvent, the strongly hydrophobic naphthalene ($K_{\text{ow}} = 2200$–2800) is surprisingly adsorbed to a larger extent in the carbons with high oxygen content. In other words, there seems to be a priori a direct relationship between the adsorption capacity of naphthalene from heptane and the polarity of the carbons. It is well known that the key factors that influence on the adsorption capacity on activated carbons are mainly twofold: (i) specific interactions, particularly H-bonding type, and (ii) dispersive/repulsive interactions between aromatic adsorbates and surface groups. Since naphthalene has not H-bonding, the trend of naphthalene uptake from heptane solution cannot be explained on the basis of specific interactions. To understand why a non-polar adsorbate as naphthalene is strongly adsorbed in adsorbents of increasing polarity, one must bear in mind several factors simultaneously; either related to changes in the hydrophobicity of the carbon surface, to competitive solvent adsorption and/or solvent-adsorbate affinity (i.e., solvation effects).

The solvation of naphthalene is greater in both organic solvents (lower ΔG_{solv}) which favours its solubility and therefore hinders the uptake in the carbonaceous adsorbent. Such higher solvation energy of naphthalene (nonpolar) in heptane and cyclohexane (nonpolar) is due to the increased interactions with the surrounding solvent shell.

Given the strong hydrophobicity of heptane ($K_{\text{ow}} = 31{,}623$), competitive adsorption of the solvent for the active sites should not be disregarded. Comparing naphthalene ($K_{\text{ow}} = 2200$) and heptane, the solvent shows much stronger hydrophobic character than the adsorbate, for which one should expect a strong competition of the former for the non-polar basal planes of the carbons. Moreover, since adsorption is performed from diluted solutions (30 ppmw/v initial concentration), the number of solvent molecules that can compete for the adsorption sites is clearly much higher than the adsorbate.

This effect of the solvent competition is more remarkable in the case of the raw carbon -B-, whose intrinsic basic nature (Table 2) turns up in a higher fraction of basal planes. Therefore, naphthalene shows a lower affinity when compared to heptane, which is traduced in a reduced adsorption capacity. In contrast, as the polarity of the surface increases, the solvent competition is minimized; by increasing the hy-

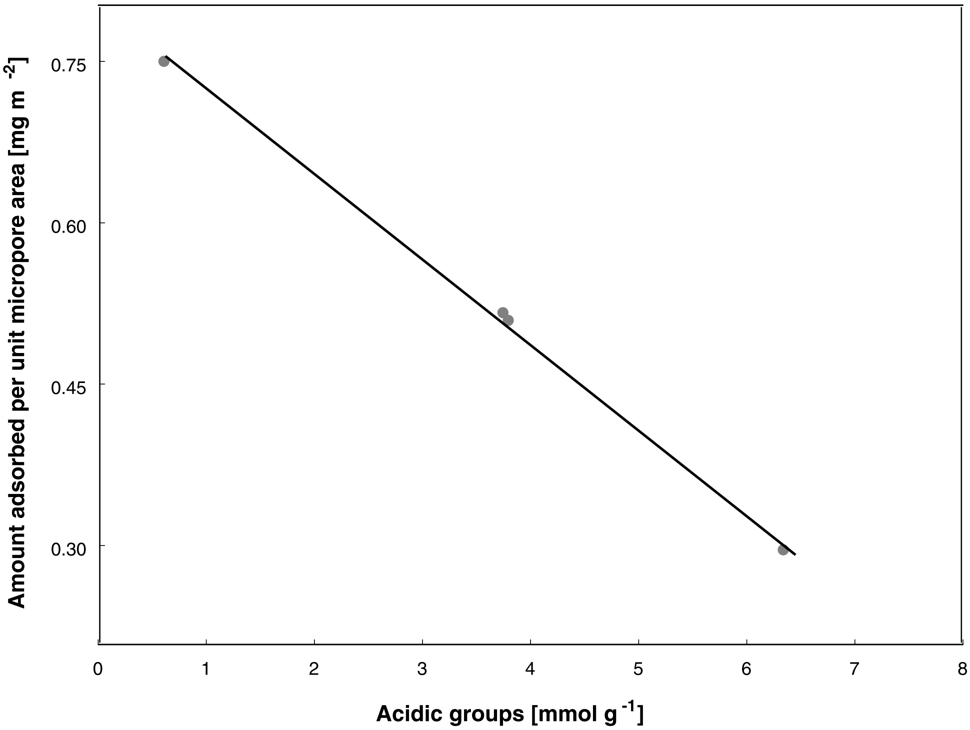


Fig. 3 Correlation between naphthalene adsorption per unit micropore area and acidic groups from aqueous solutions

drophilic character of the carbons, the affinity of heptane is reduced and the amount of naphthalene retained increased.

