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1 Analysis and modelling of non-equilibrium sorption of 2 aromatic micro-pollutants on GAC with a multi- 3 compartment dynamic model

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8 Abstract

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

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

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25 **1. Introduction**

26

27 Because of industrial and urban development, many hazardous organic substances
28 and micro-pollutants are discharged into the environment via wastewaters (Williams,
29 1990; Douben, 2003). Removing chemical contaminants from wastewaters continues
30 to be a central problem in environmental remediation and severe discharge
31 constraints are now imposed by legislation for a number of chemicals (Water
32 Framework Directive 2000) like monoaromatic and polyaromatic hydrocarbons.
33 Adsorption is a well established technique for the removal of low concentrations of
34 organic pollutants from industrial wastewater. Among the many adsorbents available,
35 activated carbon is effective in removing a large variety of organic components
36 (Seidel et al., 1985). Treatment options may range from activated carbons that differ
37 in pore structure and surface chemistry to the control of one or more chemical
38 compounds and mixtures. Granular Activated Carbon (GAC) has been shown to be
39 efficient for the removal of organic micropollutants including aromatic hydrocarbons,
40 halogenated hydrocarbons, pesticides, polychlorobiphenyl and surfactants
41 (Zimmerman et al., 2004). The optimisation of GAC processes for industrial
42 wastewater treatment demands a good knowledge of the adsorption and desorption
43 dynamics. When GAC is operated in a completely mixed reactor (ref) fed with
44 wastewater, it can be subjected to micropollutant concentrations that vary with time,
45 leading to non-equilibrium in the system. Few studies have reported the analysis of
46 this dynamics, which depends on mechanisms of internal diffusion into GAC in
47 different compartments of the granular medium: surface, macro-porosity and micro-
48 porosity.

49

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 ($500\text{-}2000\text{m}^2\text{ g}^{-1}$) (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

75 adsorption of GAC is frequent in the literature (Seredych et al., 2005; Ania et al.,
76 2007; Valderrama et al., 2007; 2008a; 2008b; Cabal et al., 2009b), dynamic models
77 that consider adsorption in multi-compartment porous media are rare. The sorption of
78 organic micropollutants onto natural and synthetic sorbents has been described as a
79 complex process in which the properties of the sorbate and the solvent play a critical
80 role. The sorption process occurs within the boundary layer around the sorbent and
81 proceeds in the liquid-filled pores or along the walls of the pores of the sorbent. As
82 the classical modelling approaches point out, the adsorption process is composed of
83 several steps:

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

91

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

99 In most studies, the adsorption rate of organic compounds from aqueous solutions is
100 modelled by using several simplistic mathematical expressions that include the
101 pseudo-first order (Lagergren, 1898), pseudo-second order (Vinod and Anirudhan,
102 2003; Wu et al., 2009), the intraparticle diffusion model (Weber, 1963; Cabal et al.,
103 2009a) and the Elovich model (Chien and Clayton, 1980). Although these kinetic
104 equations have been frequently employed to interpret adsorption data obtained under
105 non-equilibrium conditions, their theoretical origins still remain unknown (Liu and
106 Shen, 2008). The specific parameters contained in these equations can be
107 determined only by fitting on experimental data and are dependent on the operating
108 conditions, e.g. the initial sorbate concentrations. Wu et al (2009) observed that, for
109 the same sorbate/sorbent pair, the performance of a given kinetic model depended
110 on the particle sizes. Another common aspect of most studies on PAH adsorption is
111 that the solutions used were relatively concentrated (with respect to the PAH
112 solubility) and prepared using a co-solvent (alcohol), in a narrow range of
113 concentration values.

114 To describe the equilibrium adsorption, the most commonly used models are the
115 Langmuir and Freundlich models (Cornelissen et al., 2005; Pikaar et al., 2006).
116 Pikaar et al. (2006) have performed a statistical analysis on isotherm models to fit
117 sorption data for the sorption of organic compounds to activated carbon and found
118 that the dual Langmuir equation is, in general, preferable to the single and triple
119 Langmuir equations, the Freundlich equation, a Polanyi-Dubinin-Manes equation, or
120 the Toth equation. Naphthalene adsorption equilibrium in aqueous solution has been
121 studied through the Langmuir-Freundlich single solute isotherm (Derylo-Marczewska,
122 1984; Ania et al., 2007)

