

KINETICS OF NAPHTHALENE ADSORPTION ON AN ACTIVATED CARBON: COMPARISON BETWEEN AQUEOUS AND ORGANIC MEDIA

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Abstract

The purpose of this work was to explore the kinetics of naphthalene adsorption on an activated carbon from aqueous and organic solutions. Kinetic curves were fitted to different theoretical models, and the results have been discussed in terms of the nature and properties of the solvents, the affinity of naphthalene to the solutions, and the accessibility to the porosity of the activated carbon. Data was fitted to the pseudo-second-order kinetic model with good correlation coefficients for all the solution media. The faster adsorption rate was obtained for the most hydrophobic solvent (heptane). The overall adsorption rate of naphthalene seems to be controlled simultaneously by external (boundary layer) followed by intraparticle diffusion in the porosity of the activated carbon when water, ethanol and cyclohexane are used as solvents. In the case of heptane, only two stages were observed (pore diffusion and equilibrium) suggesting that the limiting stage is the intraparticle diffusion. The low value of the boundary thickness supports this observation.

Keywords: organic solvents; hydrophobicity; polarity; adsorption rate; polycyclic aromatic hydrocarbons

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) constitute an important class of highly toxic environmental pollutants, which are known to present mutagenic and carcinogenic properties. Due to their high mobility and long persistence in the environment, these compounds are included in the list of priority pollutants of the European Environmental Agency (Directive 2000/60/EC) and their concentration is regulated in drinking water (WHO, 2006). 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. Despite having been the subject of plentiful studies in the literature, investigation of the rate and mechanisms of the adsorption process itself and the role of the characteristics of the adsorbent are still ambiguous and remain unclear (Walters et al., 1984; Seredych et al., 2004, Ania et al., 2007a; Valderrama et al., 2007, 2008).

It is generally accepted that non-polar compounds, such as naphthalene, are predominantly retained due to dispersive forces, as opposed to the adsorption of polar compounds involving specific interactions (Radovic et al., 2000). 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. The preferential adsorption of a targeted probe can be significantly suppressed by competitive retention of a second component (*i.e.*, solvent) with a high affinity towards the

adsorbent (Ania et al., 2008; Cabal et al., 2009). In other words, adsorption capacity, selectivity and/or rate of retention can be dominated by the hydrophobic character of the adsorbent and the interactions with the solvent. Contrary to aqueous phase (Valderrama et al., 2007a,b, 2008; Long et al., 2008; Ania et al., 2007b, 2008), investigations on the equilibrium and kinetics of adsorption of organic pollutants from organic media are very scarce.

The goal of this study was to explore the kinetics of naphthalene retention in various media of different polarities, ranging from high (water) to low dielectric constants (cyclohexane and heptane). This compound was chosen as representative PAH in our study, given that it is one of the most frequently found in wastewater from industrial activities. By using various organic solvents, the effects of medium polarity and solvent competitiveness on the kinetics of adsorption of a non-polar aromatic compound (naphthalene) from diluted solutions were investigated.

2. EXPERIMENTAL SECTION

2.1. Materials

The adsorbent used in this work is a commercial granular activated carbon produced by physical activation of coal and supplied by Agrovin S.A (Spain). Details on the methods of characterization along with a more detailed description have been reported previously (Ania et al., 2007b) and has been summarized in the Supplementary File.

Due to the low water solubility of naphthalene, the synthetic naphthalene aqueous solutions were prepared from a stock solution in ethanol by adequate dilution in deionized

water. Final aqueous solutions contain less than 5 wt.% alcohol. All the chemicals of the highest purity were purchased from Panreac.

2.2. Adsorption studies

Kinetics measurements of naphthalene adsorption were explored from batch experiments at 30 °C using water, cyclohexane or heptane as the solvents, as described elsewhere (Ania, et al. 2008). Briefly, about 50 mg of the activated carbon were accurately weighed and placed in dark glass flasks containing a constant volume of naphthalene solution of initial concentration 30 mg L⁻¹. The suspensions were vigorously stirred (100 rpm) in a thermostatic regulated bath. Small samples of the solution (~1.5 mL) were taken out at predetermined time intervals to measure the evolution of the adsorbate concentration in the supernatant liquid, using a UV spectrometer. The extracted samples were reintroduced in the flasks in order to avoid changes in the total volume of solution. Blank experiments were also carried out to verify that losses by volatilization or adsorption on the flasks walls do not occur. The amount adsorbed, q_t , was calculated from the equation

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

where C_0 is the initial concentration, C_t the remaining concentration on the solution, V is the volume of the solution and m the mass of the adsorbent.

2.3. Kinetic theoretical models

Naphthalene adsorption kinetics on an activated carbon from diluted solutions with different media was modelled by using several simplistic mathematical expressions that include the pseudo-first (Lagergren, 1898), pseudo-second order (Vinod and Anirudhan,

2003) and the Elovich model (Chien and Clayton, 1980). In the latter, the sorption process is described as a group of mechanisms such as diffusion in the bulk solution, surface diffusion, and activated catalytic surfaces. The simplified version of the Elovich equation, proposed by Chien and Clayton (1980) was used:

$$q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t \quad (2)$$

where α and β are the parameters of the Elovich rate equation obtained by linear regression analysis of the $q_t = F(t)$ function.