These results contrast with those reported by Ahnert et al. (2003), who found an inverse relationship between the amount of benzene adsorbed and the polarity of the carbon surface. The differences with this work are (i) the initial concentration of the solutions and (ii) the hydrophobicity of the adsorbate naphthalene, being about 16 times higher than benzene. Thus, the competitive effect of the solvent becomes more important and cannot be disregarded in the complex process of adsorption from diluted solutions.

Adsorption isotherms were also measured in cyclohexane and the trend observed was similar to that attained in water. Adsorption capacity is shown to be inversely related to the surface oxygen concentration and consequently to surface polarity.

When comparing the adsorption capacities in heptane and cyclohexane, it is noticed that all carbons shows higher capacities for naphthalene uptake in cyclohexane than in heptane. For clarity, the naphthalene adsorption isotherms from heptane and cyclohexane solutions are compared in Fig. 4.

Taking into account the minimal differences in the molecular dimensions of both solvents (heptane 0.43 nm and cyclohexane 0.48 nm), and the porous features of the series of carbons (wide and open pore size distributions, cf. Table 1 and Fig. 1), this behaviour cannot be attributed to a higher accessibility of heptane to the porous structure. It should be then explained in terms of the hydrophobicity of the solvent. Being heptane more hydrophobic compared to cyclohexane, it competes more effectively with naphthalene for the hydrophobic basal plane sites on the carbon. Additionally, since naphthalene ΔG_{solv} is lower (more negative) in heptane than in cyclohexane, its solubility is more favoured and consequently the adsorption largely suppressed. This is in good agreement with expectations and similar results have been reported for other aromatic adsorbates (Ahnert et al. 2003).

The differences between the uptake from cyclohexane and heptane solutions become smaller with the oxidation of the carbons (ca. BN60). The hydrophilic carbons do have a significant polar surface, so that retention of the hydrophobic solvent becomes less favourable. In this case, the competitive effect of the solvent is minimized and the difference in the uptake of naphthalene is reduced. In this situation, the contribution of the uptake is rather related to the porous features of the carbons than to the hydrophobic/hydrophilic nature of the adsorbent and solvents.

To further corroborate these assumptions, the nature of these interactions between the adsorbate and the adsorbents was explored by thermogravimetric analysis of the exhausted samples (named as *sat* series). The desorption profiles of the samples in the three solvents studied are shown in Fig. 5.

In order to avoid a misinterpretation of these results, it must be stressed that the peaks at temperatures higher than 700 °C, which appeared in all the oxidized samples, are linked to the decomposition of the surface functionalities,

