On the Adsorption Kinetics and Equilibrium of Polyaromatic Hydrocarbons from Aqueous Solution†

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ABSTRACT: The purpose of the present work was to explore the removal of three polycyclic aromatic hydrocarbons (naphthalene, fluorene and acenaphthene) (PAHs) from aqueous solution onto an activated carbon. The adsorption performance of these compounds (both kinetic and equilibrium) has been discussed in terms of their chemical and physical properties. The results showed that the rate of adsorption was strongly dependent on the molecular size of the hydrocarbons. Thus, for example, steric hindrances associated with acenaphthene inhibited the accessibility of this compound to the high-energy sites. Under equilibrium conditions, the uptake seemed to be governed by the carbon–PAH affinity, as the lowest uptake was obtained for naphthalene which displayed the fastest adsorption rate. The interactions between the studied pollutants and the activated carbon seemed to be controlled by two factors, viz. aromaticity and water solubility. As a general rule, the higher the number of aromatic rings in the polycyclic hydrocarbon, the more favoured the adsorbate–carbon interactions. Analysis of the carbon after adsorption of the studied hydrocarbons indicated that the accessibility restrictions to the porosity of the carbon can also lead to weaker interactions with the activated carbon.

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) constitute an important class of highly toxic environmental pollutants, associated with natural (volcanic eruptions and forest fires) and anthropogenic sources such as incomplete fuel combustion, crude petroleum transformations during refinery processes, and coke-making (Douben 2003; William 1990). Many of these pollutants have mutagenic and carcinogenic properties coupled with long-term persistence in the environment, for which their accumulation poses an outstanding environmental problem. For this reason, most of these polyaromatic hydrocarbons are currently considered priority pollutants by the European Environmental Agency (European Union 2000), whilst their concentration in drinking water is regulated (WHO 2006; European Union 2000).

To date, extensive research has been carried out on the adsorption of polycyclic aromatic hydrocarbons by various adsorbent materials, including activated carbons, bentonite, kaolinite, alumina, etc. (Changchaivong and Khaodhia 2009; Zhu et al. 2004; Yuan et al. 2010; Zeledon-Toruño et al. 2007), because of their industrial and environmental importance. Nevertheless, despite the number of studies on the removal of PAHs from aqueous streams using adsorption, investigation

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of the rate and mechanisms of the adsorption process itself and the role of the characteristics of the adsorbent/adsorbate systems are still ambiguous and remain rather unclear (Walters and Luthy 1984; Seredych and Gierak 2004; Ania et al. 2007a; Valderrama et al. 2007, 2008).

In previous studies, the adsorption kinetics and equilibrium parameters were reported for the retention of naphthalene (the simplest polycyclic aromatic compound) from both aqueous and organic media using activated carbons of varied compositions (Ania et al. 2007a, 2008; Cabal et al. 2009). The aim of the present work was to extend these investigations to the adsorption performance of a family of polyaromatic hydrocarbons containing different numbers of aromatic rings (i.e. naphthalene, fluorene and acenaphthene). To attain this goal, the adsorption kinetics and equilibrium of three PAHs frequently found in wastewater from industrial activities was explored from aqueous medium using a microporous activated carbon as the adsorbent.

A proper understanding of the role of the chemical structure of PAHs on the adsorption capacity of activated carbons is critical for the selection of adsorbents in the development of advanced strategies for wastewater remediation. The adsorption kinetics and equilibrium have been evaluated and discussed in terms of several chemical and physical properties of the target pollutants, including their hydrophobity, degree of aromaticity and solubility.

2. EXPERIMENTAL

2.1. Sample preparation

A commercial activated carbon AC (particle size 0.212–0.710 mm), obtained from the physical activation of coal, was selected as the adsorbent. Before use, the carbon sample was washed in distilled water at 60 °C, dried overnight at 110 °C and stored in a desiccator. Naphthalene (NAPH), fluorene (FLU) and acenaphthene (ACE) were the PAHs chosen for study. Selected physical and chemical properties of these compounds are listed in Table 1. Due to their limited water solubility, synthetic aqueous solutions were prepared from a stock solution in ethanol by adequate dilution in de-ionized water. The final aqueous solutions contained less than 5 wt% alcohol. All the chemicals employed were of the highest purity as purchased from Sigma-Aldrich.