The intraparticle diffusion model developed by Weber and Morris (1963) was also used as a first approach for describing adsorption processes on the activated carbon. The equation can be written as follows:

$$q_t = k_p t^{1/2} + B \quad (3)$$

where k_p is the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-1/2}$) and B (mg g^{-1}) is a constant that gives idea about the thickness of the boundary layer.

3. RESULTS AND DISCUSSION

The mechanism and kinetics of liquid phase adsorption of PAH on porous adsorbents have been reported in a number of studies (Chang et al., 2004; Valderrama et al., 2007a,b, 2008; Ania et al., 2007a,b; Gok et al., 2008; Sarkar et al., 2003; Long et al., 2008). Whereas most investigations focus on the adsorption from aqueous solutions, scarce research has been carried out on organic solutions (Ania et al., 2008; Cabal et al., 2009). In this study, our aim was to investigate the effect of the hydrophobic/hydrophilic nature of the solvent on the kinetics of adsorption of naphthalene on activated carbons. Using solvents of increasing

polarity, this work envisages the perspective of the competitive adsorption arising from the interactions adsorbate-solvent and adsorbent-solvent.

The evolution of the concentration of naphthalene as a function of time, plotted as C/C_0 along time, is shown in Figure 1. It can be observed that there is an initial stage where naphthalene uptake is very fast, followed by a second one in which the uptake steadily increases up to equilibrium conditions. The fast initial stage is sharper in water medium, where the removal of naphthalene is almost complete within few hours. The longer retention times required to reach equilibrium when adsorption occurs from organic solvents point out the larger affinity of naphthalene molecules towards the organic phase (compared to the aqueous solution). This observation is also corroborated by the fact that naphthalene uptake is largely suppressed when adsorption occurs from organic solutions, compared to aqueous phase. This seems reasonable given the higher solubility of naphthalene in organic solutions (see Table S2 in the Supplementary Information file) and the simultaneous (competitive) adsorption of the solvent in dilute solutions.

Figure 2 shows the results of the naphthalene kinetics data fitted to the various theoretical models. The corresponding kinetic parameters extracted from the different equations are compiled in Table 1. The determination coefficient (R^2) and the linear regression coefficient (r^2) were used to evaluate the adequateness of the different models to fit the adsorption process. The determination coefficients were calculated by means of the equation (Chang et al., 2004):

$$R^2 = 1 - \left[\frac{\sum (y_e - y_c)^2}{\sum (y_e - y_m)^2} \right] \quad (4)$$

where y_e , y_c , and y_m are the experimental and predicted data, and the average of the experimental values, respectively.

Based on the correlation coefficients for linear regression (r^2), it is difficult to distinguish between all three models, and the sorption of naphthalene seems to be well represented by three kinetic models studied. However, the low coefficient of determination (R^2) obtained with the Elovich and pseudo-first order models suggest that they may not be suitable to describe the kinetics of naphthalene adsorption on activated carbons. In contrast, the pseudo-second order model gives satisfactory fitting with high correlation and determination coefficients. Moreover, the amount adsorbed $-q_e-$ predicted by this model agrees better with the experimental data obtained for all the solvents studied, as shown in Table 2. Thus, the pseudo-second order model is more suitable to describe the adsorption kinetics of naphthalene from liquid phase. Similar results on the retention of several PAH from aqueous phase using activated carbons and zeolites have been reported (Chang et al., 2004; Valderrama et al., 2007a,b, 2008).

Concerning the pseudo-second order rate constant, k_2 , the values quoted in Table 1 follow the sequence: heptane \gg water $>$ ethanol $>$ cyclohexane. In aqueous medium, the rate constants are comparable to those reported for various polycyclic aromatic hydrocarbons on carbon-based adsorbents (Valderrama et al., 2007a,b, 2008). Moreover, the value obtained for heptane is an order of magnitude larger than the values corresponding to the other solvents. A close look to these values indicates that there does not seem to be a direct correlation between the rate constant (k_2) and either the polarity (hydrophobic nature) of the solvent or the solubility of naphthalene (Table S2 in Supplementary Information). For

instance, the kinetics from heptane solutions (high naphthalene solubility) is almost three times faster than in water, where the solubility is significantly reduced.

Naphthalene solubility in the studied media may be linked to the Gibbs energy of solution, which being smaller in the organic solvents (lower positive values of ΔG_{sol} ; see Table S2 in the Supplementary Information) favours the solubility of naphthalene in the liquid phase and therefore hinders the uptake in the carbonaceous solid phase. Similar observations had been observed at equilibrium (Ania 2008; Cabal 2009); if the uptake is normalised vs the solubility of naphthalene in the different solvents, the data does not follow the expected trend due to solvent affinity, and the effect of the restricted accessibility is underlined.

