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2 **Adsorption of Bisphenol A on KOH-** 3 **activated tyre pyrolysis char**

4

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19 **Abstract**

20 An activated carbon (AC) with a specific surface area of $700 \text{ m}^2 \text{ g}^{-1}$ was
21 prepared by KOH activation of tyre pyrolysis char (TPC) and tested to remove
22 Bisphenol A (BPA) from aqueous solutions. BPA adsorption on this AC was evaluated
23 by studying both the adsorption isotherms at three different temperatures and the
24 decrease of BPA concentration with time, in order to determine the thermodynamic and
25 the kinetic parameters, respectively. The results were compared with those obtained
26 with pristine TPC and with a multipurpose commercial activated carbon (CAC)
27 recommended for BPA adsorption. The present KOH-activated TPC showed a great
28 potential to adsorb BPA with a monolayer capacity as high as 123 mg g^{-1} , higher than
29 that of the CAC used as a reference. BPA adsorption equilibrium data were fitted using
30 different isotherm models with two or three parameters, and the best fitting models were
31 those of Langmuir and Radke-Prausnitz. BPA adsorption was an exothermic process,
32 and the adsorption capacity decreased with increasing temperature. The adsorption
33 kinetics of BPA was adequately described by a pseudo-second order model.

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38 **Keywords:** Scrap tyre; Porous materials; Bisphenol A, Adsorption capacity; Activated
39 carbon; Adsorption kinetics.

40

41 **1. Introduction**

42 The distribution and abundance of plastic wastes in the environment has quickly
43 increased all over the world, and their harmful effects arouse a great concern. Not only
44 plastics by themselves represent a considerable source of pollution, but their additives
45 can be even more detrimental to the environment. Among them, Bisphenol A (BPA) is
46 one of the most ubiquitous chemicals worldwide, with approximately 5.5 million metric
47 tons produced in 2011 (Rochester 2013) and over 100 tons released into the atmosphere
48 by yearly production (Vandenberg et al. 2009). BPA is mainly used in the production of
49 polymers, such as polycarbonate, polyacrylate or epoxy resins. This chemical is found
50 in a huge range of products, including eyeglass lenses, CDs and DVDs, personal
51 computers, power tools, sports equipment, medical devices, and food and drink
52 containers. This continuous exposition to BPA has been reported to be a serious cause
53 of human chronic diseases (Rezg et al. 2014). BPA is a chemical intermediate, a
54 monomer, that was first developed as a synthetic oestrogen in the 1890s and reported to
55 stimulate the female reproductive system in rats in the 1930s (Rochester 2013). BPA is
56 catalogued as an endocrine disrupting compound. Besides, it is a recalcitrant water
57 contaminant, with a low biodegradability and a high resistance to chemical degradation.
58 A comprehensive study on the presence and release of BPA and other endocrine
59 disrupting compounds in drinking water was carried out by Casajuana and Lacorte
60 (Casajuana & Lacorte, 2003) who pointed out the need of better monitoring the organic
61 content in drinking water in general. High BPA concentrations have been already
62 observed in wastewater and wastewater sludge ($0.07 \mu\text{g L}^{-1}$ to $1.68 \mu\text{g L}^{-1}$ and $0.104 \mu\text{g}$
63 g^{-1} to $0.312 \mu\text{g g}^{-1}$, respectively) (Mohapatra et al. 2011).

64 Due to its ubiquitous nature and estrogenic activity potential, BPA removal has
65 been studied from several perspectives. Adsorption/degradation using metal oxides

66 (Koduru et al. 2016), biodegradation (Dai et al. 2016; Mita et al. 2015), advanced
67 oxidation (Pachamuthu et al. 2017), osmotic and ultrafiltration membranes (Zhu & Li
68 2013), amongst others, have been used for BPA removal. However, these methods are
69 not fully successful in BPA removal and have some drawbacks such as formation of
70 toxic degradation by-products, low working concentration ranges, high cost of reagents
71 and raw materials, and the need for further treatment.

72 The adsorption of organic contaminants by activated carbons (ACs) is one of the
73 most effective and widely used methods for purifying water (Bautista-Toledo et al.
74 2005). Many different materials have been used for AC production, including biomass
75 (Skodras et al. 2007), coal (Zhao et al. 2011), petrochemical resins (Kan et al. 2016),
76 industrial waste materials like scrap tyres (Mui et al. 2010b) or PET bottle wastes
77 (Mendoza-Carrasco et al. 2016). The application of char and ACs from tyre rubber for
78 wastewater treatment has been reported, including for the sorption of dyes (Mui et al.
79 2010a), organic pollutants (Alamo-Nole et al. 2011) and heavy metals (Manchón-
80 Vizquete et al. 2005). The sorption efficiency and capacity not only depend on the
81 sorbent structural and chemical properties, but are also strongly influenced by the
82 molecular characteristics of the adsorbates, such as hydrophobicity, polarity and
83 molecular structure (Lian et al. 2013). Several studies reported BPA removal by ACs
84 (Tsai et al. 2006) as well as by sewage sludge (Clara et al. 2004), porous resins (Fan et
85 al. 2011) or carbon nanomaterials, such as graphene, fullerenes and carbon nanotubes
86 (Pan et al. 2008). However, the latter carbon materials are much more expensive than
87 activated tyre pyrolysis char or any other type of activated carbon as stated by the smart
88 review of Sweetman et al. (2017) dealing with the applications of graphene, carbon
89 nanotubes and activated carbons to advanced water purification.

90 In a previous study, a series of ACs were prepared from rubber tyre pyrolysis
91 char (TPC), and their potential for adsorbing a common antibiotic, tetracycline, was
92 examined (Acosta et al. 2016). Herein, one selected AC produced from TPC was
93 applied to the adsorption of BPA. The present manuscript also comprises a thorough
94 review of BPA adsorption studies carried out so far onto ACs. We demonstrate that
95 tyre-derived ACs are a credible option for BPA adsorption, since capacities as high as
96 123 mg g^{-1} were obtained.