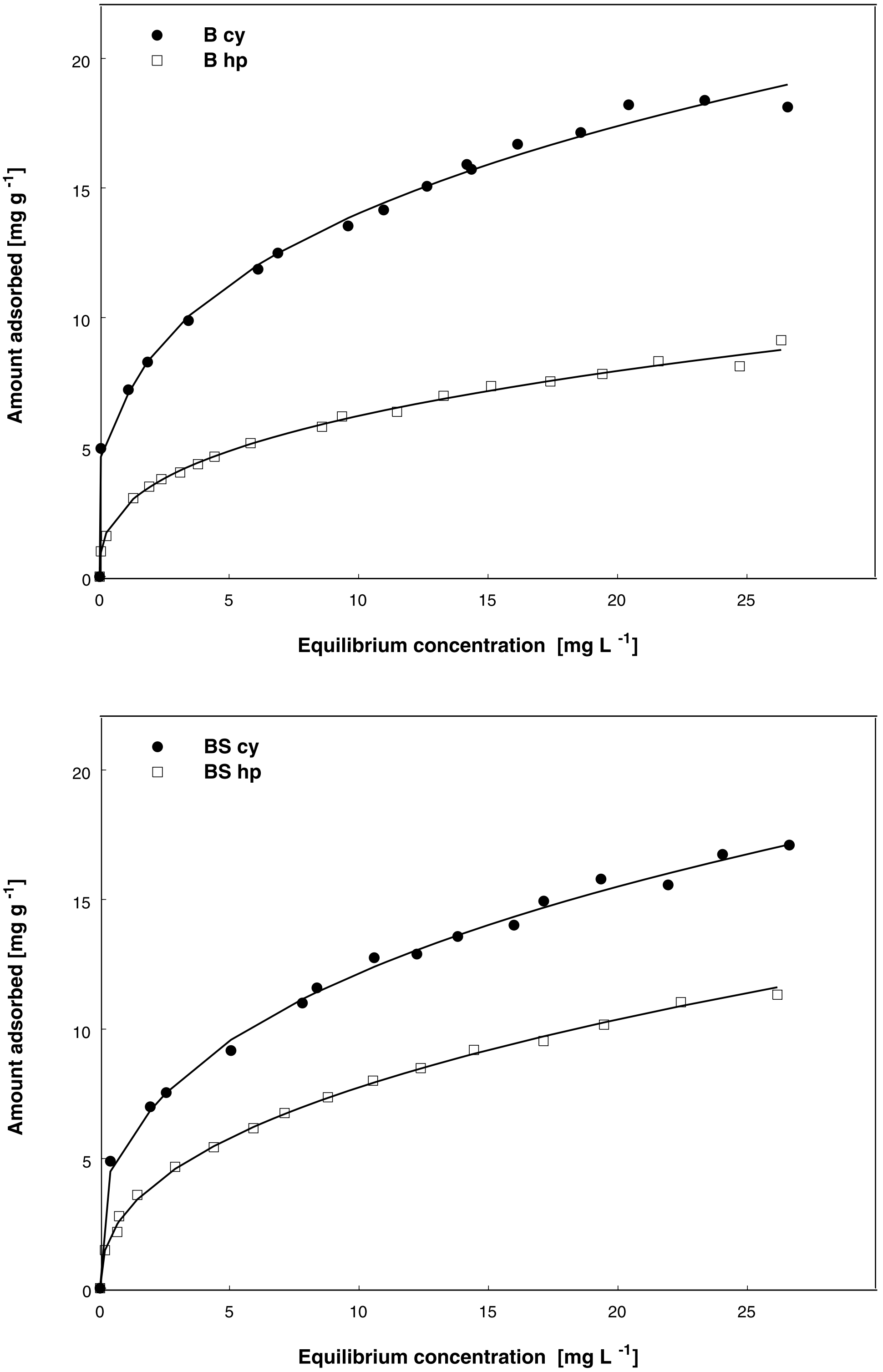
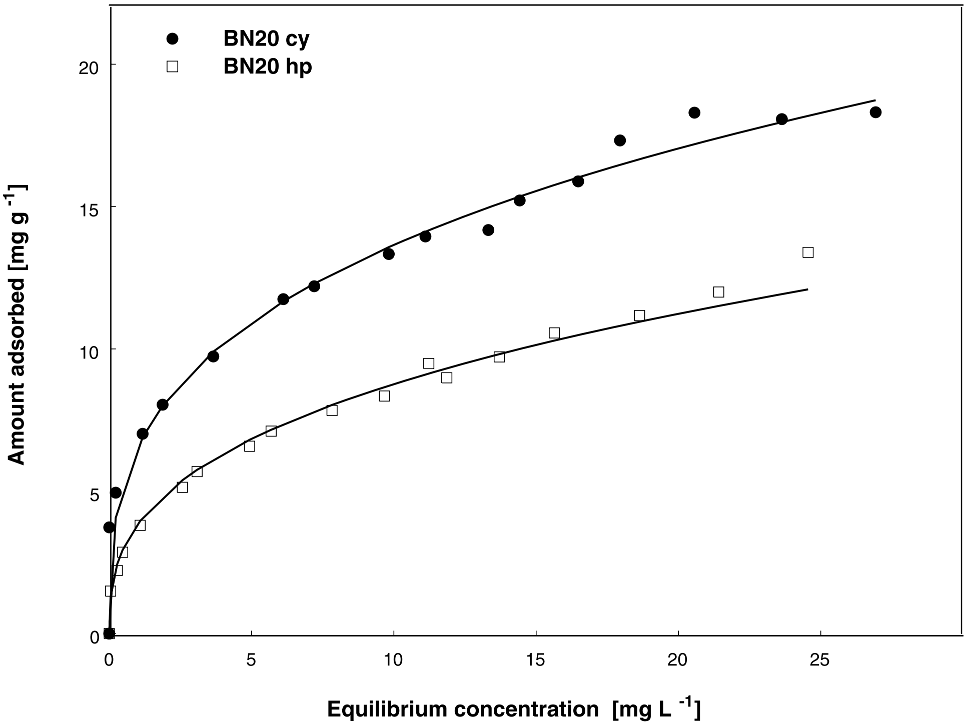


