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Analysis and modelling of non-equilibrium sorption of aromatic micro-pollutants on GAC with a multi-compartment dynamic model

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Abstract

The optimisation of granular activated carbon (GAC) processes for industrial wastewater treatment requires the development of dynamic model that considers adsorption in multi-compartment porous media. In this work, the adsorption of toluene and naphthalene on GAC is investigated. Sorption equilibrium and kinetic experiments were performed at laboratory scale using low contaminant concentrations. The experimental conditions were chosen so as to simultaneously explore the different ranges of concentrations typically encountered in industrial wastewaters. The sorption behaviour was then explained through modelling taking into account the main equilibrium and transport phenomena and three adsorption compartments: the GAC particle surface, the macro- and meso-pores, and the micropores. The pore diffusion and solid diffusion were both considered to be coupled with a linear adsorption isotherm. With one set of four parameters adjusted for an adsorbent/contaminant pair, the model satisfactorily describes the non-equilibrium adsorption/desorption processes in different operating conditions and initial conditions.

Keywords: *Kinetics, Mass transfer, Diffusion, PAH, Toluene.*

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1. Introduction

Because of industrial and urban development, many hazardous organic substances and micro-pollutants are discharged into the environment via wastewaters (Williams, 1990; Douben, 2003). Removing chemical contaminants from wastewaters continues to be a central problem in environmental remediation and severe discharge constraints are now imposed by legislation for a number of chemicals (Water Framework Directive 2000) like monoaromatic and polyaromatic hydrocarbons. Adsorption is a well established technique for the removal of low concentrations of organic pollutants from industrial wastewater. Among the many adsorbents available, activated carbon is effective in removing a large variety of organic components (Seidel et al., 1985). Treatment options may range from activated carbons that differ in pore structure and surface chemistry to the control of one or more chemical compounds and mixtures. Granular Activated Carbon (GAC) has been shown to be efficient for the removal of organic micropollutants including aromatic hydrocarbons, halogenated hydrocarbons, pesticides, polychlorobiphenyl and surfactants (Zimmerman et al., 2004). The optimisation of GAC processes for industrial wastewater treatment demands a good knowledge of the adsorption and desorption dynamics. When GAC is operated in a completely mixed reactor (ref) fed with wastewater, it can be subjected to micropollutant concentrations that vary with time, leading to non-equilibrium in the system. Few studies have reported the analysis of this dynamics, which depends on mechanisms of internal diffusion into GAC in different compartments of the granular medium: surface, macro-porosity and micro-porosity.

50 The present work focuses on two substances typically found in industrial
51 wastewaters: toluene and naphthalene. Toluene and naphthalene have been
52 characterized as potential human carcinogens and their maximum permissible
53 concentrations in drinking water range from 4.6 to 0.3 $\mu\text{g L}^{-1}$ among different countries
54 (WHO, 2006). Toluene is a very popular solvent, used in the electronics, chemical
55 and printing industries. Polycyclic aromatic hydrocarbons (PAH) are produced by
56 human activity, chiefly in the pyrolysis and combustion processes employed in
57 industry, transport and heating (Bouchez et al., 1996). These substances cause
58 severe environmental pollution because of their persistence in the environment and
59 their genotoxicity to living organisms. The chemical properties of toluene and
60 naphthalene differ by their volatility and hydrophobicity: toluene is a highly volatile
61 organic compound (VOC) while naphthalene is characterized by lower water
62 solubility and high octanol-water partitioning coefficients ($\text{Log } K_{ow}$). Naphthalene is one
63 of the most soluble of the PAH and therefore represents the worst case for PAH
64 mobility. In many studies, naphthalene is used as a model chemical for hydrophobic
65 organics. Since GAC is a heterogeneous granular medium with particle sizes ranging
66 from 0.5 to 10 mm, a bimodal pore distribution (macro and microporous) and a high
67 specific surface area (500-2000 $\text{m}^2 \text{g}^{-1}$) (Cheremisinoff and Cheremisinoff, 1993), it is
68 particularly suitable for the efficient sorption of high molecular weight organic
69 molecules with lipophilic properties, as is the case with PAH (Jonker and Koelmans,
70 2002). Ania et al. (2007) found that the adsorption of naphthalene depended strongly
71 on the pore size distribution of the adsorbent, particularly narrow microporosity.
72 Although the microporous surface constitutes a major fraction of the specific surface
73 area, adsorption of organic micropollutants also occurs on the external surface of
74 particles and macro-pore walls. Whereas the experimental characterisation of

adsorption of GAC is frequent in the literature (Seredych et al., 2005; Ania et al., 2007; Valderrama et al., 2007; 2008a; 2008b; Cabal et al., 2009b), dynamic models that consider adsorption in multi-compartment porous media are rare. The sorption of organic micropollutants onto natural and synthetic sorbents has been described as a complex process in which the properties of the sorbate and the solvent play a critical role. The sorption process occurs within the boundary layer around the sorbent and proceeds in the liquid-filled pores or along the walls of the pores of the sorbent. As the classical modelling approaches point out, the adsorption process is composed of several steps:

- Diffusion of the pollutant from bulk liquid through the thin film of liquid surrounding the GAC particle (external transfer).
- Pollutant adsorption on the particle's external surface.
- Diffusion inside the pores (internal transfer) by two main mechanisms: pore diffusion (in large pores) and/or surface diffusion (in all pores, particularly in narrow, molecular-size-like pores).
- Adsorption on the pore walls.