Besides the polarity and solubility, the size of the solvents do not explain the trend observed for k_2 constant since heptane does not account for the smallest dimension among the different media (*i.e.*, 0.28, 0.42, 0.45 and 0.48 nm for water, heptane, ethanol and cyclohexane, respectively [Webster et al., 1998; see further information in the Supplementary File]. Therefore to understand this observation, one should take into consideration a combination of several factors including polarity, solubility, accessibility and competitive effects.

On the one hand, the affinity of non-polar naphthalene towards the liquid phase (*i.e.*, bulk solution) is enhanced when non-polar organic solvents (*i.e.*, heptane and cyclohexane) are employed, as confirmed by the solubility data and Gibbs energies of solution (Table S2 in Supplementary Information). On the other hand, the hydrophilic/hydrophobic nature of the solvent cannot be disregarded in diluted solutions, where the solvent can compete with naphthalene for the active sites of adsorption on the activated carbon. The competitive effect of the solvent would be controlled by its affinity for the carbon surface (wettability)

and/or accessibility restrictions. In the case of activated carbons, non-polar solvents present higher affinity for the carbon surface; therefore the wettability of the carbon is enhanced when adsorption occurs from heptane and cyclohexane than from water and ethanol. Additionally, earlier investigations (Cabal et al., 2009) have demonstrated that the small pores (narrow micropores) are not accessible for the large cyclohexane molecules. This factor becomes important taking into account that, for this activated carbon, the contribution of narrow microporosity accounts for 30% of the overall pore volume (Table S1 and Figure S1 in the Supplementary Information). This fact should contribute to decelerate the overall adsorption rate of naphthalene on the carbon when cyclohexane is used as solvent.

Based on the 2nd order model, the initial adsorption rate (h_0) and the half adsorption time ($\tau_{1/2}$) can be estimated according to the equations:

$$h_0 = k_2 q_e^2 \quad (5)$$

$$\tau_{1/2} = 1/k_2 q_e \quad (6)$$

Half-adsorption time, $\tau_{1/2}$, is defined as the time required for the adsorption to take up half as much naphthalene as the amount adsorbed when the equilibrium is reached, and it is often used as a measure of the overall adsorption rate.

The highest initial adsorption rate (h_0) is obtained from the aqueous solution (Table 1), being between 20 and 40 times larger than for the other solvents. Again, this parameter does not follow a clear tendency with the polarity of the solvents, as ethanol and heptane show similar values which are about 1.6 times higher than in the case of cyclohexane. This could be attributed to the above-mentioned accessibility restrictions for cyclohexane

molecules that are known to hinder the amount adsorbed (Ania et al., 2008; Cabal et al., 2009). Thus, it appears that not only the equilibrium uptake is restricted but also the rate of adsorption may be affected, as both the global adsorption rate (k_2) and the initial rate of adsorption (h_0) are slowed down.

The elapsed time for half naphthalene uptake ($\tau_{1/2}$) follows the sequence: water (24 min) < heptane (67 min) << ethanol (156 min) << cyclohexane (272 min). Faster adsorption kinetics is obtained for the most hydrophilic and hydrophobic media, (water and heptane solutions, respectively) with ethanol and cyclohexane lagging behind.

In sum, the pseudo-second order model fits adequately the experimental data. The adsorption rate depends on manifold factors: the polarity of the medium (*i.e.*, solvent hydrophobicity) that governs both the affinity of naphthalene molecules towards the solution and the competition of the solvent for the adsorption sites, and by the accessibility of the probes to the porosity of the adsorbent.

Analysis of intraparticle diffusivity mechanisms

In this study, the intraparticle diffusion model (equation 3) has been used as a first approach for identifying the limiting adsorption step and the diffusion/transport mechanisms during naphthalene adsorption on an activated carbon from different media (Figure 3).

The multi-linear nature of the intraparticle diffusion plots for all the solutions indicates the simultaneous occurrence of several adsorption stages: boundary layer diffusion, followed by intraparticle diffusion in the inner porosity of the carbon materials, and finally the equilibrium. Similar behaviours have been reported for the retention of various molecules

on activated carbons (Koumanova et al., 2007; El-Khaiary, 2007). All the solvents displayed 3 differentiated stages, with the exception of heptane that exhibits only 2 linear parts. The first linear step represents the external mass transfer (adsorbate diffusion in the boundary layer); the second one accounts for the gradual adsorption stage where naphthalene molecules diffusion through the porosity of the activated carbon, and finally a horizontal line illustrates the plateau of the equilibrium (Medley and Andrews, 1959), which is nearly parallel in all the solvents. In the case of heptane, the boundary diffusion is not observed, the first linear stage being attributed to the intraparticle diffusion.

The rate constants of external mass transfer (k_s) were determined from the slope of the C/C_0 plot against time (Figure 1), fitting the data corresponding to the first linear region governed by the boundary diffusion (*i.e.*, external mass transfer is dominant). The largest value (Table 1) obtained when adsorption occurs from the aqueous solution (ca. 9 times higher than for the organic solvents) indicates a fast external diffusion, in good agreement with the experimental observations (Figure 1). In contrast, ethanol and cyclohexane displayed similar values, despite their different polarity.