Fig. 4 Comparison of naphthalene adsorption isotherms from the organic solvents: cyclohexane (cy) and heptane (hp)

since they are also observed in the profiles of the oxidized carbons before naphthalene adsorption (Ania et al. 2007b).

For all the samples, several peaks of different widths and intensities were observed after naphthalene adsorption, which were not detected before the uptake. The first peaks, centred at temperatures lower than 250 °C are attributed to the desorption of the solvents. This was confirmed by the analysis of the sample exposed to the solvent in the absence



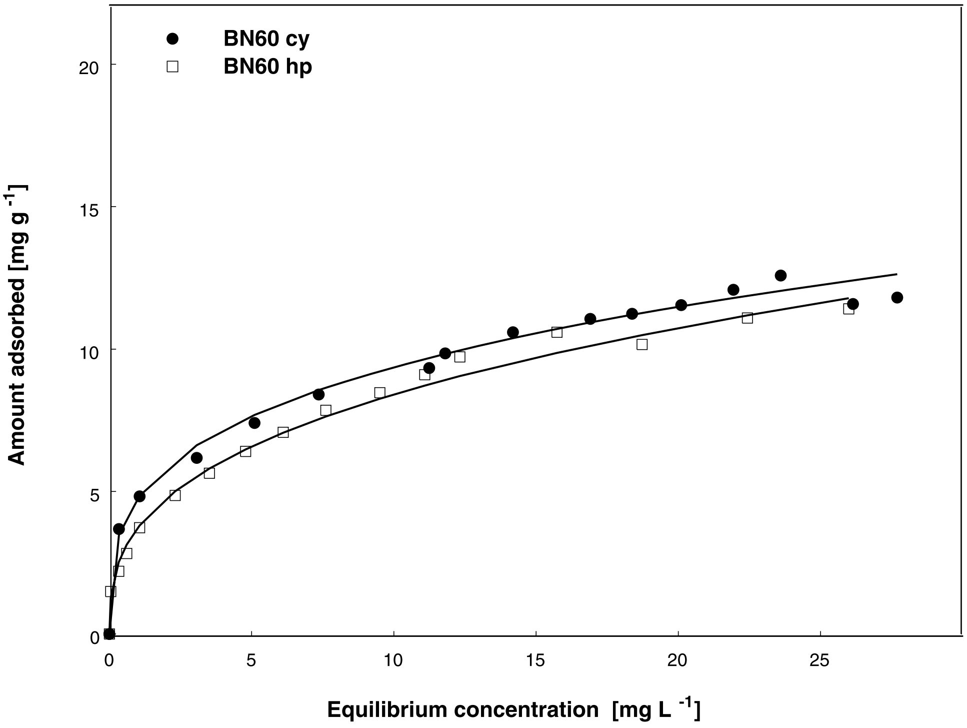


Fig. 4 (*Continued*)

of naphthalene. The second peak, centred at around 400 °C, was assigned to the removal of naphthalene physisorbed in the porous structure of the carbons. In the case of the oxidized carbons, there is a small overlap of this peak with that attributed to the decomposition of carboxylic groups, which is also present before naphthalene exposure. Nevertheless, after naphthalene adsorption the intensity of the peak increases, due to the naphthalene evolution. The assignment