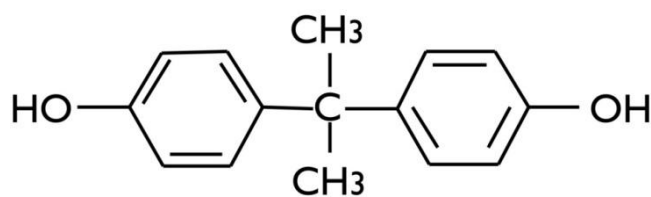
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98 **2. Experimental**

99 2.1 Adsorbents and reactants

100 Tyre wastes were pyrolysed to obtain pyrolytic oil with high calorific value. The
101 derived solid residue, here referred to as tyre pyrolysis char (TPC), was used for the
102 production of activated carbons by KOH activation. Tyre pyrolysis as well as activation
103 conditions were extensively reported elsewhere (Acosta et al. 2016; Acosta et al. 2015).
104 Briefly, the only tyre-derived AC used here was prepared at 750°C with a mass
105 impregnation ratio KOH to TPC equal to 5. This carbon was labelled CK.750.5 and was
106 selected because having the highest product $S_{TOT} = S_{BET} \times \text{carbon yield}$ of the ACs series
107 (see section 3.2.2 below). For comparative purpose of the characteristics of the activated
108 carbon produced, a commercial activated carbon (CAC), Hydrodarco C from the
109 company Cabot Norit, was used as reference of offer on the market. Hydrodarco C is
110 indeed a multi-purpose activated carbon, designed to treat industrial wastewaters.

111 BPA (99% pure; Sigma Aldrich), whose molecular structure is shown in [Figure](#)
112 [1](#), was used to prepare aqueous solutions for adsorption tests.



116 **Figure 1.** Molecular structure of Bisphenol A (BPA).

117 2.2 Materials characterisation

118 An elemental analyser (Vario EL cube, Elementar) was used to determine carbon,
119 hydrogen, nitrogen and sulphur (CHNS) contents of the tested samples. The oxygen
120 content was determined separately with the same apparatus by changing the combustion
121 conditions, and the ash content was determined by difference as described elsewhere
122 (Acosta et al. 2016). The samples were outgassed at 270°C overnight, followed by
123 nitrogen adsorption at -196°C using a 3Flex automatic device (Micromeritics).
124 Micropore volumes, V_{MIC} ($\text{cm}^3 \text{g}^{-1}$), and micropore surface area were determined by
125 application of the t -plot method, BET surface areas, S_{BET} ($\text{m}^2 \text{g}^{-1}$), by application of the
126 BET method, and the total pore volumes, V_{TOT} ($\text{cm}^3 \text{g}^{-1}$), were determined at a relative
127 pressure $P/P_0 = 0.99$ (Gregg & Sing 1982). The mesopore volumes, V_{MES} ($\text{cm}^3 \text{g}^{-1}$), were
128 determined by difference between V_{TOT} and V_{MIC} (Gregg & Sing 1982). Finally, the
129 points of zero charge, pH_{pzc} (dimensionless) were determined as reported elsewhere
130 (Acosta et al. 2016), and average pore sizes were determined using the BJH model
131 (Barrett et al. 1951) applied to the desorption branch of the isotherms. The pore size
132 distributions of the ACs were determined by application of the non-linear density
133 functional theory (NLDFIT) (Jagiello & Olivier 2013) to the nitrogen adsorption branch.
134 Secondary electrons were used for observing the topographic contrast of samples using
135 scanning electron microscopy (FET Quanta 600 FEG), under an accelerating voltage of
136 3 kV.

137 In order to characterise the surface functional groups, infrared spectra of the
138 powdered carbons were obtained with a Fourier-Transform Infrared (FTIR)
139 spectrometer (PerkinElmer Spotlight Frontier) by doing 4 scans in the wavenumber
140 range of 4000–650 cm^{-1} . The amount of proton-binding groups was also measured, and
141 the total surface charge Q (mmol L^{-1}) was calculated. From these quantities, the
142 numbers of groups having pK_a values in selected ranges could be calculated (Jagiello et
143 al. 1995). For that purpose, 0.1g of activated carbon was suspended in 50 mL of NaNO_3
144 solution (0.01 mol L^{-1}) as the supporting electrolyte and was stirred overnight to
145 equilibrate. The suspension was then titrated with NaOH (0.1 mol L^{-1}) under N_2
146 saturation (Jagiello 1994) using an automatic titrator (905 Titrand, Metrohm
147 commanded with tiamo® software V2.2).

148

149 2.3 Adsorption studies of Bisphenol A

150 BPA adsorption was thus investigated using the AC obtained showing the
151 highest total surface area S_{TOT} , which was compared to that of the commercial AC (see
152 subsection 3.2.2 below). Adsorption measurements were performed in hermetically
153 closed glass vials, using 25 and 12.5 mg of TPC char and ACs, respectively, which were
154 added to 25 mL of BPA solution. For the kinetic measurements at 25°C , initial BPA
155 concentrations of 100 mg L^{-1} and 200 mg L^{-1} were used for TPC and ACs, respectively.
156 The initial BPA concentrations used for building adsorption isotherms, i.e., at
157 equilibrium, were ranging from 5 to 80 mg L^{-1} for TPC, and from 50 to 200 mg L^{-1} for
158 ACs. Considering the low surface area of the TPC, we used twice as much the mass of
159 AC and we lowered the BPA concentration in adsorption batches to avoid its fast
160 saturation. BPA adsorption on TPC was done for the sole purpose of evaluating the

161 adsorption improvement after activation, although we are aware that a lower BPA
162 concentration should decrease the equilibrium time.

163 The adsorbents in suspension in BPA solutions were magnetically stirred in a
164 thermostatic water bath at 15, 25 or 35°C for building the equilibrium adsorption
165 isotherms and doing the related thermodynamic analysis (see section 3.5). Initial pH
166 values varied between 6.5 and 7.5, and were not adjusted for any tested material. After
167 the adsorption equilibrium was reached, BPA concentration was measured with an
168 UV/Vis spectrophotometer (Perkin Elmer Lambda 35) at a wavelength of 276 nm. To
169 eliminate the effect of any contribution from soluble materials possibly released by the
170 adsorbents, a blank was done. Particle attrition can indeed be a source of error when
171 using UV spectroscopy. However, our experimental data were fitted extremely well by
172 the selected models. We repeated several times some particular measurements, and the
173 relative error was always lower than 2%.

174 The amount of BPA adsorbed by unit mass of sorbent, $q_{t,e}$, was calculated as:

175
$$q_{t,e} = \frac{V(C_0 - C_{t,e})}{m} \quad (1)$$

176 where C_0 and $C_{t,e}$ (mg L^{-1}) are the initial and equilibrium BPA concentrations,
177 respectively, V (L) is the volume of solution and m (g) is the mass of sorbent. In order to
178 account for the adsorption kinetics of BPA, the experimental data were fitted with
179 pseudo-first and pseudo-second order kinetic models (Ho & McKay 1998; Ocampo-
180 Pérez et al. 2012). The isotherm models listed in [Table 1](#) were used to fit the
181 experimental adsorption data at equilibrium.