The time elapsed until intraparticle diffusion starts controlling the rate of adsorption increased with the hydrophobicity of the solvent, ranging from 120 min in the case of water, up to 366 and 374 min for ethanol and cyclohexane, respectively. Thus it appears that the diffusion of naphthalene molecules through the boundary layer is favoured in aqueous solution, likely due its lower affinity for water.

The intraparticle diffusion parameter, k_p , was determined from the slope of the second linear region in Figure 3 (first linear region for heptane). The calculated values (Table 1) follow the sequence water >>> heptane > cyclohexane > ethanol. A linear correlation is

obtained with the hydrophobicity of the organic solvents (Figure 4) expressed in terms of their octanol-water coefficient partition coefficient, K_{ow} . This points out that the affinity of naphthalene to the liquid phase (which increases with the hydrophobicity of the solvent) also influences the adsorption rate.

In contrast the intercept, which is associated to the boundary layer thickness (B), increases with the polarity of the solvent (Table 1). The lowest value is obtained for heptane (the intercept is almost zero), indicating a small film resistance to mass transfer surrounding the adsorbent particle. This fact, along with the absence of the mass transfer linear section in Figure 3, suggests that the stage of pore (intraparticle) diffusion is the limiting step in the rate of the global adsorption process. This also confirms that the mobility of the naphthalene/heptane system is higher, which is in good agreement with the faster overall adsorption rate evaluated from the pseudo-second order constant (Table 1).

Moreover, a linear correlation has been found between the boundary thickness (B) and the amount adsorbed evaluated at the equilibrium plateau ($r^2 = 0.992$), confirming the tendency of naphthalene molecules to remain in the organic solutions.

Thus naphthalene adsorption rate from heptane solutions can be understood in terms of the solvent properties and the occurrence of competitive adsorption. Being a highly hydrophobic molecule, heptane competes with naphthalene for the active sites on the activated carbon. Since diluted solutions are used, the diffusion of heptane inside the porosity of the carbon is expected to be favoured (higher wettability and/or affinity), and therefore the external mass transfer is enhanced (kinetic restrictions negligible). On the contrary, the pore diffusion process would be decelerated likely at expenses of the competitive effects.

As for the equilibrium plateau (last stage), this is achieved in the aqueous solution after 180 min, whereas longer times are required for the organic solvents (above 1000 min). This confirms the longer times needed for the organic solvents to reach equilibrium deduced from the experimental assays.

CONCLUSIONS

The adsorption of naphthalene on activated carbon from various solution media is best described by the pseudo-second-order reaction kinetics which provides the best correlation of the data regardless the polarity of the solvents employed. However, it is evidenced that the retention of naphthalene on different media is a complex process and the overall adsorption process can not be sufficiently described by a single kinetic model. Intraparticle diffusion played an important role, but it cannot be considered as the sole rate-limiting step during the adsorption within the studied systems.

The global adsorption rate of naphthalene appeared to be controlled simultaneously by external (boundary layer) followed by intraparticle diffusion in the porosity of the activated carbon when water, ethanol and cyclohexane are used as solvents. In the case of heptane, only two stages were observed (pore diffusion and equilibrium), suggesting that the limiting stage is the intraparticle diffusion. The low value of the boundary thickness supports this observation.

The affinity and solubility of naphthalene molecules with the solvent strongly affects both the adsorption rate and the amount adsorbed. The dependence of intraparticle diffusion constant with the solvent hydrophobicity, confirms that the adsorbate-solvent affinity

decreases the rate of adsorption. On the other hand, the linear correlation between the boundary thickness and the amount adsorbed at the equilibrium plateau also confirms the tendency of naphthalene molecules to remain in the solution when organic solvents are used as adsorption media, thereby reducing the overall amount adsorbed.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version.