2.2. Characterization

The nano-texture of the activated carbon (before and after PAH adsorption) was characterized by nitrogen and carbon dioxide adsorption isotherms measured at –196 °C and 0 °C, respectively (ASAP

| Hydrocarbon        | Chemical structure | Molecular formula | Dimensions a (nm) | log K ow | Boiling temp. (°C) | Water solubility (mg/l) |
|--------------------|--------------------|-------------------|-------------------|----------|---------------------|--------------------------|
| Naphthalene        | ![Naphthalene](image) | C_{10}H_{8}       | 0.74 × 0.92 × 0.39 | 3.5      | 218                 | 30                       |
| Fluorene           | ![Fluorene](image)  | C_{13}H_{10}      | 0.75 × 1.14 × 0.42 | 4.4      | 279                 | 2                        |
| Acenaphthene       | ![Acenaphthene](image) | C_{12}H_{10}     | 0.85 × 0.92 × 0.42 | 4.1      | 294                 | 8                        |

a Critical dimension: Webster, C.E., Drago, R.S. and Zerner, M.C. (1998) J. Am. Chem. Soc. 120, 5509.
2020 instrument, Micromeritics Instrument Corp., Norcross, GA, U.S.A.). Before such experiments, the samples were outgassed overnight under vacuum (ca. 10^{-3} Torr) at 120 °C. The resulting isotherms were used to calculate the specific surface areas, S_{BET}, and total pore volumes, V_{TOTAL}, and micropore and mesopore volumes by applying the DFT method assuming slit-shaped pore geometry. The samples were further characterized by thermogravimetric analysis (Setaram Labsys) employing the following instrument settings: heating rate = 15 °C/min; nitrogen atmosphere at a flow rate of 50 mℓ/min.

2.3. Adsorption studies

Kinetic measurements of PAH adsorption from solution were explored using batch experiments at 30 °C as described elsewhere (Ania et al. 2008). Briefly, ca. 20 mg of the activated carbon was accurately weighed and placed in a series of glass flasks containing a constant volume of the target molecule solution at a fixed initial concentration. The suspensions were vigorously stirred (100 rpm) in a thermostatic regulated bath. Small samples of each solution (~1.5 mℓ) were taken out at predetermined time intervals to measure the evolution of the adsorbate concentration in the supernatant liquid, such measurements being undertaken spectrophotometrically using a UV–vis spectrophotometer. The extracted samples were re-introduced into 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 onto the flask walls had not occurred. The amount adsorbed, q_t, was calculated from the equation:

\[ q_t = \frac{(C_0 - C_t)V}{m} \]  

where C_0 is the initial PAH concentration, C_t is the PAH concentration remaining in the solution after a time t, V is the volume of the solution and m the mass of adsorbent employed. All experiments were performed in duplicate, the average experimental error being < 5%.

Once equilibrium had been attained, adsorption isotherms were measured using a similar procedure employing different amounts of carbon samples (from 50 mg to 1 g). Details are described elsewhere (Ania et al. 2008). The equilibrium data were fitted to the so-called Langmuir–Freundlich (LF) single solute isotherm (Derylo-Marczewska et al. 1984) which may be written as:

\[ \frac{q_e}{q_m} = \frac{(KC)^n}{1 + (KC)^n} \]  

where q_e is the amount of solute adsorbed per g adsorbent, q_m is the maximum adsorption per unit mass of the adsorbent, K is the Langmuir-type constant defined by the van’t Hoff equation, while the exponent n represents the heterogeneity of the site energies.

2.4. Theoretical kinetics models

The adsorption kinetics of the selected PAHs from dilute aqueous solution onto the activated carbon were modelled by the pseudo-second-order model (Ho 2006). The intra-particle 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 (Valderrama et al. 2008; Tan et al. 2009):

\[ q_t = k_p t^{1/2} + B \]
where $k_p$ is the intra-particle diffusion rate constant [mg/(g min$^{1/2}$)] and $B$ (mg/g) is a constant that provides a measure of the boundary layer thickness.