Within a perfectly stirred reactor at constant temperature, adsorption rate is controlled by extra- or intra-particle diffusion steps. The relative importance of these steps depends on the adsorbent structure (particle diameter, pore length and diameter), solute properties (solute diffusivities) and hydrodynamic conditions. The design of a full-scale process requires knowledge not only of the equilibrium state but also of the dynamics of the solute adsorption/desorption processes, which depend strongly on the different steps described above.

In most studies, the adsorption rate of organic compounds from aqueous solutions is modelled by using several simplistic mathematical expressions that include the pseudo-first order (Lagergren, 1898), pseudo-second order (Vinod and Anirudhan, 2003; Wu et al., 2009), the intraparticle diffusion model (Weber, 1963; Cabal et al., 2009a) and the Elovich model (Chien and Clayton, 1980). Although these kinetic equations have been frequently employed to interpret adsorption data obtained under non-equilibrium conditions, their theoretical origins still remain unknown (Liu and Shen, 2008). The specific parameters contained in these equations can be determined only by fitting on experimental data and are dependent on the operating conditions, e.g. the initial sorbate concentrations. Wu et al (2009) observed that, for the same sorbate/sorbent pair, the performance of a given kinetic model depended on the particle sizes. Another common aspect of most studies on PAH adsorption is that the solutions used were relatively concentrated (with respect to the PAH solubility) and prepared using a co-solvent (alcohol), in a narrow range of concentration values.

To describe the equilibrium adsorption, the most commonly used models are the Langmuir and Freundlich models (Cornelissen et al., 2005; Pikaar et al., 2006). Pikaar et al. (2006) have performed a statistical analysis on isotherm models to fit sorption data for the sorption of organic compounds to activated carbon and found that the dual Langmuir equation is, in general, preferable to the single and triple Langmuir equations, the Freundlich equation, a Polanyi-Dubinin-Manes equation, or the Toth equation. Naphthalene adsorption equilibrium in aqueous solution has been studied through the Langmuir-Freundlich single solute isotherm (Derylo-Marczewska, 1984; Ania et al., 2007)

However, few works have developed physical deterministic models for the explanation of the adsorption kinetics of toluene and naphthalene on activated carbon. Some studies have been conducted on simulation and prediction of pilot plant and full-scale adsorber data, e.g. Crittenden et al. (1987), who used a homogeneous solid diffusion model (HDSM) of GAC adsorption of dichloroethylene in a contaminated groundwater matrix. Valderrama et al. (2008a), have studied PAH removal through GAC adsorption and found that the rate-determining step of PAH extraction is the sorbent-phase diffusion. They used two non-equilibrium adsorption models: the Homogeneous Particle Diffusion Model (HPDM) and the Shell Progressive Model (SPM) and have determined PAH effective particle diffusion coefficients (D_{eff}) in the range 1.1×10^{-13} – $6.0 \times 10^{-14} \text{ m}^2 \cdot \text{s}^{-1}$. Though many papers dealing with adsorption of organic substances from aqueous solutions have been published (Seredych et al., 2005; Ania et al., 2007; Valderrama et al., 2007; 2008a; 2008b; Cabal et al., 2009b); the rate and the mechanisms of the adsorption process itself remain unclear. Therefore, it would be appropriate to evaluate a model capable of predicting the equilibrium and kinetic sorption performance of GAC for aqueous trace organic molecules based on fundamental sorbent and sorbate properties.

Therefore, in this paper, aromatics with one and two rings (toluene and naphthalene) are evaluated in a set of sorption and desorption tests on GAC in completely stirred cells, with the following objectives:

- to determine the adsorption behaviour, i.e. kinetic and equilibrium parameters, on an extended time scale (short term to long term), in extreme concentration conditions (low to high) expected to be found in ground and industrial wastewater, i.e. typically in the range of 0.2 – 200 g m^{-3} ,

- to quantify the main phenomena through a mechanistic modelling approach,
- and to build a model containing a reduced number of adjusted parameters (parameters with a physical meaning) which simulates the adsorption/desorption behaviour in different operating conditions. This model should be easy to handle and resolve and should also allow for its integration in larger models of more complex systems (for example adsorber modelling, or coupling with other bio-physicochemical phenomena).

2. Materials and experimental methods

Adsorbates and adsorbents

Toluene and naphthalene were supplied by Sigma Aldrich. Toluene from the BTEX group solvents was chosen as a typical mono-aromatic hydrocarbon, naphthalene was chosen as a model compound for a light molecule of the group of polyaromatic hydrocarbons. All the above chemicals were more than 99% pure. Organic stock solutions were prepared in ultrapure water in a concentration range of approximately 0.2 to 200g m⁻³.