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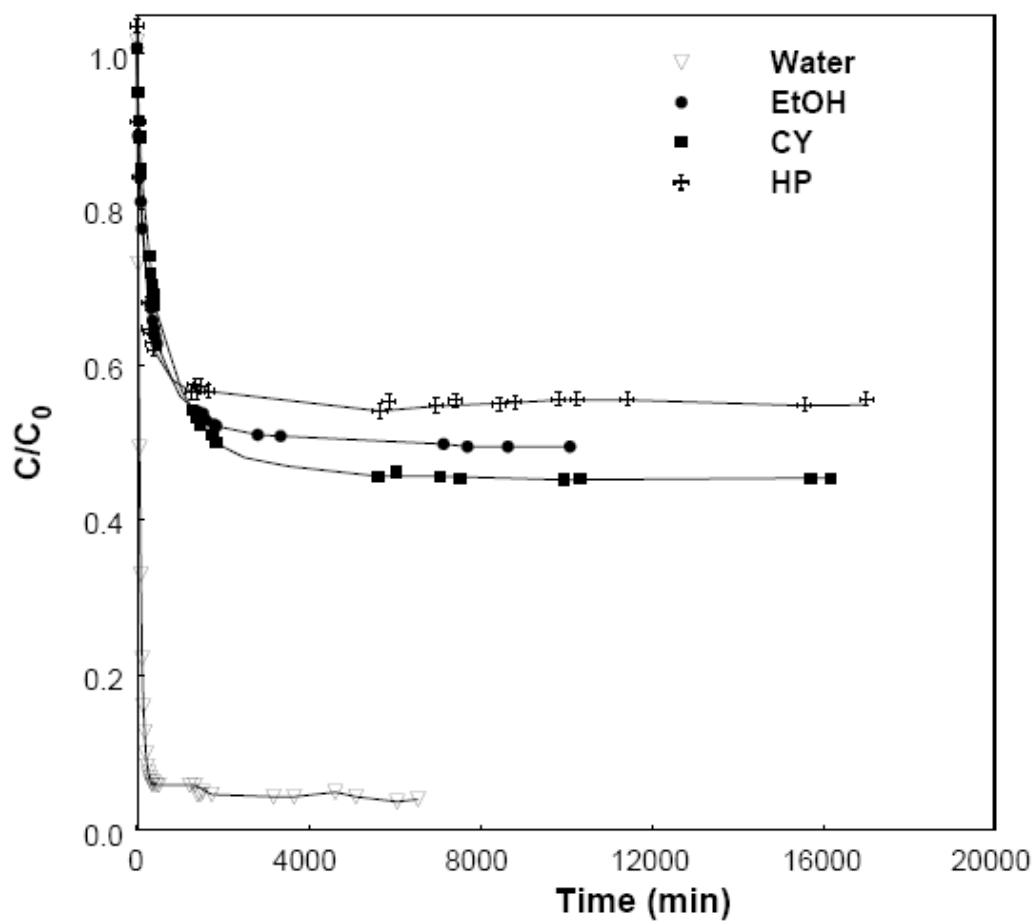
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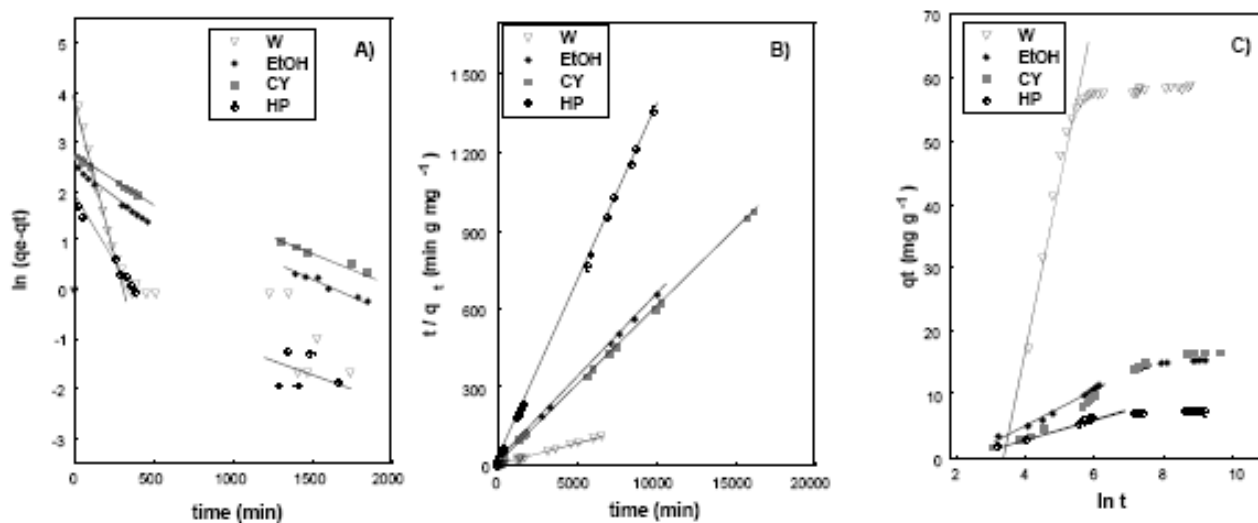
374 **Captions to Figures**

375 **Figure 1.** Concentration evolution of naphthalene in the different solvents.