182

183

Isotherm	Nonlinear form	Parameters and units			Reference
Langmuir (<i>La</i>)	$q_e = \frac{q_{max} k_L C_e}{1 + k_L C_e}$	q_{max} [$mg\ g^{-1}$]	k_L [$L\ mg^{-1}$]		(Langmuir 1916)
Freundlich (<i>Fr</i>)	$q_e = k_F C_e^{1/n_f}$	k_F [$mg\ g^{-1}$]	n_f^{-1}		(Freundlich 1907)
Sips (<i>Si</i>)	$q_e = \frac{q_{max} k_s C_e^{1/n_s}}{1 + k_s C_e^{1/n_s}}$	q_{max} [$mg\ g^{-1}$]	k_s [$L\ mg^{-1}$]	n_s^{-1}	(Sips 1950)
Dubinin-Radushkevich (<i>DR</i>)	$q_e = q_{max} \exp \left\{ - \left[\frac{RT \ln (C_s/C_e)}{E} \right]^2 \right\}$	q_{max} [$mg\ g^{-1}$]	E [$kJ\ mol^{-1}$]		(Dubinin & Radushkevich 1947)
Dubinin-Astokhov (<i>DA</i>)	$q_e = q_{max} \exp \left\{ - \left[\frac{RT \ln (C_s/C_e)}{E} \right]^n \right\}$	q_{max} [$mg\ g^{-1}$]	E [$kJ\ mol^{-1}$]	n	(Dubinin 1975)
Redlich – Peterson (<i>Re-Pe</i>)	$q_e = \frac{K_R C_e}{1 + a_R C_e^\beta}$	K_R [$mg\ g^{-1}$]	a_R [$L\ mg^{-1}$]	β	(Redlich & Peterson 1959)
Radke-Prausnitz (<i>Ra-Pr</i>)	$q_e = \frac{q_{mRP} K_{RP} C_e}{(1 + K_{RP} C_e)^{m_{RP}}}$	q_{mRP} [$mg\ g^{-1}$]	K_{RP} [$L\ mg^{-1}$]	m_{RP}	(Radke & Prausnitz 1972)

185

186 2.4 Thermodynamic study

187 The thermodynamic parameters: Gibbs free energy (ΔG°), enthalpy (ΔH°) and
 188 entropy (ΔS°), were calculated by the following equations.

$$189 \quad K_C = \frac{C_{Ad}}{C_e} \quad (2)$$

$$190 \quad \ln K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (3)$$

$$191 \quad \Delta G^\circ = -RT \ln K_C \quad (4)$$

192 where K_C (dimensionless) is the equilibrium adsorption constant, which is the ratio of
 193 the residual equilibrium concentration of BPA in the solution, C_{Ad} ($mg\ L^{-1}$), to the

194 amount of BPA adsorbed onto the activated carbon at equilibrium, C_e (mg L^{-1}); T (K) is
195 the temperature, and R ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) is the molar gas constant.

196

197 2.5 Regeneration and reuse study

198 CK.750.5 regeneration study was carried out as described elsewhere (Itodo and
199 Oketunde, 2017). The first adsorption was carried out with 12.5 mg of CK.750.5 that
200 were introduced in 25 mL of a 200 mg L^{-1} BPA solution and stirred at 25°C for 24 h.
201 The spent carbon was then separated and put in contact with 0.05 mL of a 0.1 mol L^{-1}
202 HCl aqueous solution and stirred for 24 h at 25°C . The solution was filtered, and the
203 carbon was thoroughly washed with distilled water until neutral pH, and dried in an
204 oven for 12 h at 85°C under vacuum. Finally, the regenerated carbon was submitted to
205 BPA adsorption again, and the same adsorption-regeneration cycles were repeated 5
206 times.

207

208 **3. Results and discussion**

209 3.1 Pyrolysis process and products

210 Rubber tyre was pyrolysed in conditions presented in a previous publication
211 (Acosta et al. 2015), and the detailed results were also given there. In summary, in the
212 selected experimental conditions, 49.8 wt. % of oil, 40.1 wt. % of char and 10.1 wt. %
213 of gas were obtained. The pyrolytic oil had a high heating value (HHV): 42.9 MJ kg^{-1} ,
214 on average, which is similar to that reported by some authors (Aylón et al. 2010; Quek
215 & Balasubramanian 2013). The energy yield of this pyrolytic oil ($\text{HHV} (\text{MJ kg}^{-1}) \times \text{oil}$
216 yield (wt. \%)) (Quek & Balasubramanian 2013) represents the amount of energy (in MJ)

217 that can be obtained per kg of scrap tyre used in the process. In the present case, the
218 energy yield was obtained from the oil yield in the pyrolysis process and was found to
219 be 22.7 % (MJ kg⁻¹).

220 This pyrolytic oil had an average density and viscosity of 0.949 g cm³ and 2.29
221 ×10⁻³ Pa s, respectively, similar to values already reported for other pyrolytic oils and
222 close to those of commercial diesel fuel (Li et al. 2005). Finally, pyrolytic oil presented
223 an acidity of 0.961 mg KOH g⁻¹ (a value representing the amount of KOH to neutralise
224 1 g of oil) above the permissible limit of 0.5 mg KOH g⁻¹ for being directly used as
225 diesel fuel without oil upgrading, which is an essential but standard and cost-effective
226 way to reduce its high acid content (Bacha et al. 2007). Tyre char composition was
227 mainly 78.9 wt. % of fixed carbon, 6.9 wt. % of volatiles and 13.7 wt. % of ashes. The
228 high carbon content of tyre char makes it a potentially good AC precursor.

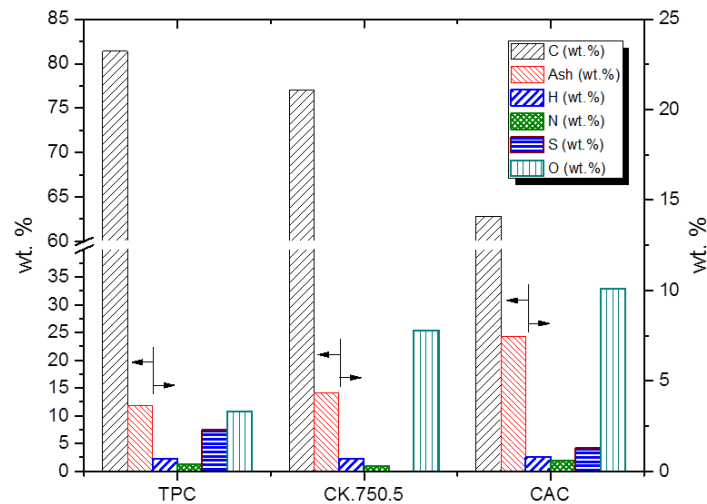
229 3.2 Characteristics of tyre pyrolysis char and activated carbons

230 3.2.1 Elemental analysis

231 The ultimate compositions of TPC, CK.750.5 and CAC are presented in [Figure](#)
232 [2](#). In comparison, tyre scrap rubber contained 6% of ash and organic matter composed
233 of 86 wt.% C (among which less than 30% is fixed carbon), 7.6 wt.% H, 3.2 wt.% O,
234 1.7 wt.% N and 1.6 wt.% S (Acosta et al. 2015).