The determination coefficient ($R^2$) and the linear regression coefficient ($r^2$) were used to evaluate the adequatness of the different theoretical models for fitting the data for the adsorption process. The determination coefficients were calculated by means of the following equation (Chang et al. 2004):

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

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

3. RESULTS AND DISCUSSION

A detailed analysis of the pore structure of the selected activated carbon has been reported previously (Ania et al. 2007a). Here, we merely report the main physicochemical and textural parameters obtained from an interpretation of the gas adsorption data (Table 2). Briefly, the selected activated carbon had a well-developed microporous structure, being characterized by a basic character as inferred from the value of the point of zero charge and its low oxygen content (low density of oxygen-containing surface functionalities). Based on previous findings (Ania et al. 2007a), these properties suggest that this activated carbon would be an adequate adsorbent for the retention of non-polar compounds such as polycyclic aromatic hydrocarbons. This implies that any likely competitive effect due to water adsorption (i.e. solvent–adsorbent interactions) would be minimized and thus preferential adsorption of the investigated PAH would be expected as the main adsorption mechanism.

3.1. Adsorption kinetics

The evolution of the concentration of NAPH, ACE and FLU as a function of time, plotted as $C/C_0$ versus time, is depicted in Figure 1. Three different zones may be identified for the studied

| Parameter       | Value     |
|-----------------|-----------|
| $S_{BET}$       | 1156 m$^2$/g |
| $V_{TOTAL}$     | 0.646 cm$^3$/g |
| $V_{MICROPORES}$| 0.337 cm$^3$/g |
| $V_{MESOPORES}$ | 0.134 cm$^3$/g |
| Carbon          | 96.5 wt% |
| Hydrogen        | 0.6 wt% |
| Nitrogen        | 0.7 wt% |
| Oxygen          | 1.9 wt% |
| $pH_{PZC}$      | 9.1       |

*Evaluated at a relative pressure of 0.95.

bEvaluated by applying the DFT method to the nitrogen adsorption data.
compounds (the corresponding steps for NAPH are more clearly seen in the inset in Figure 1). An initial stage (Zone 1), where the uptake was very fast, led to a fall in the initial concentration of 70% for ACE and FLU and of 80% for NAPH. This fast initial stage was followed by a second stage (Zone 2) where the amount adsorbed increased gradually and slowly until the changes in the solution concentration were negligible and equilibrium had been attained (Zone 3). For all three compounds, the time required to attain equilibrium was longer than that reported for mesoporous organosilicas and hyper-crosslinked polymeric sorbents (Valderrama et al. 2007, 2008; Vidal et al. 2011). This could be due to the differences in the porosity of the activated carbon used in this study, which was characterized by a high surface area and microporous structure. Comparing the three compounds, longer retention times were required to reach equilibrium for ACE and FLU (ca. 300 h) than for NAPH, where the total amount adsorbed was almost attained within a few hours. This finding contrasts with the rather similar aqueous solubility of these compounds (Table 1), and points out that the affinity of the pollutants towards the solid phase is not governed solely by this parameter.

Various theoretical models (including the pseudo-first- and pseudo-second-order kinetics models, and the Elovich equation) were fitted to the experimental kinetics data. Whereas the adsorption rates of the three studied PAHs seemed to be well represented by all the different theoretical models tested, as reflected by the respective values of the linear regression coefficients ($r^2$), low coefficients of determination ($R^2$) were obtained other than for the pseudo-second-order kinetics model. Thus, this model was considered to be the most suitable for describing the adsorption kinetics of the three PAHs from aqueous solution. Similar results on the retention of several PAHs from the aqueous phase using activated carbons and zeolites have been reported (Valderrama et al. 2007, 2008; Chang et al. 2004).

The kinetics parameters for the pseudo-second-order model are listed in Table 3. It is noteworthy that both the pseudo-second-order rate constant, $k_2$, and the initial adsorption rate, $h_0$, of naphthalene were two orders of magnitude larger than the corresponding values for ACE and FLU. This confirms the much faster adsorption kinetics for NAPH, as mentioned above. To further understand this finding, the nature of the different PAHs (their solubilities, aromaticity,
hydrophobicity and molecular dimensions) were closely studied and linked to the experimental observations on the adsorption rate.

In this regard, the selected PAHs were characterized by a low water solubility and a varied number and distribution of aromatic rings. According to the data listed in Table 1, the solubilities of the PAHs followed the trend: FLU < ACE < NAPH. However, the adsorption rate did not follow this trend, thereby suggesting that solubility was not the sole parameter governing the adsorption kinetics.