The Granular Activated Carbon (GAC) employed as the adsorbent was supplied by Pica and had the characteristics presented in Table 2. The GAC was obtained from coconut which was thermally activated and had a mean granulometry of 0.5-0.8mm. The BET (Brunauer–Emmett–Teller) surface area (1707m² g⁻¹) was obtained from N₂ adsorption isotherms at 77K on an ASAP2010 micrometrics apparatus. The isotherms were used to calculate the total pore volume, specific surface area and pore size distributions with t-plot and HK (Horwath-Kawazoe) modelling. Prior to

addition to the vials, the GAC was rinsed three times with ultra-pure water to remove dissolved contaminants and fine particles, which could have affected the adsorption capacity of the activated carbon (Summers and Roberts, 1988; Srivastava and Tyagi, 1995). The GAC was then dried at 105°C for 24h prior to storage in a dessicator until use (Cooney and Xi, 1994). It is generally accepted that activated carbon has a bimodal pore size distribution and contains pores ranging from several microns to a few angstroms. According to the classification by the International Union of Pure and Analytical Chemistry (IUPAC), there are three types of pores: micropores having dimensions less than 2nm, macropores larger than 500nm, and mesopores lying between these two limits.

Adsorption of pollutants on GAC

Adsorption measurements of toluene and naphthalene from aqueous solutions on carbon adsorbents were performed at 25°C in a stirred batch system, which consisted of 120mL amber glass vials filled without headspace and closed with Teflon-coated septa. Experiments were conducted in laboratory ultrapure water (tap water treated by ion exchange and UV). All points were obtained in duplicate or triplicate. A control sample without GAC was identically prepared for each experiment. The different aqueous solutions of pollutants without solid were first stirred on a rotary stirrer for 72h. Measurement by GCMS determined the real initial concentration of the solution before the adsorption experiment, taking into account the artefacts associated with the adsorption of pollutants on the different components of the reactor (Huang et al., 1988). The GAC was then weighed with an accuracy of +/- 0.001g and added into the vials. Tightly closed, the vials were shaken for 2-168h for the kinetic study. This revealed that the concentration values stabilised

(suggesting that equilibrium was reached) in 15h for NAP and 24h for Toluene (see below). After stirring, the tubes were centrifuged for 20min at 2500rpm. The residual pollutant concentration of the supernatant was then determined by GCMS analysis and the adsorbed amount was calculated from the difference between initial and residual concentrations. The adsorbed quantity Q_{exp} is given by the following equation:

$$Q_{\text{exp}} = (C_{0,\text{exp}} - C_{\text{exp}}) \cdot \frac{V}{S}, \quad (1)$$

Where $C_{0,\text{exp}}$ and C_{exp} are the initial and equilibrium concentrations respectively (g m^{-3}), V the volume of solution (m^3) and S the mass of solid (g).

Analytical procedures

Pollutant concentrations were determined using a gas chromatograph (Varian 3900), equipped with a mass spectrometer detector (Saturn 2100T) using helium (99.999% purity) as carrier gas coupled with an automatic headspace sampler (Quma HSS40). Separation was accomplished using a $30\text{m} \times 0.25\text{mm} \times 0.25\mu\text{m}$ column (fused silica VARIAN, type VF-5MS (5% phenyl 95% dimethylpolysiloxane)). The water samples (10mL) were transferred to 20mL glass vials with Teflon-coated septa and aluminium seals. The samples were equilibrated for 30min at 80°C and an aliquot of 1mL of the headspace gas was injected into the gas chromatograph. The detection limit was $1\mu\text{g L}^{-1}$. The accuracy for measurements of split samples containing a concentration of $1.5\mu\text{g L}^{-1}$ was $\pm 0.1\mu\text{g L}^{-1}$. All vials were first washed and dried in a 500°C oven to remove all traces of organics.

SEM analysis

A JEOL 5410LV Scanning Electron Microscope was used to observe the surface morphology of GAC (Figure 1.a). Prior to analysis, samples were dried in a vacuum oven at room temperature and then gold coated.

3. Modelling

The model applied was based on the four-step conceptual model:

- External diffusion of the pollutant through the thin liquid film surrounding the GAC particle.
- Pollutant adsorption on the particle's external surface.
- Internal diffusion by two main mechanisms: pore diffusion (in large pores) and surface diffusion.
- Adsorption on the pore walls.

And on the following supplementary assumptions:

- The adsorbent particles are spherical (particle diameter is given by the arithmetic mean value of the mesh size) (Figure 1.b).
- Pores of different sizes are parallel, i.e. transfer between different types of pore is not considered.
- Two main diffusion mechanisms should be taken into account. For large pores (macro- and meso-pores) only the pore diffusion is considered because it is several orders of magnitude faster than the solid diffusion. As the two mechanisms occur in parallel, the slower one can be ignored. For the narrow (micro) pores, only solid diffusion is considered.

- Two pore categories are considered: 1) macropores (the ratio of volume to surface area is very small for the macropores of the adsorbent studied); 2) micropores (pore size < 2nm).

Consequently, the model contains three adsorption compartments: the external surface, the macro/meso pores and the micropore surfaces.