235 After activation, the ash content increased in the TPC-derived material until 14.1
236 wt. %. Activation also induced a decrease of carbon content, while the oxygen content
237 increased from around 3.3 to 7.8 wt. %, due to the formation of functional groups on the
238 carbon surface. In a similar way, the sulphur content decreased with respect to TPC,
239 which is attributed mainly to the volatility of this element. The same behaviour has been
240 reported for ACs prepared under oxidising atmospheres (San Miguel et al. 2002).

241 Finally, the values of pH_{PZC} were 7.2 and 7.8 for TPC and CK.750.5, respectively,
 242 similar to those reported after chemical activation of scrap tyre rubber (Troca-Torrado et
 243 al. 2011). In contrast, the CAC had a pH_{PZC} of 10.7, which indicates possible activation
 244 in oxidising conditions (Bautista-Toledo et al. 2005).



245
 246 **Figure 2.** Ultimate analysis of tyre pyrolysis char and of the two activated
 247 carbons investigated here.

248

249 3.2.2 Surface area and porosity

250 After activation, the yield of sample CK.750.5 was 53 wt. %. The N_2
 251 adsorption/desorption isotherms at -196°C of TPC, CK.750.5 and CAC are presented in
 252 **Figure 3(a)**. This figure presents the adsorption data with the X axis in logarithmic scale
 253 to better observe the pore volume filled at very low P/P_0 , from 10^{-7} , indicating the
 254 presence of very narrow pores in CK.750.5 and CAC. CK.750.5 and CAC exhibited
 255 isotherms of mixed Types I and IV, according to the IUPAC classification, and
 256 presented a linear part up to 150 and $100\text{ cm}^3\text{ g}^{-1}$, respectively, at relative pressures
 257 close to 0.01. TPC presented a predominantly Type IV isotherm according to the
 258 IUPAC classification, characteristic of mesoporous materials with a poorly developed
 259 microporous structure (San Miguel et al. 2001). The linear portion of those isotherms in

260 the range of medium P/P_0 (0.15-0.60) suggested multilayer adsorption in the mesopores.
261 Only CAC showed a developed hysteresis loop (Type H4) within the range of relative
262 pressures from 0.4 to 1, indicating the existence of a developed mesoporosity with slit-
263 like mesopores. Type H4 loops are observed for many activated carbons and some other
264 nanoporous adsorbents. (Sing & Williams 2004). CK.750.5 and TPC showed a sharp
265 rise of the isotherms at P/P_0 close to 1, which is indicative of capillary condensation
266 occurring in the meso- and macropores. Narrow hysteresis loops, Type H3, were
267 observed for these two materials and therefore useful information can be obtained only
268 by the application of the NLDFT method (Sing & Williams 2004). The pore-size
269 distributions confirmed the presence of mesoporosity in CK.750.5 and TPC, with a
270 maximum of porosity centred around 10 – 40 nm (Acosta et al. 2016).

271 [Figure 3\(b\)](#) presents the textural properties of TPC and ACs in terms of BET surface
272 area, micropore and mesopore volumes. CK.750.5 exhibited a higher micro- and
273 mesoporosity than CAC, and also a S_{BET} higher by $215 \text{ m}^2 \text{ g}^{-1}$. The CAC, Hydrodarco C,
274 was supposed to present a surface area of $600 \text{ m}^2 \text{ g}^{-1}$, but the latter was found to be only
275 $484 \text{ m}^2 \text{ g}^{-1}$. S_{BET} of CACs largely depends on the batch but also depends on the interval of
276 relative pressures (P/P_0) used for applying the BET theory. We chose a range of P/P_0
277 ensuring that the C parameter was positive: we plotted $V_{ads} \times (1-P/P_0)$ as a function of P/P_0 ,
278 V_{ads} being the STP adsorbed volume, and took the range of P/P_0 values wherein $V_{ads} \times (1-$
279 $P/P_0)$ increased with P/P_0 . Therefore, we totally trust the accuracy of our results. The
280 microporous surface area of CK.750.5, determined by the t -plot method, was almost
281 twice that of CAC, 414 and $210 \text{ m}^2 \text{ g}^{-1}$, respectively. The skeletal density was close to 2
282 for all materials (Acosta et al. 2016), while average pore sizes were 31.6, 18.3 and 6.7
283 nm, for TCP, CK.750.5 and CAC.

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285

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a)

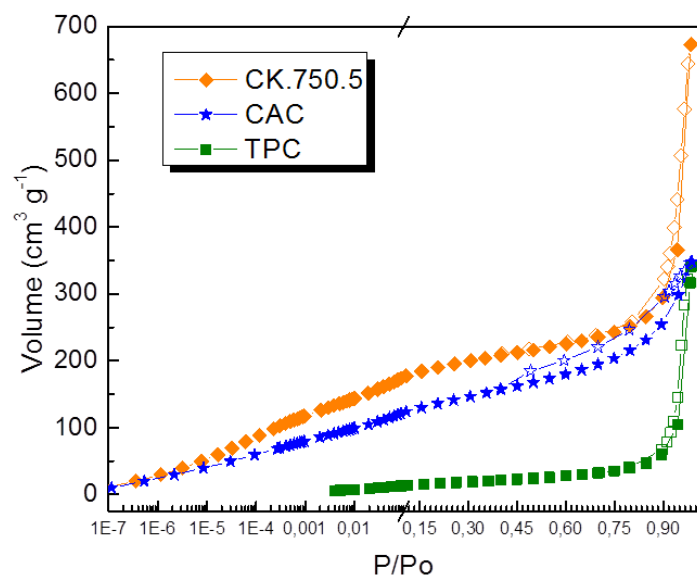
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b)