123 However, few works have developed physical deterministic models for the
124 explanation of the adsorption kinetics of toluene and naphthalene on activated
125 carbon. Some studies have been conducted on simulation and prediction of pilot
126 plant and full-scale adsorber data, e.g. Crittenden et al. (1987), who used a
127 homogeneous solid diffusion model (HDSM) of GAC adsorption of dichloroethylene
128 in a contaminated groundwater matrix. Valderrama et al. (2008a), have studied PAH
129 removal through GAC adsorption and found that the rate-determining step of PAH
130 extraction is the sorbent-phase diffusion. They used two non-equilibrium adsorption
131 models: the Homogeneous Particle Diffusion Model (HPDM) and the Shell
132 Progressive Model (SPM) and have determined PAH effective particle diffusion
133 coefficients (D_{eff}) in the range $1.1 \cdot 10^{-13}$ – $6.0 \cdot 10^{-14} \text{m}^2 \cdot \text{s}^{-1}$. Though many papers
134 dealing with adsorption of organic substances from aqueous solutions have been
135 published (Seredych et al., 2005; Ania et al., 2007; Valderrama et al., 2007; 2008a;
136 2008b; Cabal et al., 2009b); the rate and the mechanisms of the adsorption process
137 itself remain unclear. Therefore, it would be appropriate to evaluate a model capable
138 of predicting the equilibrium and kinetic sorption performance of GAC for aqueous
139 trace organic molecules based on fundamental sorbent and sorbate properties.

140

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

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

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

155

156 **2. Materials and experimental methods**

157

158 *Adsorbates and adsorbents*

159 Toluene and naphthalene were supplied by Sigma Aldrich. Toluene from the BTEX
160 group solvents was chosen as a typical mono-aromatic hydrocarbon, naphthalene
161 was chosen as a model compound for a light molecule of the group of polyaromatic
162 hydrocarbons. All the above chemicals were more than 99% pure. Organic stock
163 solutions were prepared in ultrapure water in a concentration range of approximately
164 0.2 to 200g m⁻³.

165

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

173 addition to the vials, the GAC was rinsed three times with ultra-pure water to remove
174 dissolved contaminants and fine particles, which could have affected the adsorption
175 capacity of the activated carbon (Summers and Roberts, 1988; Srivastava and Tyagi,
176 1995). The GAC was then dried at 105°C for 24h prior to storage in a dessicator until
177 use (Cooney and Xi, 1994). It is generally accepted that activated carbon has a
178 bimodal pore size distribution and contains pores ranging from several microns to a
179 few angstroms. According to the classification by the International Union of Pure and
180 Analytical Chemistry (IUPAC), there are three types of pores: micropores having
181 dimensions less than 2nm, macropores larger than 500nm, and mesopores lying
182 between these two limits.

183

184 *Adsorption of pollutants on GAC*

185 Adsorption measurements of toluene and naphthalene from aqueous solutions on
186 carbon adsorbents were performed at 25°C in a stirred batch system, which
187 consisted of 120mL amber glass vials filled without headspace and closed with
188 Teflon-coated septa. Experiments were conducted in laboratory ultrapure water (tap
189 water treated by ion exchange and UV). All points were obtained in duplicate or
190 triplicate. A control sample without GAC was identically prepared for each
191 experiment. The different aqueous solutions of pollutants without solid were first
192 stirred on a rotary stirrer for 72h. Measurement by GCMS determined the real initial
193 concentration of the solution before the adsorption experiment, taking into account
194 the artefacts associated with the adsorption of pollutants on the different components
195 of the reactor (Huang et al., 1988). The GAC was then weighed with an accuracy of
196 +/- 0.001g and added into the vials. Tightly closed, the vials were shaken for 2-168h
197 for the kinetic study. This revealed that the concentration values stabilised

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

$$204 \quad Q_{\text{exp}} = (C_{0,\text{exp}} - C_{\text{exp}}) \cdot \frac{V}{S}, \quad (1)$$

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

207

208 *Analytical procedures*

209 Pollutant concentrations were determined using a gas chromatograph (Varian 3900),
210 equipped with a mass spectrometer detector (Saturn 2100T) using helium (99.999%
211 purity) as carrier gas coupled with an automatic headspace sampler (Quma HSS40).
212 Separation was accomplished using a $30\text{m} \times 0.25\text{mm} \times 0.25\mu\text{m}$ column (fused silica
213 VARIAN, type VF-5MS (5% phenyl 95% dimethylpolysiloxane)). The water samples
214 (10mL) were transferred to 20mL glass vials with Teflon-coated septa and aluminium
215 seals. The samples were equilibrated for 30min at 80°C and an aliquot of 1mL of the
216 headspace gas was injected into the gas chromatograph. The detection limit was
217 $1\mu\text{g L}^{-1}$. The accuracy for measurements of split samples containing a concentration
218 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
219 remove all traces of organics.