The external transfer is characterised by:

- the specific surface area a_s ($\text{m}^2 \text{m}^{-3}$) corresponding to the geometric surface area of the particles of radius R (m),
- the external mass transfer coefficient k_{ext} (m s^{-1}) associated with this surface.

According to the principles stated above, the dynamic adsorption model was composed of the following equations.

-Macro- and meso-pore diffusion and adsorption (in spherical coordinates):

$$\varepsilon_p \frac{\partial C_p}{\partial t} + \sigma_p \rho \frac{\partial Q_p}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_e \frac{\partial C_p}{\partial r} \right) \quad (2)$$

with the boundary conditions:

$$r=0, \frac{\partial C_p}{\partial r} = 0 \quad (3)$$

$$r=R, D_e \frac{\partial C_p}{\partial r} = k_{\text{ext}} (C - C_p|_R) \equiv \text{flux}_p \quad (4)$$

C is the bulk concentration (g m^{-3}). For the meso- and macro-pore compartment: C_p and Q_p are the pore concentration (g m^{-3}) and adsorbed quantity (g m^{-2}) at local coordinates of time t (s) and space r (m), D_e is the effective diffusion coefficient ($\text{m}^2 \text{s}^{-1}$), ε_p is the porosity, ρ (g m^{-3}) is the particle density, σ_p is the specific surface area ($\text{m}^2 \text{g}^{-1}$), flux_p ($\text{g m}^{-2} \text{s}^{-1}$) is the flux exchanged between the pore compartment and the bulk liquid phase.

271 -Micropores (pore width comparable with the molecular size) solid diffusion

$$272 \quad \frac{\partial Q_{mp}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_s \frac{\partial Q_{mp}}{\partial r} \right) \quad (5)$$

273 with the boundary conditions:

$$274 \quad - \quad r=0, \quad \frac{\partial Q_{mp}}{\partial r} = 0 \quad (6)$$

$$275 \quad - \quad r=R, \quad D_s \frac{\partial Q_{mp}}{\partial r} = \frac{k_{ext}}{\sigma_{mp} \rho} (C - C_{mp}^e \big|_R) \quad (7)$$

276 The flux exchanged between the micropores and the bulk liquid is:

$$277 \quad k_{ext} (C - C_{mp}^e \big|_R) \equiv \text{flux}_{mp} \quad (8)$$

278 For the micropore compartment (subscript mp): Q_{mp} is the locally adsorbed quantity
 279 (g m^{-2}), $C_{mp}^e \big|_R$ is the concentration at R in equilibrium with Q_{mp} at R, D_s is the
 280 surface diffusion coefficient ($\text{m}^2 \text{s}^{-1}$), σ_{mp} is the specific surface area ($\text{m}^2 \text{g}^{-1}$), flux_{mp}
 281 ($\text{g m}^{-2} \text{s}^{-1}$) is the flux exchanged between the micropore compartment and the bulk
 282 liquid.

283 -External transfer and surface adsorption:

$$284 \quad \frac{dQ_{ext}}{dt} = k_{ext} (C - C_{ext}^e) \frac{a_s}{\sigma_{ext} \rho} \quad (9)$$

$$285 \quad k_{ext} (C - C_{ext}^e) \equiv \text{flux}_{ext} \quad (10)$$

286 Q_{ext} is the quantity adsorbed (g m^{-2}) on the external surface of particles (variable only
 287 in time), C_{ext}^e is the liquid film concentration near the particle side in equilibrium with
 288 Q_{ext} , σ_{ext} is the external specific area available for adsorption ($\text{m}^2 \text{g}^{-1}$), flux_{ext} ($\text{g m}^{-2} \text{s}^{-1}$)
 289 is the flux exchanged between the particle external surface and the bulk liquid.

290 -Bulk liquid mass balance:

The variation of pollutant concentration in the bulk liquid is due to the pollutant fluxes transferred towards the particle's external surface and to the pores.

$$\varepsilon \frac{dC}{dt} = -(a_s \text{flux}_{\text{ext}} + a_s \text{flux}_p + a_s \text{flux}_{\text{mp}}) \quad (11)$$

The adsorption isotherm is taken to be linear for the concentration range limited by the weak solubility. Saturation was not observed in any set of experiments. The adsorption constant K_e is expressed in $\text{m}^3 \text{m}^{-2}$ and represents a partition coefficient between the liquid and the surface. Adsorption is also considered to be rapid and reversible while a physical interaction mechanism is involved; the local equilibrium assumption is adopted in the model. The same linear adsorption equation was applied for all compartments, for example in the macro and mesopores:

$$Q_p = K_e C_p \quad (12)$$

$$\frac{dQ_p}{dt} = K_e \frac{dC_p}{dt} \quad (13)$$

The disadvantage of the present model with respect to its resolution and practical applications is the presence of two-dimensional variables C_p , Q_p and Q_{mp} (time and radius). Previous modelling studies of adsorption systems (Do and Rice, 1986; Goto et al., 1990) revealed the possibility of transforming the models based on partial differential equations (time and space) into simple differential equations (time) in the case of linear absorption, for both pore diffusion and solid diffusion mechanisms.