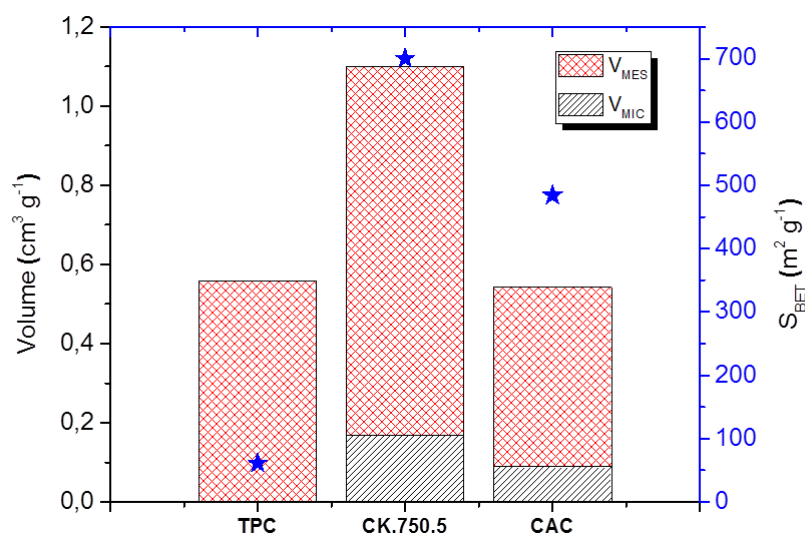
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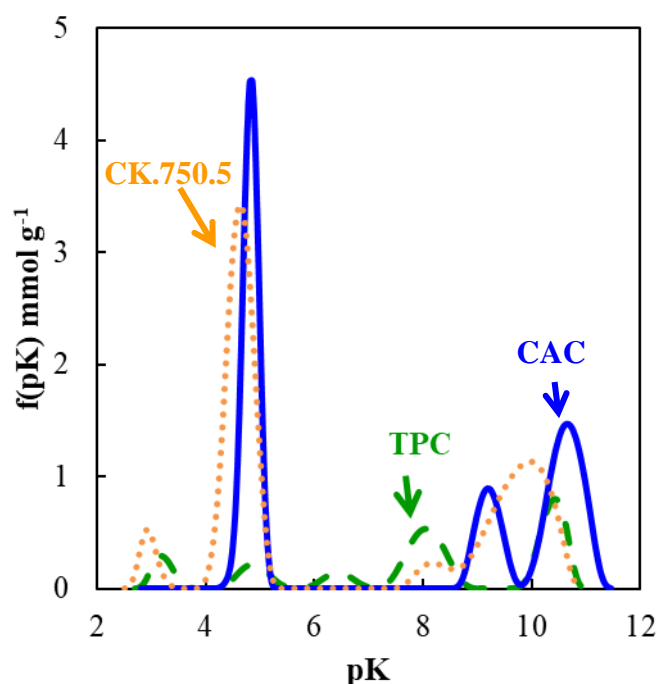
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Figure 3. (a) N₂ adsorption/desorption isotherms of TPC, CK.750.5 and CAC at -196°C. For emphasising their differences in the range of low relative pressures, corresponding to microporosity, the scale of P/P₀ is logarithmic below 0.1 and linear above. (b) Textural characterisation of the same materials: V_{MIC} = micropore volume, V_{MES} = mesopore volume, and surface area (blue stars).

Figure 4 shows the results of the potentiometric titration for the three carbon materials studied therein. TPC had a total number of groups equal to 1.47 mmol g⁻¹ (as shown in Table 2), an amount far lower than what was determined for ACs: 3.37 and

307 3.99 mmol g⁻¹ for CAC and CK.750.5, respectively, in good agreement with the higher
308 O and H contents observed by elemental analysis for ACs. The nature of the functional
309 groups was also different. TPC had more basic (1.09 mmol g⁻¹) than acidic (0.38 mmol
310 g⁻¹) groups.



311

312 **Figure 4.** Density of functional groups as a function of pK_a , for TPC, CAC and
313 CK.750.5

314

315 The pK_a distributions showed the predominance of strongly basic species such as
316 lactol- or hydroxyl-containing functional groups with $pK_a > 8$ (Seredych et al. 2016).
317 CAC presented almost balanced acidic and basic groups, and CK.750.5 had more acidic
318 than basic groups. As it happened with TPC, strongly basic species, with $pK_a > 8$, were
319 present in both ACs but acidic functions, with $pK_a < 5$, also existed. CAC and CK.750.5
320 presented 1.65 and 2.12 mmol g⁻¹ of acidic groups, which represent 49 and 53% of the
321 total groups. The higher number of functional groups present in CK.750.5 might seem
322 to disagree with the flatter IR profile shown in Figure S1 of the Supplementary

323 Information. However, FTIR spectroscopy may be quantitative as far as the
 324 corresponding data can be normalized with respect to the most intense band, which
 325 cannot be done here with so poorly characteristic spectra.

326 Table 2: Peak position and numbers of groups (in parentheses: (mmol g⁻¹)).

Sample	$pK_a < 3$	pK_a 3-5	pK_a 5-7	pK_a 7-8	pK_a 8-10	pK_a 10-12	acidic	basic	All
TPC	-	3.2 (0.14) 4.9 (0.15)	6.4 (0.09)	-	8.0 (0.15)	10.0 (0.46) 10.5 (0.48)	0.38	1.09	1.47
CK.750.5	2.9 (0.20)	4.6 (2.12)	-	-	8.2 (0.15)	10.0 (1.52)	2.12	1.67	3.99
CAC	-	4.82 (1.65)	-	-	9.2 (0.53)	10.6 (1.19)	1.65	1.72	3.37

327

328 From a practical and economic point of view, as important as the surface area is
 329 the material yield. The total surface area, S_{TOT} , was calculated by multiplying S_{BET} by
 330 the carbon yield. S_{TOT} was introduced elsewhere (Fierro et al. 2010) and can be used as a
 331 performance criterion for any process of porous carbon preparation. Several authors
 332 reported ACs prepared from tyre char having surface areas higher than ours (Mui et al.
 333 2010b; Ariyadejwanich et al. 2003; González et al. 2006; San Miguel et al. 2003; Chan
 334 et al. 2011; Teng et al. 2000). However the total surface area (S_{TOT}) obtained in this
 335 study (371 m² g⁻¹), which represents the surface area obtained considering the mass loss
 336 during the activation process, is in the range of the results reported in the literature, and
 337 even higher in some cases, as indicated in Table 3. According to San Miguel et al. (San
 338 Miguel et al. 2001) the different surface areas that were reported may be attributed to
 339 differences in the activation and pyrolysis conditions, including furnace and tyre rubber
 340 characteristics.

341

342

343 **Table 3.** Main characteristics of tyre-derived ACs found in the literature and comparison
 344 with the present study.