220

221

222

223 *SEM analysis*

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

227

228 **3. Modelling**

229

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

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

237

238 And on the following supplementary assumptions:

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

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

251

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

254 The external transfer is characterised by:

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

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

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

$$261 \quad \varepsilon_p \frac{\partial C_p}{\partial t} + \sigma_p \rho \frac{\partial Q_p}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_e \frac{\partial C_p}{\partial r} \right) \quad (2)$$

262 with the boundary conditions:

$$263 \quad - \quad r=0, \quad \frac{\partial C_p}{\partial r} = 0 \quad (3)$$

$$264 \quad - \quad r=R, \quad D_e \frac{\partial C_p}{\partial r} = k_{\text{ext}} (C - C_p|_R) \equiv \text{flux}_p \quad (4)$$

265 C is the bulk concentration (g m^{-3}). For the meso- and macro-pore compartment: C_p
 266 and Q_p are the pore concentration (g m^{-3}) and adsorbed quantity (g m^{-2}) at local
 267 coordinates of time t (s) and space r (m), D_e is the effective diffusion coefficient ($\text{m}^2 \text{s}^{-1}$),
 268 ε_p is the porosity, ρ (g m^{-3}) is the particle density, σ_p is the specific surface area
 269 ($\text{m}^2 \text{g}^{-1}$), flux_p ($\text{g m}^{-2} \text{s}^{-1}$) is the flux exchanged between the pore compartment and the
 270 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:

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

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

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

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

278 For the micropore compartment (subscript mp): Q_{mp} is the locally adsorbed quantity

279 (g m^{-2}), $C_{mp}^e |_R$ 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:

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

$$293 \quad \varepsilon \frac{dC}{dt} = -(a_s \text{flux}_{\text{ext}} + a_s \text{flux}_p + a_s \text{flux}_{\text{mp}}) \quad (11)$$

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

$$301 \quad Q_p = K_e C_p \quad (12)$$

$$302 \quad \frac{dQ_p}{dt} = K_e \frac{dC_p}{dt} \quad (13)$$

303

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

310

311 In this simplified approach, mean concentrations are used instead of the radially
 312 varying concentrations. One of the consequences is the possibility of using the "linear
 313 driving force" model (Gleuckauf, 1947) associated with a global mass transfer
 314 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:

$$332 \quad Q = \sigma_p \bar{Q}_p + \sigma_{mp} \bar{Q}_{mp} + \sigma_{ext} Q_{ext} + \varepsilon_p \frac{S}{\rho} \bar{C}_p \quad (23)$$

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:

$$339 \quad OF = \frac{1}{n} \sum_1^n \left(\frac{|C_{sim} - C_{exp}|}{C_{exp}} \right)^2 \quad (24)$$

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

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

357

358 **4. Results and discussion**

359

360 As explained previously, two kinds of experiments were performed: (1) a kinetic study
361 in which the evolution of the eluate concentration was measured versus time; (2) a
362 pseudo-isotherm study in which the evolution of the eluate concentration was
363 measured when the ratio GAC/liquid (i.e. S/L) varied, for a given initial concentration
364 $C_{0,exp}$ and a given constant contact time. Examples of experimental results are given
365 in Figure 2 for toluene and naphthalene: kinetics obtained for different initial
366 concentration values ($C_{0,exp}$) and isotherms obtained for different $C_{0,exp}$ and contact
367 times.

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

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

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

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

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

387

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

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

393 The effective diffusion coefficients (shown in Table 3) for the two types of pores
394 considered in the model were calculated using the formula of Eq.14 and Eq.15. The
395 values are reasonable for the type of porosity and diffusion mechanism considered.
396 For reference, the molecular diffusion coefficients in water are $9.5 \cdot 10^{-10} \text{m}^2 \text{s}^{-1}$ and
397 $6.6 \cdot 10^{-10} \text{m}^2 \text{s}^{-1}$ for toluene and naphthalene respectively.