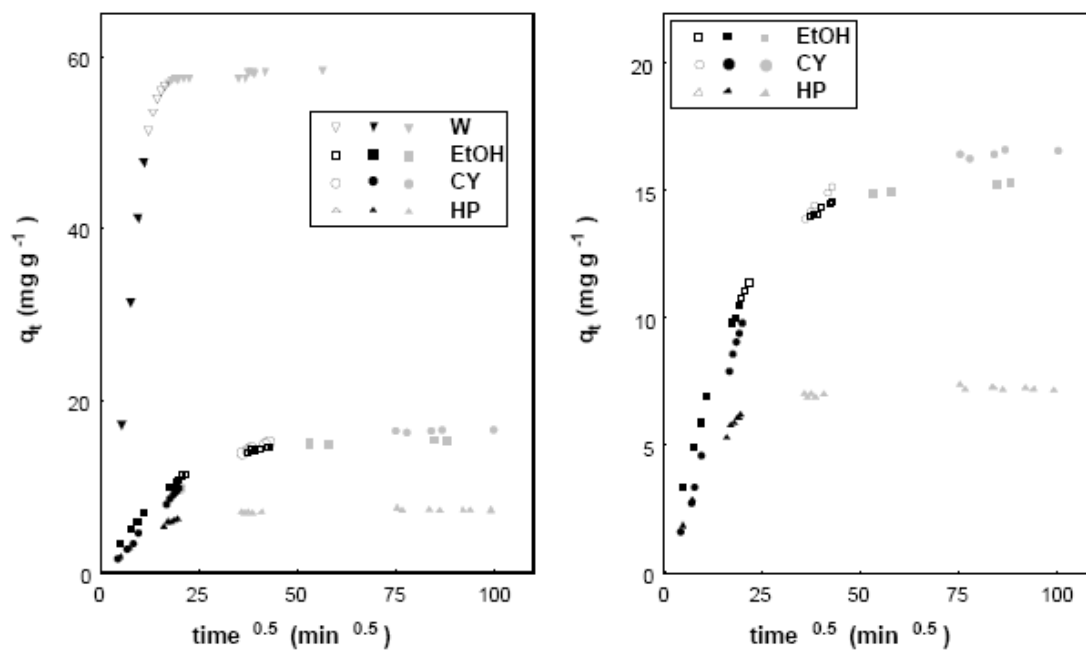


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377 **Figure 2.** Kinetic experimental data fitted to A) pseudo-first-order model, B)
378 pseudo-second-order model, and C) Elovich model on the different solvents
379 water (W), ethanol (EtOH), cyclohexane (CY) and heptane (HP).



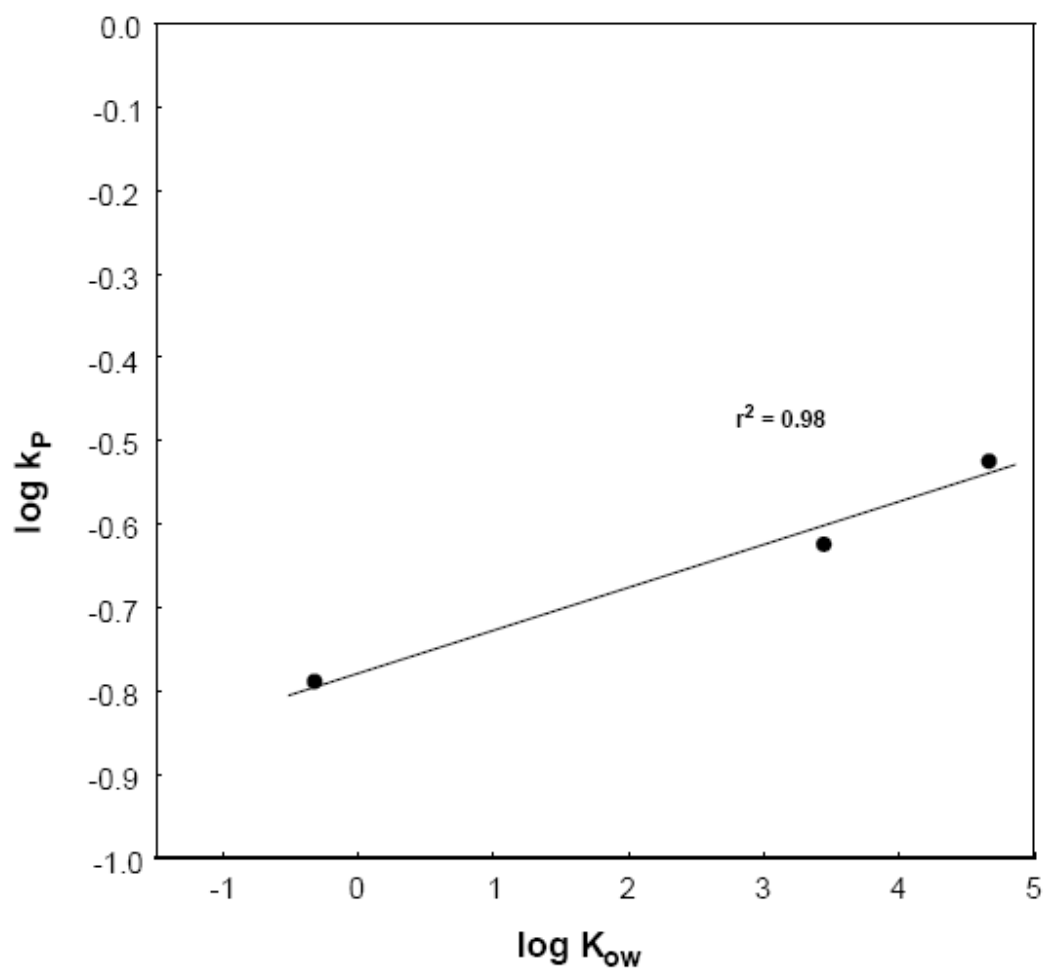
380 **Figure 3.** Intraparticle diffusion plots for the adsorption of naphthalene in
 381 different solvents: water (W), ethanol (EtOH), cyclohexane (CY) and heptane
 382 (HP). The distinctive stages areas appear in different colors.