Another aspect considered was the degree of aromaticity of the pollutants. This parameter would be expected to define the nature of the interactions between individual PAHs and the activated carbon. Indeed, the thermodynamic driving force for the adsorption of a given PAH would be expected to be based on (i) repulsive interactions with water and (ii) dispersive (non-localized) interactions between the graphene sheets of the activated carbon and the aromatic rings of the hydrocarbons (Coughlin and Erza 1968). According to Clar’s rule (Clar 1964, 1972), the degree of aromaticity of polycyclic aromatic compounds is defined by the number of resonance structures with the most disjointed aromatic π-sextets, i.e. benzene-like moieties. The larger the number of resonance structures involving benzene rings, the higher the degree of aromaticity. According to this rule, NAPH and ACE show similar aromaticities with 10 π-delocalized electrons and three different resonant structures having one π-sextet, whereas FLU shows the highest aromaticity with 12 π-delocalized electrons and four resonant structures having up to two π-sextets. Based on the solubility and aromaticity data, FLU and ACE possessed the most thermodynamically favourable features for their adsorption onto the activated carbon. Nevertheless, the experimental data show that the adsorption rate of NAPH was faster than that of FLU and ACE.

In addition to solubility, the dimensions of these compounds were also taken into account (Table 1). Of the PAHs studied, NAPH was the simplest fused-ring aromatic compound, being composed of two aromatic benzene rings. In contrast, ACE and FLU involved two benzene rings fused to a cyclopentane ring in two different orientations. On taking this fact into account, the computed dimensions of these compounds followed the order: NAPH < FLU ~ ACE (Table 1).

| TABLE 3. Parameters from Fitting (a) the Pseudo-second-order Model to the Kinetic Data and (b) the Langmuir–Freundlich Equation to the Equilibrium Adsorption Isotherms* |
|---------------------------------------------------------------|
| **(a) Pseudo-second-order model** |
| $\text{k}_2 \times 10^{-6}$ | $h_0$ [g/(mg min)] | $t^{0.5}$ (min$^{0.5}$) | $r^2$ | $R^2$ |
| NAPH | 135 | 18.31 | 20 | 0.999 | 0.964 |
| ACE | 1.4 | 0.21 | 1872 | 0.991 | 0.943 |
| FLU | 2.2 | 0.15 | 1730 | 0.990 | 0.909 |
| **(b) Langmuir–Freundlich equation** |
| $q_m$ (mg/g) | n | Fitted range | $r^2$ |
| NAPH | 481 | 0.83 | 0–25 ppm | 0.985 |
| ACE | 575 | 0.91 | 0–15 ppm | 0.998 |
| FLU | 532 | 0.42 | 0–15 ppm | 0.977 |

* $k_2$ = pseudo-second-order rate constant; $h_0$ = initial adsorption rate; $t^{0.5}$ = half-life time; $q_m$ = maximum adsorption capacity per mass of adsorbent.
This trend matches the experimentally obtained values for the pseudo-second-order kinetics constants and suggests that steric hindrance might apply to the diffusion of the large ACE and FLU compounds along the activated carbon porous structure.

In order to identify the limiting adsorption step and the diffusion/transport mechanisms during the adsorption of PAHs onto the activated carbon, the experimental data were also analyzed by the external mass transfer and the intra-particle diffusion models (Figure 2). The rate constant for external mass transfer \( (k_s) \) was determined from the first step of the adsorption process (Zone 1 in Figure 1) from the slope of the plot of \( C/C_0 \) versus time (Aksu and Kabasakal 2004; McKay and Poots 1984). This step corresponds to the region where the migration of the pollutant from the bulk solution to the carbon surface is dominant (i.e. boundary diffusion). The calculated values followed the sequence: NAPH \( (73 \text{ min}^{-1}) \gg \gg \) FLU \( (16 \text{ min}^{-1}) > \) ACE \( (6 \text{ min}^{-1}) \), thus confirming the fast external diffusion of NAPH (probably due to its smaller molecular dimensions) and FLU (due to its lower solubility) over ACE, in good agreement with the experimental observations. A similar trend was observed for the time span before intra-particle diffusion started to control the adsorption rate, being shorter for NAPH than ACE and FLU (i.e. 90 min versus 420 min). This supports the view that the diffusion of NAPH molecules through the boundary layer was favoured in comparison to FLU and ACE, probably due to its smaller size.