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

400

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

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

408

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

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

419

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

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

439
440 Among the adjusted parameters, the adsorption constant, K_e , and the mass transfer
441 coefficient for macro- and meso-pores $k_{o,p}$ (or the effective diffusion coefficient D_e)
442 are the most sensitive. Figure 4.a shows a sensitivity study carried out for the kinetic
443 curve of naphthalene. Each curve was calculated by multiplying the parameters K_e ,
444 D_e , D_s and k_{ext} by 10, one by one. The sensitivity of a given parameter is not the
445 same over the whole time scale and this result was expected.

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

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

459

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

465

466 **5. Conclusions**

467

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

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

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

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

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

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

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

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

517

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519

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References

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526 **Water Framework Directive 2000. Directive 2000/60/EC of the European Parliament**
527 **and of Council of 23 October 2000 establishing a framework for community action in**
528 **the field of water policy. Official Journal of the European Communities, p. 1–72.**

529 **Ania, C.O., Cabal, B., Pevida, C., Arenillas, A., Parra, J.B., Rubiera, F., Pis, J.J., 2007.**
530 **Effects of activated carbon properties on the adsorption of naphthalene from aqueous**
531 **solutions. Applied Surface Science 253, 5741.**

532 **Bouchez, D., Vittorioso, P., Courtial, B., Camilleri, C., 1996. Kanamycin rescue: A**
533 **simple technique for the recovery of T-DNA flanking sequences. Plant Molecular**
534 **Biology Reporter 14, 115-123.**

535 **Cabal, B., Ania, C.O., Parra, J.B., Pis, J.J., 2009a. Kinetics of naphthalene adsorption on**
536 **an activated carbon: Comparison between aqueous and organic media. Chemosphere**
537 **76, 433-438.**

538 **Cabal, B., Budinova, T., Ania, C.O., Tsyntsarski, B., Parra, J.B., Petrova, B., 2009b.**
539 **Adsorption of naphthalene from aqueous solution on activated carbons obtained from**
540 **bean pods. Journal of Hazardous Materials 161, 1150-1156.**

541 **Cheremisinoff, N.P., Cheremisinoff, P.N., 1993. Carbon adsorption for pollution control.**

542 **Chien, S.H., Clayton, W.R., 1980. Application of Elovich Equation to the Kinetics of**
543 **Phosphate Release and Sorption in Soils. Soil Sci Soc Am J 44, 265-268.**

544 **Cooney, D.O., Xi, Z.P., 1994. Activated Carbon Catalyzes Reactions of Phenolics during**
545 **Liquid-Phase Adsorption. Aiche Journal 40, 361-364.**

546 **Cornelissen, G., Gustafsson, Ouml, 2005. Predictions of large variations in biota to**
547 **sediment accumulation factors due to concentration dependent black carbon adsorption**
548 **of planar hydrophobic organic compounds; Environmental Toxicology and Chemistry**
549 **24, 495-498.**

550 **Crittenden, J.C., Hand, D.W., Arora, H., Lykins, B.W., 1987. Design Considerations for**
551 **Gac Treatment of Organic-Chemicals. Journal American Water Works Association 79,**
552 **74-82.**

553 **Derylo-Marczewska, A., M. Jaroniec, D. Gelbin and A. Seidel, 1984. Heterogeneity**
554 **effects in single-solute adsorption from dilute solutions on solids. Chem. Scr 24, 239-246.**

555 **Ding, L.P., Bhatia, S.K., Liu, F., 2002. Kinetics of adsorption on activated carbon:**
556 **application of heterogeneous vacancy solution theory. Chemical Engineering Science, 57,**
557 **3909-3928**

558 **Do, D.D., Rice, R.G., 1986. Validity of the Parabolic Profile Assumption in Adsorption**
559 **Studies. Aiche Journal 32, 149-154.**

560 **Douben, 2003. PAHs: An Ecotoxicological Perspective. Ecological and Environmental**
561 **Toxicology Series. P.E.T. Douben.**