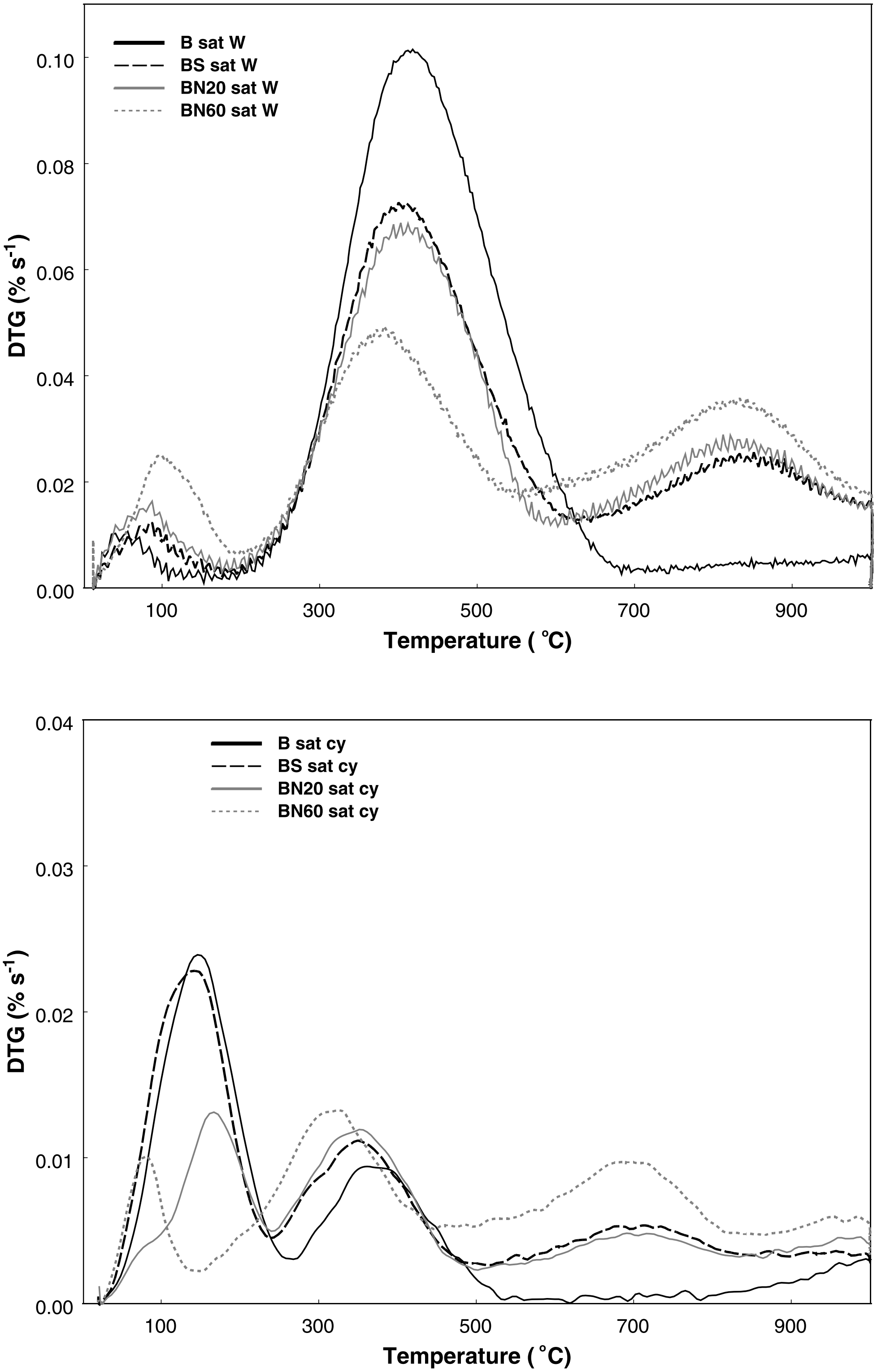
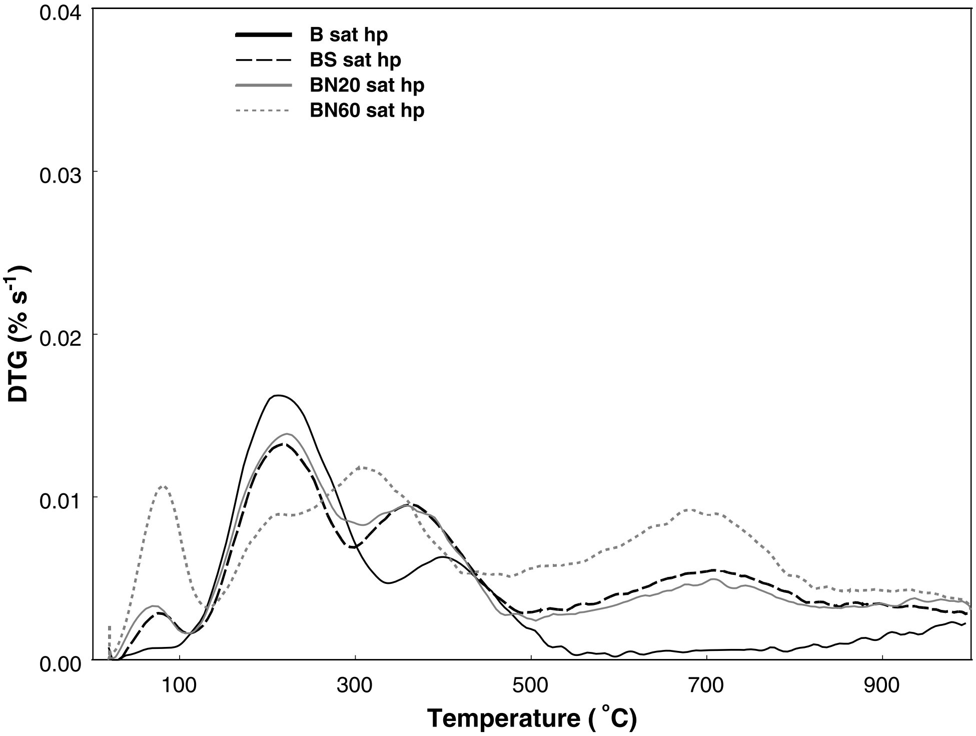