Intra-particle diffusion is the most plausible rate-controlling stage during the second step of the adsorption process (Zone 2 in Figure 1). The model developed by Weber and Morris implies that the amount adsorbed onto the activated carbon would be linearly dependent on the square root of time [equation (3)]. However, the multi-linear nature of the intra-particle diffusion plots for all the hydrocarbons studied depicted in Figure 2 indicates the simultaneous occurrence of several adsorption stages, as discussed above in the analysis of the overall kinetics process (i.e. boundary layer diffusion, followed by intra-particle diffusion into the inner porosity of the carbon materials,

![Figure 2](image_url)

**Figure 2.** Intra-particle diffusion plots for the adsorption of NAPH (squares), FLU (circles), and ACE (triangles) from aqueous solution. The distinctive stages appear in different shading for the data points for each pollutant. The intra-particle diffusion parameters [equation (3)] have been obtained from the slope of the second linear region (depicted as black symbols); the corresponding fitting equations are indicated for each PAH.
and subsequently equilibrium). The intra-particle diffusion parameter, $k_p$, was determined from the slope of the second linear region in Figure 2 (filled symbols), with the calculated values being of the same order of magnitude for the three hydrocarbons studied [i.e. 2.8, 2.3 and 1.3 mg/(g min) for NAPH, ACE and FLU, respectively], with the slightly higher value for NAPH being probably due to its smaller dimensions. These results suggest that pore (intra-particle) diffusion does not seem to be the main step controlling the overall adsorption rate (as the three PAH have similar $k_p$ values). Moreover, the intercept evaluated from this second linear region — which is associated with the boundary layer thickness — was similar for ACE and FLU and smaller than that for NAPH. This is in good agreement with the higher $k_s$ value, i.e. rate constant for external mass transfer, of the latter and suggests that the overall adsorption kinetics are controlled by external diffusion of the hydrocarbons from the bulk solution to the vicinity of the carbon adsorbent.

Finally, the equilibrium plateau (Zone 3 in Figure 1) was attained after ca. 6 h for NAPH, whereas 12 days were needed in the adsorption of ACE and FLU.

### 3.2. Adsorption equilibrium

Figure 3 illustrates the equilibrium adsorption isotherms of NAPH, ACE and FLU onto the activated carbon studied. The experimental data have been normalized against the maximum solubility of each PAH as determined experimentally (Table 1) in order to illustrate the affinity of the adsorbent to the activated carbon more clearly (Carrott et al. 2005). All the isotherms are of Type L in the Giles classification, showing a plateau at high equilibrium concentrations of the individual PAHs. The adsorptive capacity of the activated carbon towards the different PAHs was obtained by fitting the Langmuir–Freundlich model [equation (2)] to the experimental data. The results obtained are listed in Table 3 along with the linear range and correlation coefficients. The excellent fit indicates that application of the Langmuir–Freundlich model to the studied systems was appropriate.

![Figure 3](https://via.placeholder.com/150)

*Figure 3.* (a) Equilibrium adsorption isotherms at room temperature for NAPH, FLU and ACE onto the activated carbon studied. The symbols represent the experimental data while the solid lines correspond to the fit of the Langmuir–Freundlich equation. (b) To allow comparison, the data have been normalized against the maximum solubility of each PAH as determined experimentally.
It can be seen that the highest adsorption capacities were exhibited by ACE and FLU rather than NAPH, this trend being the same as that observed at low initial solution concentrations. This tendency under equilibrium conditions was the reverse of that observed under kinetics conditions, i.e. the smallest uptake was obtained for NAPH which also displayed the fastest adsorption rate. This observation was more clearly seen when the equilibrium adsorption isotherms were normalized against the maximum solubility of each compound [Figure 3(b)].

To obtain a better explanation of the adsorption equilibrium behaviours, it is necessary to evaluate the different factors affecting the adsorption process. Taking into account the non-polar nature of the PAHs, the most suitable adsorption mechanism is the model proposed by Coughlin and Ezra (1968) based on the \( \pi-\pi \) interactions between the polyaromatic structure of the hydrocarbons and the \( \pi \)-electron density of the graphene layer of the activated carbon. As mentioned above, FLU showed the largest affinity towards the activated carbon due to its high degree of aromaticity (12 \( \pi \)-electrons), whereas ACE and NAPH each possess 10 \( \pi \)-electrons. Despite these differences in the aromaticity of the studied PAHs, similar adsorption characteristics were obtained for FLU and ACE. Thus, retention would appear to be related to the number of aromatic rings in the structures of the PAHs, since large capacities were exhibited by the activated carbon towards the hydrocarbons composed of three fused rings, followed by NAPH with two fused rings.