- 562 Gleuckauf, J.I.C.a.E., 1947. The influence of incomplete equilibrium on the front
563 boundary of chromatograms and the effectiveness of separation. *J Chem Soc*, 1315–
564 1321.
- 565 Goto, M., Smith, J.M., Mccoy, B.J., 1990. Parabolic Profile Approximation (Linear
566 Driving-Force Model) for Chemical-Reactions. *Chemical Engineering Science* 45, 443-
567 448.
- 568 Huang, C.W., Hung, Y.T., Lo, H.H., 1988. Contact Oxidation Process Followed by
569 Activated Carbon Adsorption for Textile Waste-Water Treatment. *Acta Hydrochimica
570 Et Hydrobiologica* 16, 593-605.
- 571 Jonker, M.T.O., Koelmans, A.A., 2002. Extraction of polycyclic aromatic hydrocarbons
572 from soot and sediment: Solvent evaluation and implications for sorption mechanism.
573 *Environmental Science & Technology* 36, 4107-4113.
- 574 Lagergren, 1898. Zur theorie der sogenannten adsorption gelöster stoffe. *K. Sven* 24, 1-
575 39.
- 576 Liu, Y., Shen, L., 2008. From Langmuir Kinetics to First- and Second-Order Rate
577 Equations for Adsorption. *Langmuir* 24, 11625.
- 578 Pikaar, I., Koelmans, A.A., van Noort, P.C.M., 2006. Sorption of organic compounds to
579 activated carbons. Evaluation of isotherm models. *Chemosphere* 65, 2343-2351.
- 580 Roustan, M., 2003. Transfert gaz-liquide dans les procédés de traitement des eaux et des
581 effluents gazeux, Lavoisier, 798p.
- 582 Seidel, A., Tzscheutschler, E., Radeke, K.-H., Gelbin, D., 1985. Adsorption equilibria of
583 aqueous phenol and indol solutions on activated carbons. *Chemical Engineering Science*
584 40, 215.
- 585 Seredych, M.M., Gun'ko, V.M., Gierak, A., 2005. Structural and energetic
586 heterogeneities and adsorptive properties of synthetic carbon adsorbents. *Applied
587 Surface Science* 242, 154.
- 588 Srivastava, S.K., Tyagi, R., 1995. Competitive adsorption of substituted phenols by
589 activated carbon developed from the fertilizer waste slurry. *Water Research* 29, 483.
- 590 Summers, R.S., Roberts, P.V., 1988. Activated Carbon Adsorption of Humic
591 Substances.1. Heterodisperse Mixtures and Desorption. *Journal of Colloid and Interface
592 Science* 122, 367-381.
- 593 Valderrama, C., Cortina, J.L., Farran, A., Gamisans, X., Heras, F.X.D.L., 2008a.
594 Kinetic study of acid red "dye" removal by activated carbon and hyper-cross-linked
595 polymeric sorbents Macronet Hypersol MN200 and MN300. *Reactive & Functional
596 Polymers* 68, 718-731.
- 597 Valderrama, C., Cortina, J.L., Farran, A., Gamisans, X., Lao, C., 2007. Kinetics of
598 sorption of polyaromatic hydrocarbons onto granular activated carbon and Macronet
599 hyper-cross-linked polymers (MN200). *Journal of Colloid and Interface Science* 310, 35-
600 46.

- 601 Valderrama, C., Gamisans, X., de las Heras, X., Farran, A., Cortina, J.L., 2008b.
602 Sorption kinetics of polycyclic aromatic hydrocarbons removal using granular activated
603 carbon: Intraparticle diffusion coefficients. *Journal of Hazardous Materials* 157, 386-
604 396.
- 605 Vinod, V.P., Anirudhan, T.S., 2003. Adsorption Behaviour of Basic Dyes on the Humic
606 Acid Immobilized Pillared Clay. *Water, Air, & Soil Pollution* 150, 193.
- 607 Weber, W.J.J., J.C. Morris, 1963. Kinetics of adsorption on carbon from solution. *J.*
608 *Sanit. Eng. Div.* 89, 31-60.
- 609 WHO, 2006. *Guidelines for Drinking water Quality*. World Health Organization Press,
610 Switzerland.
- 611 Williams, P.T., 1990. Sampling and Analysis of Polycyclic Aromatic-Compounds from
612 Combustions Systems - a Review. *Journal of the Institute of Energy* 63, 22-30.
- 613 Wu, F.C., Tseng, R.L., Huang, S.C., Juang, R.S., 2009. Characteristics of pseudo-second-
614 order kinetic model for liquid-phase adsorption: A mini-review. *Chemical Engineering*
615 *Journal*
- 616 Zimmerman, J.R., Ghosh, U., Millward, R.N., Bridges, T.S., Luthy, R.G., 2004. Addition
617 of Carbon Sorbents to Reduce PCB and PAH Bioavailability in Marine Sediments:
618 Physicochemical Tests. *Environmental Science & Technology* 38, 5458.
619

Figure captions

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620

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

623

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

625 *Figure 2.b:* Adsorption pseudo-isotherms of toluene at 25°C (●) $C_{0,exp}=21\text{g m}^{-3}$ /contact

626 time=600h, (◆) 200g m^{-3} /94 h, (■) 10g m^{-3} / 48h ,(▲) 7g m^{-3} / 48h.