In this simplified approach, mean concentrations are used instead of the radially varying concentrations. One of the consequences is the possibility of using the "linear driving force" model (Gleuckauf, 1947) associated with a global mass transfer coefficient k_0 between the bulk liquid and the pores:

$$315 \quad \frac{1}{k_{0,p}} = \frac{1}{k_{\text{ext}}} + \frac{R}{5D_e} \quad (14)$$

$$316 \quad \frac{1}{k_{0,mp}} = \frac{1}{k_{\text{ext}}} + \frac{R}{5D_s} \quad (15)$$

317 Where $k_{0,p}$ and $k_{0,mp}$ are the overall transfer coefficient for macro- and meso-pores
 318 and for micropores respectively (m s^{-1}).

319 With these assumptions, the final form of the model becomes:

$$320 \quad \varepsilon_p \frac{d\bar{C}_p}{dt} + \sigma_p \rho \frac{d\bar{Q}_p}{dt} = a_s k_{0,p} (C - \bar{C}_p) \quad (16)$$

$$321 \quad \frac{d\bar{Q}_p}{dt} = K_e \frac{d\bar{C}_p}{dt} \quad (17)$$

$$322 \quad \frac{d\bar{Q}_{mp}}{dt} = \frac{a_s k_{0,mp}}{\sigma_{mp} \rho} (C - \bar{C}_{mp}^e) \quad (18)$$

$$323 \quad \bar{C}_{mp}^e = \frac{\bar{Q}_{mp}}{K_e} \quad (19)$$

$$324 \quad \frac{dQ_{\text{ext}}}{dt} = \frac{a_s k_{\text{ext}}}{\sigma_{\text{ext}} \rho} (C - C_{\text{ext}}^e) \quad (20)$$

$$325 \quad C_{\text{ext}}^e = \frac{Q_{\text{ext}}}{K_e} \quad (21)$$

$$326 \quad \frac{dC}{dt} = \frac{\varepsilon - 1}{\varepsilon} [a_s k_{0,p} (C - \bar{C}_p) + a_s k_{0,mp} (C - \bar{C}_{mp}^e) + a_s k_{\text{ext}} (C - C_{\text{ext}}^e)] \quad (22)$$

327

328 The overscored concentrations $\bar{C}$ and $\bar{Q}$ represent concentrations averaged over the
 329 particle with respect to the radial coordinate and hence depend only on the time
 330 coordinate. The total adsorbed quantity Q (g g^{-1}) results from a mass balance
 331 calculation over the different particle compartments:

$$Q = \sigma_p \bar{Q}_p + \sigma_{mp} \bar{Q}_{mp} + \sigma_{ext} Q_{ext} + \varepsilon_p \frac{S}{\rho} \bar{C}_p \quad (23)$$

333

334 The model contains a set of parameters available from experimental data and
335 measurements, listed with their values in Table 2.

336 The system of equations (Eq.16-22) was numerically resolved in MATLAB®. A multi-
337 parameter optimisation procedure was used for fitting the four specific parameters,
338 i.e. K_e , $k_{o,p}$, $k_{o,mp}$ and k_{ext} , based on the objective function OF to be minimized:

$$OF = \frac{1}{n} \sum_{i=1}^n \left(\frac{|C_{sim} - C_{exp}|}{C_{exp}} \right)^2 \quad (24)$$

340 where n is the number of experimental data, and C_{sim} and C_{exp} are the simulated and
341 measured bulk concentrations respectively.

342 The model should represent the adsorption process for any initial conditions
343 (adsorption and desorption processes) and contact durations. The complete sets of
344 adsorption experimental data (i.e. kinetics and pseudo-isotherm results) were used
345 for the fitting procedure: about 100 and 70 points for toluene and naphthalene
346 respectively. Desorption experimental data were then used for model validation.

347

348 The model presents the advantages of considering different kinds of pores with their
349 transport specificities and using mean concentrations of a given compartment, thus
350 simplifying the numerical resolution. The principal weakness is that the porous
351 system is considered to be built up only of parallel pores while, in reality, connections
352 also exist between pores. Ding et al. (2002) used a model based on two types of
353 interconnected porosity. This model is more realistic but its numerical resolution is
354 not trivial (partial differential equations of second order with complex boundary

conditions). Its use for common applications and extensions for adsorber design could be very difficult.

4. Results and discussion

As explained previously, two kinds of experiments were performed: (1) a kinetic study in which the evolution of the eluate concentration was measured versus time; (2) a pseudo-isotherm study in which the evolution of the eluate concentration was measured when the ratio GAC/liquid (i.e. S/L) varied, for a given initial concentration $C_{0,exp}$ and a given constant contact time. Examples of experimental results are given in Figure 2 for toluene and naphthalene: kinetics obtained for different initial concentration values ($C_{0,exp}$) and isotherms obtained for different $C_{0,exp}$ and contact times.