References	Activating agent	S_{BET} ($m^2 g^{-1}$)	Yield (%)	S_{TOT} ($m^2 g^{-1}$)
This study	KOH	700	53	371
(Mui et al. 2010b)	CO ₂	1014	33	335
(Ariyadejwanich et al. 2003)	H ₂ O	1177	31.4	370
(González et al. 2006)	H ₂ O	1317	12.5	165
(San Miguel et al. 2003)	H ₂ O	1022	18	184
(Chan et al. 2011)	H ₂ O	962	15	144
(Teng et al. 2000)	KOH	474	-	-

345

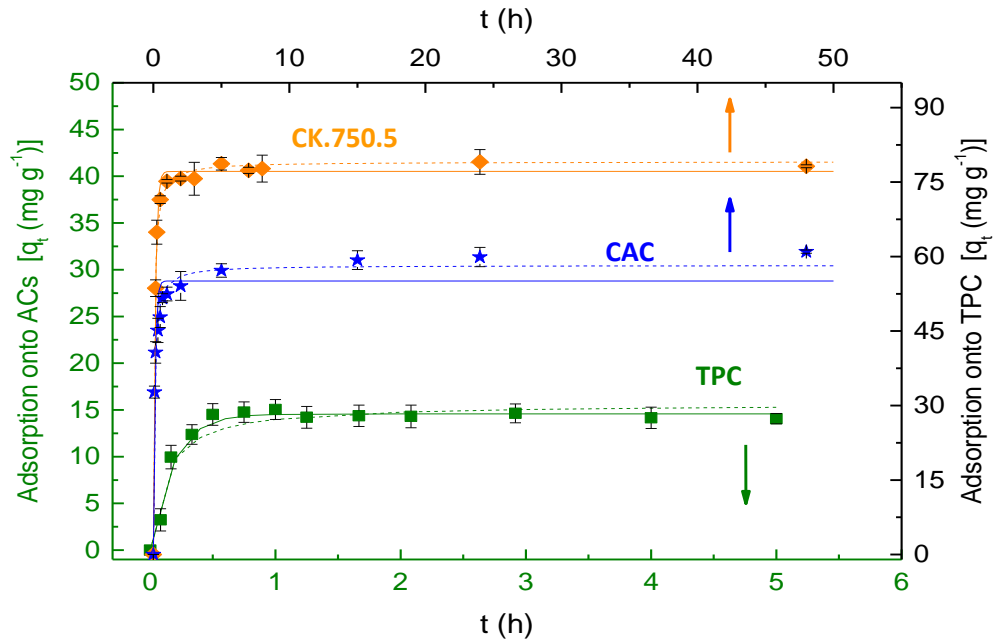
346

347 3.3 Kinetics of BPA adsorption

348 **Figure 5** a) shows the amount of BPA adsorbed per unit mass of adsorbent, q_t
 349 ($mg g^{-1}$), versus contact time, t (h), onto TPC, CK.750.5 and CAC. Equilibrium
 350 adsorption time was obtained after 4 h for TPC, and after 10 h for both CK.750.5 and
 351 CAC. **Table 4** presents the corresponding experimental adsorption capacities at
 352 equilibrium for all materials. **Figure 5** b) shows the BPA removal efficiency
 353 corresponding to the data of **Figure 5** a). The BPA removal was around 7.5% for TPC,
 354 and around 15 and 20% for CAC and CK.750.5, respectively. Those modest BPA
 355 removals imply that higher ratios of sorbent to BPA solutions should be used to reach a
 356 more complete BPA elimination.

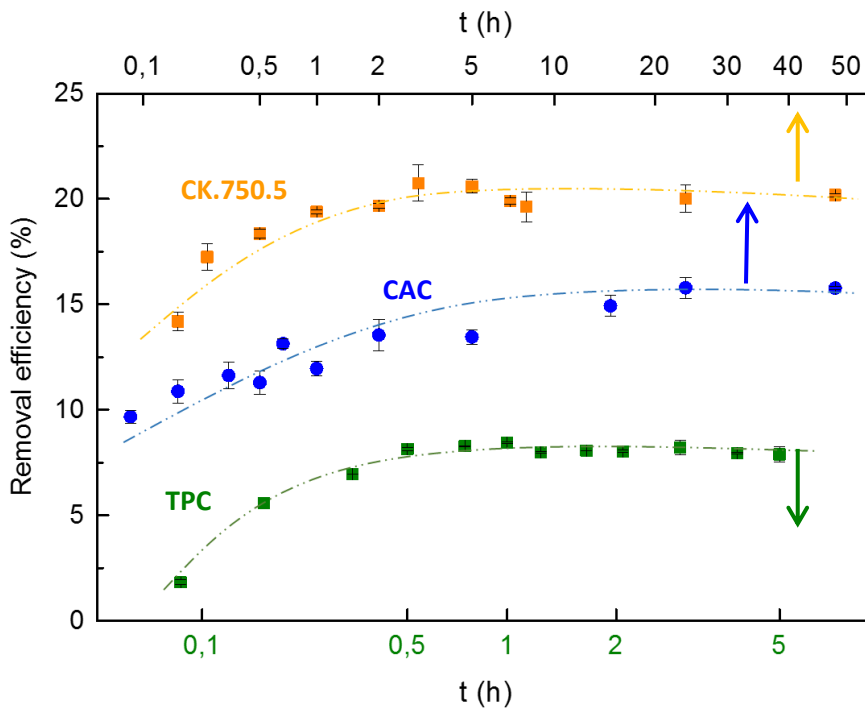
357

a)



358

359 b)



360

361 **Figure 5.** a) Adsorbed amounts of BPA at 25°C as a function of time, on TPC,
 362 CK.750.5 and CAC. Continuous and dotted lines represent the pseudo-first and
 363 pseudo-second order models, respectively. b) BPA removal at 25°C as a function
 364 of time, on TPC, CK.750.5 and CAC. Discontinuous lines are just guides for the
 365 eye. Experimental conditions were: $C_0 = 100 \text{ mg L}^{-1}$ and 200 mg L^{-1} for TPC
 366 and ACs, respectively; stirring speed 170 rpm, temperature 25°C, and pH 6.5 –
 367 7.5. The data of TPC correspond to the top horizontal axis and the right vertical
 368 axis.

369 Table 4 also gathers the parameters derived from the fits of pseudo-first and
 370 pseudo-second order models to the experimental data, as well as the corresponding
 371 coefficients of determination, R^2 . The pseudo-second order model fitted the adsorption
 372 behaviour of ACs better, whereas the pseudo-first order model fitted that of TPC better.
 373 This suggests that adsorption of BPA onto TPC occurs mainly by a process of physical
 374 diffusion monolayer, while there is a rate-limiting step in the case of ACs, possibly
 375 chemical adsorption involving valence forces through exchange of electrons between
 376 sorbent and sorbate (Sulaymon et al. 2012). The adsorption capacities increased in the
 377 order TPC < CAC < CK.750.5 (14.57 < 58.24 < 79.11 mg g⁻¹, respectively), indicating a
 378 faster saturation of TPC, mainly due to its lower S_{BET} .

379

380 Table 4. Adsorption rate constants, correlation coefficients and amounts of BPA
 381 adsorbed at equilibrium obtained by pseudo first- and pseudo second-order models.