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

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

629 time=48h, (▲) 30g m^{-3} / 144h.

630

631 *Figure 3.a:* Simulation of adsorption behaviour: (a) Naphthalene concentration (g m^{-3}) in

632 liquid compartments with two different Solid/Liquid ratios: $S/L=0.04\text{g L}^{-1}$ (black lines) and

633 $S/L=4\text{g L}^{-1}$ (grey lines) with $C_0 = 22\text{g m}^{-3}$.

634 *Figure 3.b:* Naphthalene distribution between the particle compartments with $C_0 = 22\text{g m}^{-3}$

635 and $S/L=0.04\text{g L}^{-1}$.

636

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

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

639 *Figure 4.b:* Pseudo-isotherms of adsorption and desorption of naphthalene at 25°C (●)

640 adsorption experimental data $C_{0,exp}=6\text{g m}^{-3}$ /contact time =48h; (♦)first desorption; (□)second

641 desorption; simulated data are represented in line.

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Table captions

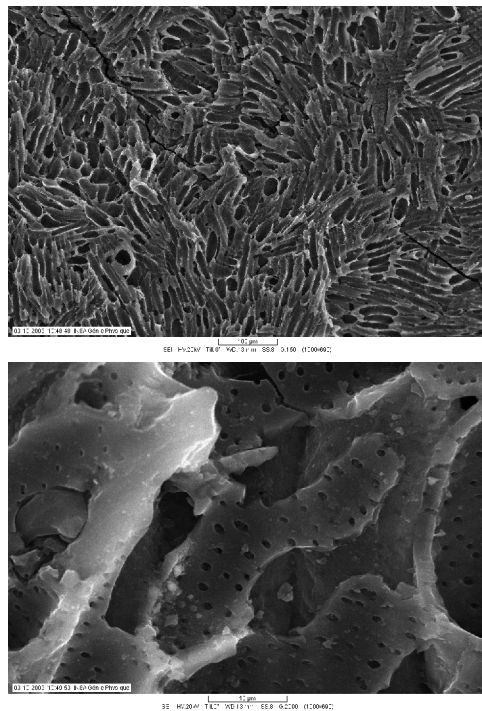
Table 1: Model variables

Table 2: Parameters available from experimental data and measurements

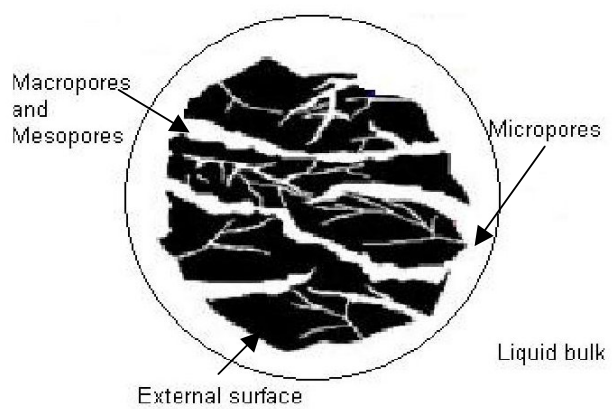
Table 3: Parameters estimated by model fitting procedure and estimated diffusion coefficients

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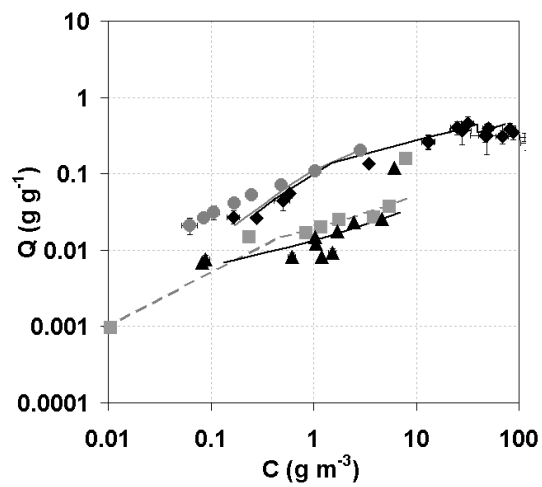
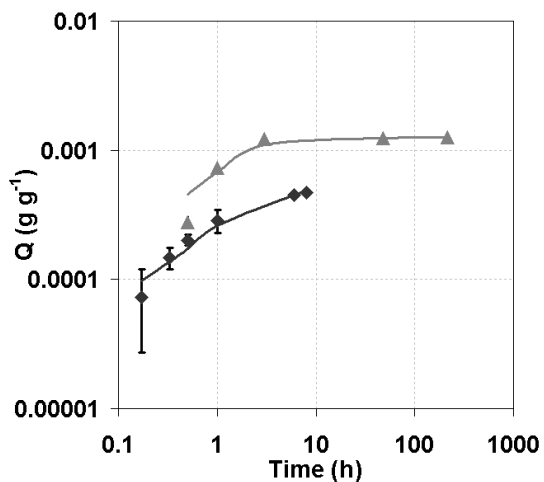