Fig. 5 DTG under nitrogen of the samples after naphthalene adsorption (sat series) from water (W), cyclohexane (cy) and heptane (hp) solutions

of the desorption peaks to naphthalene and the solvents was confirmed analysing the gases evolved from TPD by a FTIR detector coupled to the TG analyser.

It is interesting to underline that the temperature of the desorption peak slightly shifts downward to smaller temperatures with the polarity of the carbons, for the three solvents

Fig. 5 (*Continued*)



studied, being higher in B sample for the three series of solvents. This is consistent with that the forces responsible of naphthalene adsorption are stronger in more hydrophobic carbons.

4 Conclusions

We have confirmed the importance of the hydrophobic/hydrophilic nature of the carbon surface (i.e, surface polarity) in the retention of a non-polar adsorbate such as naphthalene. Both solvent-adsorbate and solvent-adsorbent interactions become critical in determining the adsorption capacity of aromatic compounds, due to (i) the occurrence of competitive solvent adsorption and (ii) to solvation effects based on the affinity of the solvent towards the adsorbate.

Different trends and values were obtained with liquids of different polarities and carbons with several surface heterogeneities. In the absence of oxygen functionalities on the carbon surface, the interaction of naphthalene with the carbon sites (basal planes) is highly dependent on the solvent affinity for the active sites and on the free energy of solvation.

When adsorption is performed from aqueous solutions, specific interactions of bulk water with the carbon surface (via hydrogen-bonding) appear. In this case, with the creation of surface functional groups on the carbon upon oxidation, the appetence of the adsorbent for polar molecules such as water increased, and therefore the adsorption capacity from aqueous solutions decreased significantly.

On the other hand, when adsorption is performed from organic solutions, the large energy of solvation of naphthalene in nonpolar solvents results in higher solubility and therefore in reduced adsorption, when compared to aqueous solutions. Moreover there exists also a competition with the solvent for the active sites that occasionally hinders the retention of the targeted probe. The appetence of carbon surface for non-polar solvents decreases with oxidation, thereby favouring naphthalene adsorption as opposed to the trend observed in water medium.

Acknowledgements COA thanks the CSIC I3P Program, co-financed by the European Social Fund, for a postdoctoral contract. Prof. Béguin is kindly acknowledged for providing XPS.

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