	Pseudo-first order			Pseudo-second order			
	q_e (exp.) (mg g ⁻¹)	$k_1 \times 10^{-2}$ (h ⁻¹)	R^2	q_e (predicted) (mg g ⁻¹)	$k_2 \times 10^{-4}$ (g (mg h) ⁻¹)	R^2	q_e (predicted) (mg g ⁻¹)
TPC	14.05	5.5	0.97	14.57	54.0	0.93	15.64
CK.750.5	78.19	7.1	0.99	77.17	19.0	0.99	79.11
CAC	60.99	8.3	0.93	55.09	22.0	0.99	58.24

382

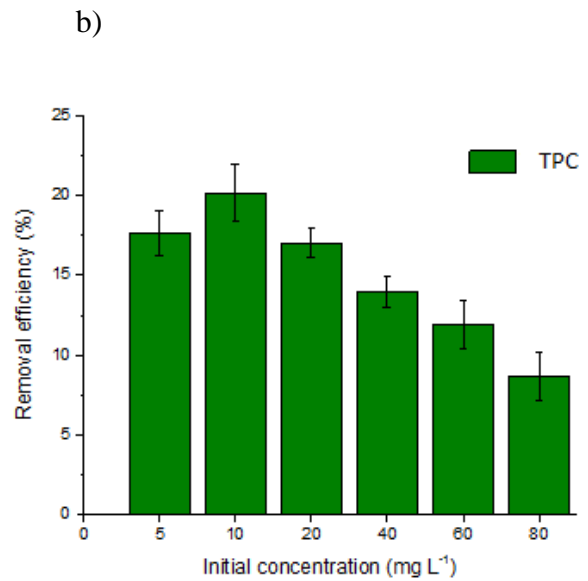
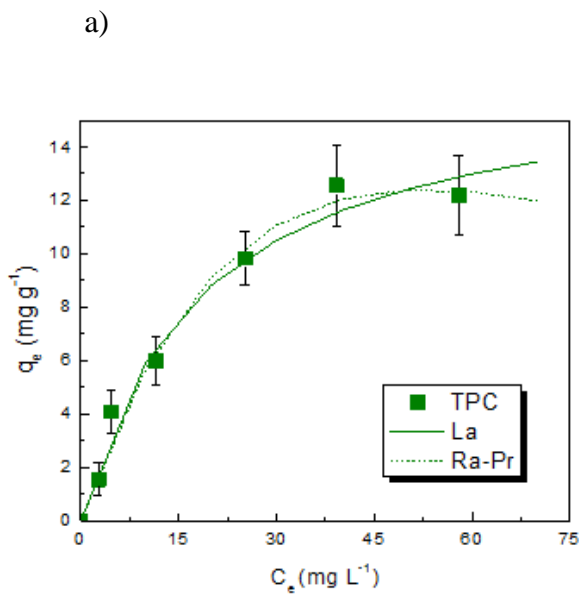
383 3.4 BPA adsorption at equilibrium

384 3.4.1 General features of BPA adsorption isotherms

385 BPA adsorption capacity on TPC and ACs was calculated using Equation (1), and
 386 the adsorption isotherms were obtained at 25°C. The adsorption capacity, q_e (mg g⁻¹),
 387 was plotted versus the equilibrium concentration of the solute, C_e (mg L⁻¹), for TPC in
 388 Figure 6(a) and for both CK.750.5 and CAC in Figure 6(c). As it can be observed, the

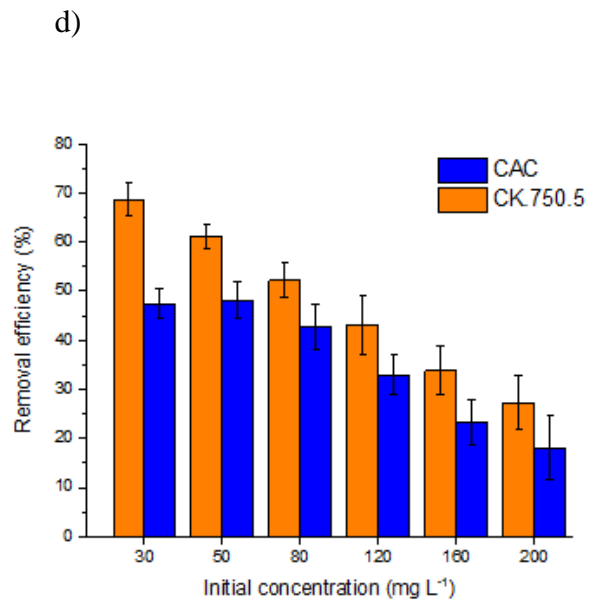
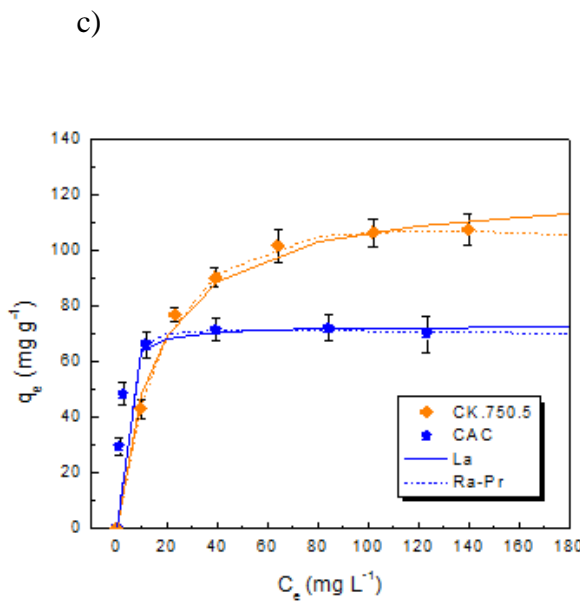
389 increase of initial concentration leads to an increase of the BPA adsorption capacity,
 390 which is due to a major saturation of the adsorbent surface.

391



392

393



394

395

396 **Figure 6.** (a) BPA adsorption isotherm and b) BPA removal (%) on TPC.
 397 Experimental conditions were: $C_0 = 5 - 80$ mg L⁻¹, stirring speed 170 rpm for 8
 398 h, temperature 25°C, and pH 6.5 - 7.5. (c) BPA adsorption isotherms and d)
 399 BPA removal (%) on CK.750.5 and CAC. Experimental conditions were: $C_0 =$
 400 $30 - 200$ mg L⁻¹, stirring speed 170 rpm for 50 h, temperature 25°C, and pH
 401 6.5 - 7.5. Continuous and dotted lines represent Langmuir (*La*) and Radke-
 402 Prausnitz (*Ra-Pr*) adsorption isotherm models, respectively.