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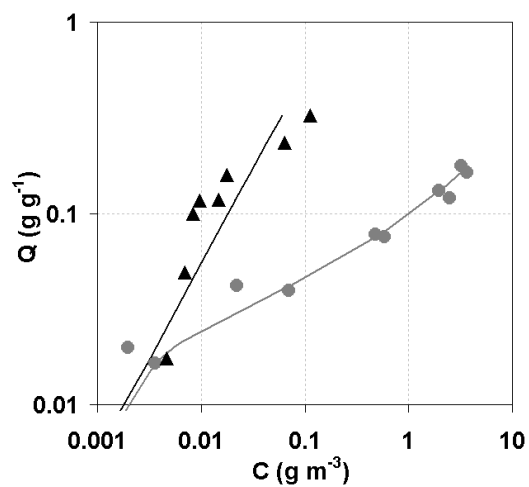
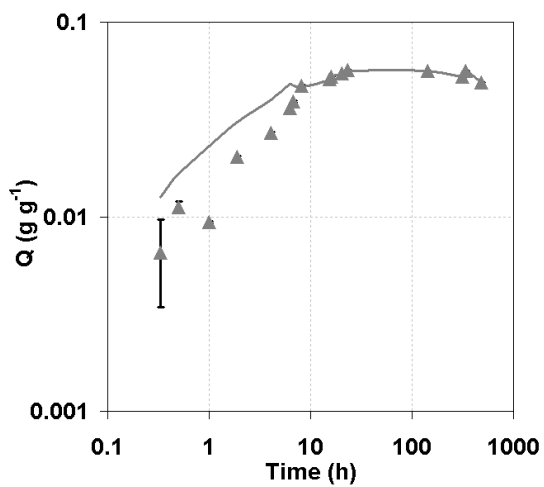
1.b