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384

385 **Figure 4.** Correlation between the interparticle diffusion rate constant and the polarity of
386 the media, determined as the octanol-water-coefficient $\log K_{ow}$.



387

Table 1. Parameters of pseudo-first-order, pseudo-second-order, and Elovich models for naphthalene adsorption from different solvents: k_i rate constants; h_0 initial adsorption rate; $\tau_{1/2}$ half-life time; α and β , the initial sorption rate and surface coverage respectively; and B the boundary layer thickness

	Water	Ethanol	Cyclohexane	Heptane
Pseudo first order				
<i>(first step)</i>				
$k_{11} * 10^3 \text{ (min}^{-1}\text{)}$	11.7	2.4	2.0	5.8
r^2	0.984	0.993	0.996	0.995
R^2	0.362	0.469	0.946	0.497
<i>(second step)</i>				
$k_{12} * 10^3 \text{ (min}^{-1}\text{)}$	--	1.3	1.1	--
r^2	--	0.960	0.981	--
Pseudo second order				
$k_2 * 10^4 \text{ (g mg}^{-1} \text{ min}^{-1}\text{)}$	7.2	4.1	2.1	20.4
$h_0 \text{ (mg g}^{-1} \text{ min}^{-1}\text{)}$	2.49	0.100	0.063	0.110
$\tau_{1/2} \text{ (min)}$	24	156	272	67
r^2	0.999	0.999	0.999	0.999
R^2	0.916	0.992	0.997	0.993
Elovich				
$\alpha \text{ (g mg}^{-1}\text{)}$	1.69	0.33	0.17	0.33
$\beta \text{ (mg g}^{-1} \text{ min}^{-1}\text{)}$	0.05	0.36	0.31	0.82
r^2	0.984	0.994	0.986	0.940
R^2	--	0.814	0.8	--
Intraparticle diffusion				
$k_p \text{ (mg g}^{-1} \text{ min}^{-0.5}\text{)}$	1.26	0.16	0.24	0.30
$B \text{ (mg g}^{-1}\text{)}$	36.3	7.8	5.2	0.5
r^2	0.964	0.993	0.991	0.994
External diffusion				
$k_s * 10^4 \text{ (min}^{-1}\text{)}$	66.3	7.75	7.59	--

Table 2. Comparison of experimental adsorption capacities $-q_e$ (mg g^{-1})- with those predicted by theoretical models for the retention of naphthalene from the different solutions

Solvent	Experimental	Pseudo 1st order	Pseudo 2nd order
Water	58.36	46.93	58.82
Ethanol	15.41	11.96	15.70
Cyclohexane	16.63	15.11	17.15
Heptane	7.22	5.84	7.34

Supplementary Information

Details of the characteristics of the adsorbent.

The adsorbent used in this work is a commercial granular activated carbon, specially tailored for the treatment of industrial wastewater and drinking water. It was produced by physical activation of coal and supplied by Agrovin S.A (Spain). A particle size fraction of 0.71-1 mm was used for the experiments. Details on the methods of characterization along with a more detailed description have been reported previously (Ania et al., 2007b). Here we are summarizing the main details for data interpretation.

Table S1. Main chemical and textural parameters of the activated carbon

BET surface area [m^2g^{-1}]	1156
Helium density [cm^3g^{-1}]	2.18
Total pore volume [cm^3g^{-1}]	0.646
Micropore volume [cm^3g^{-1}]*	0.337
Mesopore volume [cm^3g^{-1}]*	0.134
Ash content [wt.%]	11.4
Oxygen [wt.%]	1.9
pH _{PZC}	9.1

* evaluated by the DFT method applied to the N_2 adsorption data

Ania, C.O., Cabal, B., Pevida, C., Arenillas A, Rubiera F., Parra, J.B., Pis, J.J. 2007b. Removal of naphthalene from aqueous solution on chemically modified activated carbons. *Wat. Res.*, 41, 333-340.