The experimental results show the dependence of the adsorption kinetics and isotherms on the initial concentration. The explanation of the experimental results is not obvious especially for the atypical behaviour of the isotherms. A tentative application of commonly used isotherm models like those of Langmuir or Freundlich was unsuccessful because the fitted constants were found to be dependent on the concentration domain. The commonly used kinetic models (first or second order) are unable to correctly describe the shape of the kinetic curves on the whole time scale and exhibit a dependence on the concentration domain.

The fact that the isotherms apparently depend on the initial concentration and on the contact time demonstrates that the experimental system was not at equilibrium and this was decisive for the development and application of the conceptual model

presented. So, the term “pseudo-isotherm” is more suitable than “isotherm” and will be used hereafter.

The modelling results and the experimental data are represented in Figure 2 for the kinetic study (Figures 2.a and 2.c) and for the pseudo-isotherms (Figures 2.b and 2.d). The model represents the experimental data in a satisfactory manner.

Table 3 shows the values of the adjusted parameters by molecule. It is important to note that only one set of parameters for each molecule allows the model to correctly predict the overall data obtained in different conditions.

The relevance of the adjusted values of the parameters was assessed through their physical significance.

The constant K_e , having the units of $\text{m}^3 \text{m}^{-2}$, is not comparable with other adsorption constant values (in L kg^{-1}) presented in the literature because of the different adsorption models applied and the hypotheses concerning the equilibrium state.

The effective diffusion coefficients (shown in Table 3) for the two types of pores considered in the model were calculated using the formula of Eq.14 and Eq.15. The values are reasonable for the type of porosity and diffusion mechanism considered. For reference, the molecular diffusion coefficients in water are $9.5 \cdot 10^{-10} \text{m}^2 \text{s}^{-1}$ and $6.6 \cdot 10^{-10} \text{m}^2 \text{s}^{-1}$ for toluene and naphthalene respectively.

Finally, the k_{ext} value corresponds to typical values for liquid transfer around solid particles in stirred liquids, which are commonly between 10^{-6} and 10^{-4}m s^{-1} .

The adsorption in a non-homogenous porous matrix is a sequential process in terms of mass transfer and sorbate distribution among the different compartments. If, during the first moments, it is essentially the external surface that is occupied by the

sorbate, the prolonged contact time favours a redistribution of the molecules over the different compartments driven by the concentration gradient. This phenomenon depends on the diffusion coefficients and slows down the attainment of an equilibrium state.

The curves in Figures 3.a and 3.b were obtained by simulation using the experimental conditions of the kinetic study in the case of naphthalene ($C_0 = 22\text{g m}^{-3}$, $S/L=0.04\text{g L}^{-1}$) and using the fitted values of the model parameters (as listed in Table 3). For comparison, a simulation was also made with $S/L=4\text{g L}^{-1}$ and is represented by the grey lines in Figure 3.a.

Figure 3.b shows the total quantity adsorbed Q (Eq.23) and the distribution of the sorbent among the different compartments of the GAC particles as calculated by the model: on the external surface ($\sigma_{\text{ext}} Q_{\text{ext}}$), adsorbed on macro- and meso-pore surfaces ($\sigma_p \bar{Q}_p$), retained in macro- and meso-pore liquid ($V_p \bar{C}_p$), adsorbed in micropores ($\sigma_{\text{mp}} \bar{Q}_{\text{mp}}$).

Two kinetic domains can be distinguished at different time scales: firstly a short period of several hours corresponding to a massive adsorption on the external surface, followed by a steep decrease in the bulk concentration due to macropore adsorption. A pseudo-equilibrium state is observed after about 100h (for $S/L=0.04\text{g L}^{-1}$) when the bulk concentration seems to be stabilised but, in fact, a slow increase in the micropore adsorption still occurs. A significant evolution of the macroscopic parameters (bulk concentration) would be observed only at very long time periods due to the very slow diffusion in the micropores. The influence of solid to liquid ratio on the macroscopic behaviour of the adsorption process is significant, the

pseudo-equilibrium state being more rapidly attained for high S/L (grey curves in Fig 3.a). The model used here considers that the different types of pores are independent (parallel), i.e. the micropores and macropores do not communicate inside the porous system but communicate directly with the bulk liquid. This is an “optimistic” model because the concentration gradient for microporous diffusion is at its maximum (in non-equilibrium adsorption, the bulk liquid is always more concentrated than that in the macropores). The simulations show that, even with this optimistic hypothesis, molecules like PAH in aqueous solutions are mostly adsorbed in the macro- and meso-porosity (for short time periods) and thus the use of microporous GAC is not necessary.

Among the adjusted parameters, the adsorption constant, K_e , and the mass transfer coefficient for macro- and meso-pores $k_{o,p}$ (or the effective diffusion coefficient D_e) are the most sensitive. Figure 4.a shows a sensitivity study carried out for the kinetic curve of naphthalene. Each curve was calculated by multiplying the parameters K_e , D_e , D_s and k_{ext} by 10, one by one. The sensitivity of a given parameter is not the same over the whole time scale and this result was expected.