651 *Figure 1*



2.a

2.b

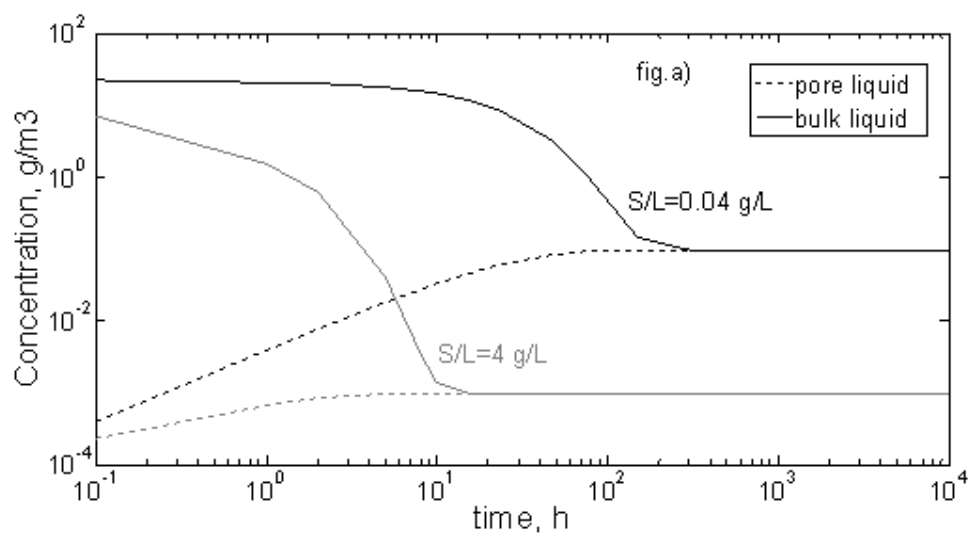


2.c

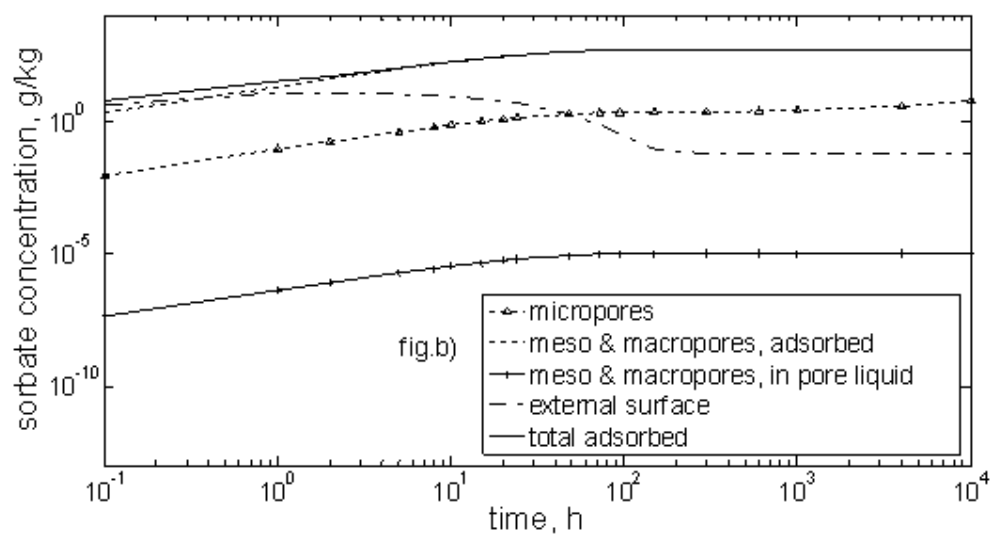
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652 Figure 2
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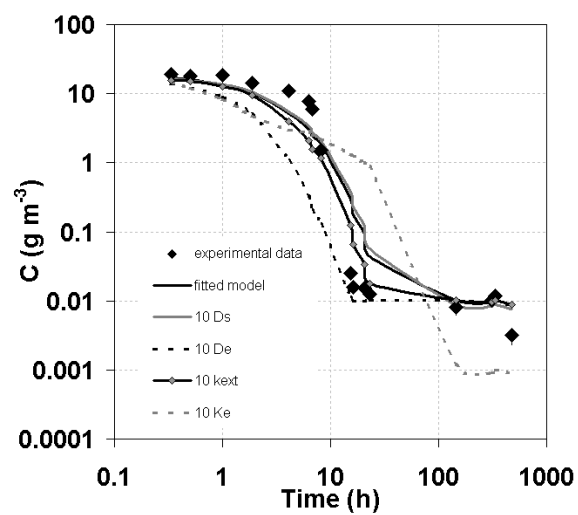


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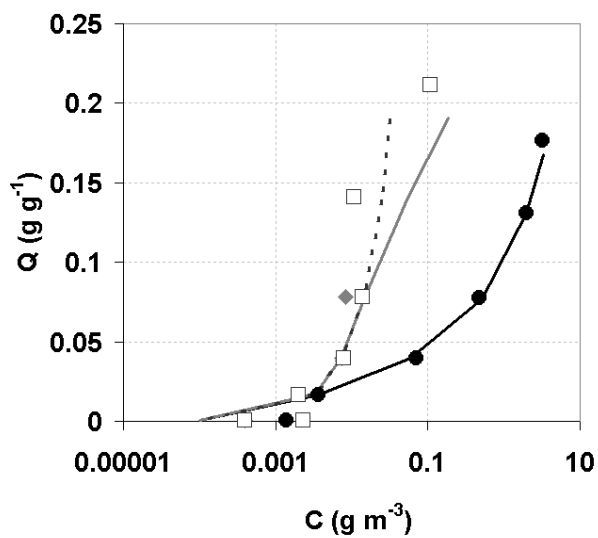
655 Figure 3.

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4.a



4.b

657 Figure 4

658

658

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

659

659

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	$\text{m}^2 \text{g}^{-1}$	$\sigma_{\text{ext}} = 0.5(a_s / \rho)$

660

660 *Table 3: Parameters estimated by model fitting procedure and estimated diffusion*
 661 *coefficients*
 662

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	$m^2 \cdot s^{-1}$	$1.2 \cdot 10^{-12}$	$1.2 \cdot 10^{-12}$

663