Besides the influence of adsorbate–adsorbent interactions, the accessibility of the adsorbent molecules to the internal porous structure of the activated carbon also plays an important role. Thus, the hindered accessibility of FLU and ACE (due to their molecular size) leads to their slow adsorption kinetics relative to that of NAPH. However, under equilibrium conditions, the overall amount adsorbed is controlled by the affinity between the PAH and the activated carbon. This hypothesis was corroborated by the CO\(_2\) adsorption isotherms of the activated carbon after PAH adsorption (Figure 4). Thus, the CO\(_2\) isotherms of the activated carbon after the adsorption of ACE and FLU exhibited Henry-type characteristics, indicating that when the carbon was loaded with

![Figure 4. Adsorption isotherms for CO\(_2\) at 0 °C onto the activated carbon studied as measured before and after the adsorption of NAPH, FLU and ACE.](image-url)
these two compounds, the porosity was blocked and hence the carbon exhibited very little CO$_2$ adsorption. In contrast, when the carbon was exposed to NAPH, the amount of gas adsorbed was more pronounced, while the isotherm of the loaded carbon still presented the typical shape expected for a microporous carbon (indicating that a fraction of the microporosity was still accessible to CO$_2$).

Further information about the interactions between the activated carbon and the various PAHs was obtained by thermogravimetric analysis of the carbon after adsorption (Figure 5). The desorption profile of the raw carbon exhibited a single peak at ca. 80–100 °C due to the removal of the moisture retained on the carbon, characteristic of carbon materials with a low density of surface functionalities (Bandosz 2006). After exposure to the different polyaromatic hydrocarbons, all the desorption profiles showed a well-differentiated peak above 300 °C corresponding to desorption of the aromatic compound. The relatively high desorption temperatures of the three PAHs compared to their boiling temperatures (Table 1) confirms that they were adsorbed into the microporosity of the activated carbon. The temperature of the desorption peak of ACE (i.e. 360 °C) was significantly lower than that for FLU and NAPH (i.e. 410 °C and 425 °C, respectively), suggesting that ACE exhibited a weaker interaction with the activated carbon than FLU or NAPH. This contrasts with the above-mentioned affinity of these compounds based on their degrees of aromaticity (expected to be similar for ACE and NAPH) according to Clar’s rule. The different desorption temperatures exhibited by ACE and FLU are expected to be related to their degrees of aromaticity. On the other hand, the difference between ACE and NAPH could be due to accessibility restrictions. In this regard, NAPH molecules (with a small size) can access the narrow micropores in the activated carbon, thereby enhancing the NAPH–carbon interactions (as the adsorbate dimensions match the pore size) (Ania et al. 2007b). However, in the case of ACE, weaker interactions arise due to its adsorption in lower energy sites as a consequence of steric hindrance.

**CONCLUSIONS**

The adsorption kinetics and equilibrium of polycyclic aromatic hydrocarbons with different chemical structures from aqueous solution were evaluated using an activated carbon as the adsorbent. It was concluded, in general, that adsorbate–carbon interactions were favoured by a...
greater number of aromatic rings in the polycyclic hydrocarbon. However, such favoured affinity
did not necessarily imply a greater extent of adsorption under equilibrium conditions or a faster
adsorption rate, which both followed different trends.

The overall adsorption rate of the studied PAHs seemed to be closely related to their molecular
dimensions (which could hinder their accessibility to the adsorbent porosity), rather than to the
parameters that control the adsorbate–adsorbent affinity (such as the solubility and the aromaticity).
The rate of adsorption of NAPH was faster than that of ACE and FLU, despite the fact that retention
of this compound would be the least favoured thermodynamically. Some accessibility restrictions
applied in the case of ACE and FLU due to their larger dimensions, thereby blocking their
adsorption in high-energy sites (i.e. in the inner microporosity of the carbon). In the overall kinetics
process, the rate-controlling stage appeared to be external diffusion of the hydrocarbons from
the bulk solution to the carbon surface. Pore (intra-particle) diffusion was rather similar for the three
hydrocarbons studied.

On the other hand, the nature of the hydrocarbon–activated carbon interactions and the overall
amount adsorbed at equilibrium were governed by the solubility of the hydrocarbon (which controls
the affinity of the adsorbate molecules towards the solid phase) and the degree of aromaticity. As a
consequence, ACE and FLU exhibited the largest uptake associated with a much slower retention
rate according to the kinetics data.

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