The effective diffusion coefficient affects the first period when meso- and macro-pore adsorption takes place. An increase in the adsorption coefficient results in a slowing down of the adsorption kinetics (Valderrama et al., 2008b) and, obviously, in another equilibrium (pseudo-equilibrium) state. The least sensitive parameter is the solid diffusion coefficient and this is explained by a low adsorption in the micropores, at least for the time scale studied. The external mass transfer parameter is not sensitive either; k_{ext} for liquid films in stirred systems takes values between 10^{-4} and 10^{-6} m s^{-1} (Roustan, 2003) and, in this range, the simulations are within the experimental data domain. The GAC used in industrial applications has narrow size dispersion so the

particle radius should not be a sensitive parameter for a given GAC type. Calculations made with $2R$ and $R/2$ gave the same sensitivity results as k_{ext} (in formula 14 and 15 it is obvious that the diffusion coefficient makes the major contribution to the overall transport).

The model was then confronted with desorption experiments (naphthalene) in order to validate it and to evaluate its predictive performance. The complex experimental protocol composed of an adsorption step followed by two successive desorption steps was simulated using the previously adjusted parameters. As Figure 4.b shows, the simulation results are in agreement with the experimental values.

5. Conclusions

The experimental study of the adsorption/desorption process in various operating conditions and the modelling and simulation work lead to the conclusions drawn below.

1) The adsorption/desorption of aromatic compounds in aqueous solutions on GAC is a complex process which cannot be represented by simple and usual kinetic models (pseudo-first-order, second order, intraparticle diffusion or Elovich) over a wide range of initial concentrations and time periods. These models are not predictive because the equations and parameters contained in them lack physical meaning.

2) Pseudo-equilibrium states were observed on kinetic curves after about twenty hours of contact. Experimental isotherms determined with different initial concentrations and for different contact times clearly show that reaching the equilibrium state requires hundreds of hours.

3) A multi-compartment dynamic model allowed the deconvolution of the experimentally observed curves and explains the occurrence of many kinetic domains. These kinetic domains are related to the GAC structure and correspond to the different dynamic processes: on the particle surface, in the macro-meso pores and in the micropores. It was expected a priori and then demonstrated by modelling that, at short times, the external surface adsorbs the major part of the solute, then a redistribution of the adsorbed quantity takes place by migration inside the macro-meso pores and then in the micropores, tending towards an equilibrium state in the long term.

4) Concerning the structure of the model, a set of four parameters characterising the solute-sorbent interaction (linear adsorption constant and transport parameters) are necessary and cannot be obtained by direct measurements. These parameters are evaluated by fitting the model on a set of experimental data. Once the set of four parameters has been determined, the model becomes predictive for the molecule-GAC pair, being able to simulate the sorption (adsorption-desorption) process in different conditions of concentrations (large range of $C_{0,exp}$), liquid/solid ratios, contact times, initial conditions, etc. This is what was demonstrated by the successful simulation of successive adsorption-desorption experiments in the case of naphthalene.

5) The modelling and simulation results confirm the experimental observations and show that, for short time periods, the major adsorbed quantity is located on the external surface and in the macro-meso pores. This conclusion is important for further process design, for the choice of the GAC according to its porous structure and in relation with the process contact time.

6) The model takes into account the dominant phenomena occurring in the system studied and the specific properties of the adsorbent related to the porous system, being sufficiently complete to describe this kind of system. The principal weakness lies in the parallel pore assumption, the main consequence of which could be a slight overestimate of the microporous adsorption (supposition not verified). However, in the case of the system studied (PAH in aqueous solution adsorbed on GAC), the microporous adsorption is still very low and hardly useful for a real application. Consequently, the model presented is considered well suited to modelling adsorption/desorption processes for aqueous PAH solutions on GAC.

7) Besides its predictive character, the model is mathematically simple and easy to solve, and hence it can be easily used in more complex models describing treatment processes and coupled bio-physico-chemical phenomena or it can be used with different adsorption equilibrium laws (non-linear in this case).

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Figure captions

Figure 1.a: Scanning electron micrographs of the activated carbon PICAS35; b) scheme of a GAC particle

Figure 2.a: Adsorption kinetics of toluene at 25°C, (♦) $C_{0,exp}=5\text{g m}^{-3}$ (▲) $C_{0,exp}=13\text{g m}^{-3}$

Figure 2.b: Adsorption pseudo-isotherms of toluene at 25°C (●) $C_{0,exp}=21\text{g m}^{-3}$ /contact time=600h, (♦) 200g m^{-3} /94 h, (■) 10g m^{-3} / 48h ,(▲) 7g m^{-3} / 48h.

Figure 2.c: Adsorption kinetics of naphthalene at 25°C, (▲) $C_{0,exp}=20\text{g m}^{-3}$.

Figure 2.d: Adsorption pseudo-isotherms of naphthalene at 25°C (●) $C_{0,exp}=6\text{g m}^{-3}$ /contact time=48h, (▲) 30g m^{-3} / 144h.

Figure 3.a: Simulation of adsorption behaviour: (a) Naphthalene concentration (g m^{-3}) in liquid compartments with two different Solid/Liquid ratios: $S/L=0.04\text{g L}^{-1}$ (black lines) and $S/L=4\text{g L}^{-1}$ (grey lines) with $C_0 = 22\text{g m}^{-3}$.