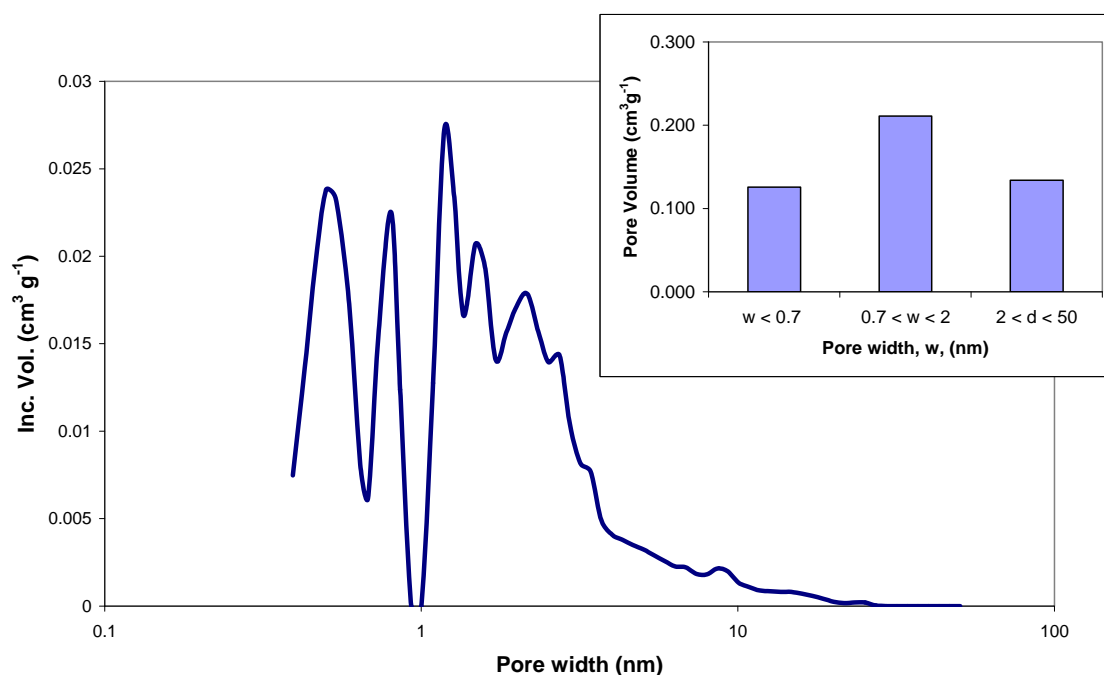


Figure S1. Pore Size distribution of the activated carbon used in this work, obtained by application of the DFT model to the N₂ adsorption data at 196 °C. Inset: Cumulative pore volumes.

Selected properties of the studied solvents

Table S2. Physical properties of the selected solvents^a, naphthalene solubility^b, and naphthalene solution enthalpies (ΔG_{sol})^c on the corresponding solvents

	Heptane	Cyclohexane	Ethanol	Water
$d_{\text{min}}[\text{nm}]^d$	0.43	0.48	0.45	0.28
Dielectric constant (ϵ)	1.9	2	2	78.5
Density (g/cm ³)	0.680	0.774	0.784	1.000
Molar Volume (cm ³ mol ⁻¹)	146.6	108.1	58.4	18
Kow	31623	2200	0.48	--
ΔG_{sol} (kJ/mol) *	5.06	4.72	8.53	30.69
Naphthalene Solubility (mole fraction x_i)	0.130	0.149	0.032	4.2×10^{-6}

^a R.C. Reid, J.M. Prausnitz, B.E. Poling, *The Properties of Gases and Liquids*, McGraw-Hill, New York, 1986.

^b IUPAC-NIST Solubility Database <http://srdata.nist.gov/solubility/index.aspx>. Last access 18th March 2009

^c Solomonov BN, Sedov IA, *The hydrophobic effect Gibbs energy*, *Journal of Molecular Liquids* 139 (2008) 89–97

^d Webster CE, Drago RS, Zerner MC. *J Am Chem Soc* 1998;120:5509–16.

* ΔG_{sol} , the Gibbs energy of solution, is defined as the Gibbs energy change for transfer of 1 mole of a solute from its standard state (solid, liquid, or vapor) to an infinitely diluted solution in a given solvent at 298 K and 1 bar), which being smaller in the organic solvents (lower positive values of ΔG_{sol} ; see Table S2) favours the solubility of naphthalene in the liquid phase and therefore hinders the uptake in the carbonaceous solid phase. The large positive value in the case of the aqueous solution indicates that solubility is an endothermic process and that it is not favoured in aqueous media.

Solomonov BN, Sedov IA, The hydrophobic effect Gibbs energy, Journal of Molecular Liquids 139 (2008) 89–97

Critical dimensions (sizes) of the molecules

The concept of solvent dimension is associated to the molecule size, shape and configuration, which determine whether a molecule will fit into a small pore of a fixed size. Kinetic diameters or Lennard-Jones potentials constants, have frequently been employed to determine the accessibility of molecules to pores and are related to the minimum equilibrium diameter of a molecule, r_{min} given by a Leonard-Jones potential, assuming that the molecule is effectively spherical. Kinetic diameters do not take into account molecular orientation, and this orientation is crucial in determining whether a molecule will fit into a small pore of fixed size. For large, non-spherically symmetrical molecules, kinetic diameters will not be useful in determining whether the molecule can enter a pore. Thus, the critical dimensions are considered as a better criterion of molecular exclusion.

The critical diameter is the smallest diameter of a cylinder through which the molecule can pass through without distortion [*C. Song, S. Kirby, Microporous Mater. 2 (1994) 467*]. The description of the critical dimensions involves the diameter of the circumscribed circle of the cross-section of minimum area of a molecule. The evaluation of these values is calculated from the available bond lengths, bond angles and van der Waals radii. [*Webster CE, Drago RS, Zerner MC. J Am Chem Soc 1998;120:5509–16*].