Figure 3.b: Naphthalene distribution between the particle compartments with $C_0 = 22\text{g m}^{-3}$ and $S/L=0.04\text{g L}^{-1}$.

Figure 4.a: Sensitivity analysis on adsorption kinetics of naphthalene ($C_{0,exp}=20\text{g m}^{-3}$).

Experimental data (♦) and simulated data (black line), effect of K_e , D_e , D_s and k_{ext} .

Figure 4.b: Pseudo-isotherms of adsorption and desorption of naphthalene at 25°C (●) adsorption experimental data $C_{0,exp}=6\text{g m}^{-3}$ /contact time =48h; (♦) first desorption; (□) second desorption; simulated data are represented in line.

Table captions

Table 1: Model variables

Table 2: Parameters available from experimental data and measurements

Table 3: Parameters estimated by model fitting procedure and estimated diffusion coefficients

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651 *Figure 1*

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652 Figure 2
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Figure 3.

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Table 1: Model variables

Variable	Description	Unit
C	Concentration in the bulk liquid	g m^{-3}
C_{ext}^e	Equilibrium concentration close to the external surface	g m^{-3}
C_p	Concentration in the mesopores and macropores	g m^{-3}
$\bar{C}_p$	Mean concentration in the mesopores and macropores	g m^{-3}
C_{mp}^e	Equilibrium concentration in the liquid phase at the micropore inlet	g m^{-3}
$\bar{C}_{mp}^e$	Equilibrium mean concentration in the liquid phase at the micropore inlet	g m^{-3}
Q	Total quantity adsorbed	g g^{-1}
Q_{ext}	Quantity adsorbed on the particle external surface	g m^{-2}
Q_p	Quantity adsorbed in the mesopores and macropores	g m^{-2}
$\bar{Q}_p$	Mean quantity adsorbed in the mesopores and macropores	g m^{-2}
Q_{mp}	Quantity adsorbed in the micropores	g m^{-2}
$\bar{Q}_{mp}$	Mean content in the micropores	g m^{-2}
r	Radial direction	m
t	Time	s

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Table 2: Parameters available from experimental data and measurements

Parameter	Description	Unit	Experimental value or estimation
a_s	Specific surface area of GAC particles	$\text{m}^2 \text{m}^{-3}$	$a_s = f_a (3/R)$; $a_s = 39340$
f_a	Shape factor	-	4.3; estimated by microscope imaging (Figure 1.a)
$C_{0,\text{exp}}$	Concentration of the pollutant solution used for adsorption (desorption) experiments	g m^{-3}	Different experimental values
C_{exp}	Final concentration in an experimental sample	g m^{-3}	Different experimental values
V	Volume of liquid in the experimental sample	m^3	Different experimental values
R	Particle mean radius	m	$3.25 \cdot 10^{-4}$ (manufacturer data)
S	GAC mass in the experiments	g	Different experimental values
V_p	Volume of mesopores and macropores	$\text{m}^3 \text{g}^{-1}$	$1.1 \cdot 10^{-7}$ (BET evaluation)
ρ	GAC particle density	g m^{-3}	420000 (manufacturer's data)
ε	Bulk liquid volume fraction		$\varepsilon = \frac{V}{(V + S/\rho)}$
ε_p	Mesopore- and macropore porosity		$\varepsilon_p = \rho V_p$
σ_p	Mesopore and macropore specific surface area	$\text{m}^2 \text{g}^{-1}$	394 (BET evaluation)
σ_{mp}	Micropore specific surface area	$\text{m}^2 \text{g}^{-1}$	1576.6 (BET evaluation)
σ_{ext}	External surface specific area available for adsorption	$\text{m}^2 \text{g}^{-1}$	$\sigma_{\text{ext}} = 0.5(a_s / \rho)$

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Table 3: Parameters estimated by model fitting procedure and estimated diffusion coefficients

Parameter	Description	Unit	Toluene	Naphthalene
K_e	Adsorption equilibrium constant	m	$2.3 \cdot 10^{-4}$	$1.38 \cdot 10^{-2}$
$k_{o,p}$	Mesopore/macropore overall mass transfer coefficient	$m \cdot s^{-1}$	$1.9 \cdot 10^{-7}$	$2.2 \cdot 10^{-6}$
$k_{o,mp}$	Micropore overall mass transfer coefficient	$m \cdot s^{-1}$	$1.9 \cdot 10^{-8}$	$1.9 \cdot 10^{-8}$
k_{ext}	External mass transfer coefficient	$m \cdot s^{-1}$	$1.0 \cdot 10^{-5}$	$7.0 \cdot 10^{-6}$
D_e	Effective mesopore/macropore pore diffusion coefficient	$m^2 \cdot s^{-1}$	$1.3 \cdot 10^{-11}$	$2.1 \cdot 10^{-10}$
D_s	Effective surface diffusion coefficient	$m^2 \cdot s^{-1}$	$1.2 \cdot 10^{-12}$	$1.2 \cdot 10^{-12}$