403

404 Figure 6 also shows the BPA removal efficiency as a function of the initial
405 concentration of BPA for TPC (b), and for CK.750.5 and CAC (d). Upon increasing the
406 BPA initial concentration from 5 to 80 mg L⁻¹, the BPA removal efficiency on TPC
407 decreased from around 20 to 10%. Using ACs instead, the BPA removal was
408 considerably higher although it also decreased when the initial concentration of BPA
409 increased, from around 70 to 30% for CK.750.5 and from around 50 to 20% for CAC.
410 The parameters for the seven models presented in Table 1 and their corresponding
411 determination coefficients are given in Table 5. In the case of Dubinin-Radushkevitch
412 (*DR*) and Dubinin-Astakov (*DA*) adsorption isotherm equations, the saturation
413 concentration, C_s , of BPA was 0.3 g L⁻¹ (Dehghani et al. 2016), which is the maximum
414 BPA solubility in water at 25°C.

415

416 3.4.2 Discussion of BPA adsorption onto TPC and ACs

417 TPC was investigated separately due to its significantly different porosity with
418 respect to ACs. The coefficient of determination, R^2 , presented in Table 5, gives the
419 fitting of experimental data with respect to theoretical data. From the results obtained, it
420 is clear that all models led to quite good fits ($R^2 > 0.97$), except the Freundlich model
421 (0.94). According to the models comprising only two parameters, *La* and *DR*, the
422 maximum adsorption capacities were 17.00 and 16.70 mg g⁻¹, respectively, while the
423 maximum adsorption capacities obtained using *Si* and *DA* models were 15.53 and 14.54
424 mg g⁻¹, respectively. The energies of BPA adsorption onto TPC were 8.25 and 8.87 kJ
425 mol⁻¹ according to *DR* and *DA* models, respectively. These values suggest a
426 physisorption on the material, and similar results have indeed been obtained by applying
427 the same models to materials such as chitosan (14.14 kJ mol⁻¹) (Dehghani et al. 2016)
428 and BPA-imprinted microbeads (7.22 kJ mol⁻¹) (Bayramoglu et al. 2016).

429 The isotherm model parameters for CK.750.5 and CAC are also shown in [Table](#)
430 [5](#). Most models allowed a good fit, with R^2 indeed higher than 0.96, except for the
431 Freundlich (*Fr*) model ($R^2 = 0.79$). Langmuir (*La*) model led to one of the best fits, with
432 which the maximum monolayer capacities were found to be 123.19 and 73.31 mg g^{-1} for
433 CK.750.5 and CAC, respectively. These values are lower than those reported for
434 commercial activated carbons having surface areas higher than $900 \text{ m}^2 \text{ g}^{-1}$ (Tsai et al.
435 2006).
436
437 [Table 5](#). Isotherm model parameters obtained for the adsorption data of materials
438 presented in this work at 25°C .

	Isotherm equation	Parameters					R^2	
TPC	<i>La</i>	q_{max} [mg g^{-1}]	17.006	k_L [L mg^{-1}]	0.054		0.975	
	<i>Fr</i>	k_F [mg g^{-1}]	1.813	n_f^{-1}	0.496		0.936	
	<i>Si</i>	q_{max} [mg g^{-1}]	15.530	k_s [L mg^{-1}]	0.046	n_s^{-1}	1.132	0.976
	<i>DR</i>	q_{max} [mg g^{-1}]	16.688	k [kJ mol^{-1}]	8.252			0.971
	<i>DA</i>	q_{max} [mg g^{-1}]	14.540	E [kJ mol^{-1}]	8.875	n	2.614	0.976
	<i>Re-Pe-</i>	k_R [mg g^{-1}]	0.917	a_R [L mg^{-1}]	0.054	β	1.000	0.979
	<i>Ra-Pr</i>	q_{mRP} [mg g^{-1}]	149.520	k_{RP} [L mg^{-1}]	0.005	m_{RP}	4.946	0.982
CK.750.5	<i>La</i>	q_{max} [mg g^{-1}]	123.197	k_L [L mg^{-1}]	0.065		0.982	
	<i>Fr</i>	k_F [mg g^{-1}]	30.836	n_f^{-1}	0.268		0.865	
	<i>Si</i>	q_{max} [mg g^{-1}]	107.827	k_s [L mg^{-1}]	0.037	n_s^{-1}	1.296	0.964
	<i>DR</i>	q_{max} [mg g^{-1}]	117.355	k [kJ mol^{-1}]	9.138			0.962
	<i>DA</i>	q_{max} [mg g^{-1}]	108.527	E [kJ mol^{-1}]	8.684	n	3.286	0.999
	<i>Re-Pe-</i>	k_R [mg g^{-1}]	7.992	a_R [L mg^{-1}]	0.065	β	1.000	0.982
	<i>Ra-Pr</i>	q_{mRP} [mg g^{-1}]	205.743	k_{RP} [L mg^{-1}]	0.031	m_{RP}	1.266	0.996
CAC	<i>La</i>	q_{max} [mg g^{-1}]	73.310	k_L [L mg^{-1}]	0.677		0.990	
	<i>Fr</i>	k_F [mg g^{-1}]	40.291	n_f^{-1}	0.134		0.787	
	<i>Si</i>	q_{max} [mg g^{-1}]	71.754	k_s [L mg^{-1}]	0.610	n_s^{-1}	1.266	0.997
	<i>DR</i>	q_{max} [mg g^{-1}]	76.410	k [kJ mol^{-1}]	16.114			0.909
	<i>DA</i>	q_{max} [mg g^{-1}]	73.170	E [kJ mol^{-1}]	14.845	n	3.200	0.976
	<i>Re-Pe-</i>	k_R [mg g^{-1}]	49.609	a_R [L mg^{-1}]	0.677	β	1.000	0.990
	<i>Ra-Pr</i>	q_{mRP} [mg g^{-1}]	83.485	k_{RP} [L mg^{-1}]	0.532	m_{RP}	1.035	0.996

440 *La* isotherm refers to homogeneous adsorption and assumes the formation of a
441 monolayer within which adsorption can only occur on a finite number of definite
442 localised and equivalent sites (Foo & Hameed 2010), indicating that the different
443 adsorption capacity of CK.750.5 with respect to CAC should be mainly attributed to a
444 different surface area. K_L and K_F values for CAC were larger than for CK.750.5,
445 indicating for CAC a higher affinity between adsorbate and adsorbent (Tsai et al. 2006).
446 The mechanism proposed by Coughlin and Ezra (Coughlin & Ezra 1968) suggests that
447 adsorption is based on π - π dispersion interactions between the electrons of the aromatic
448 rings in the adsorbate and those of carbon basal planes in ACs. The protonation
449 equilibria of BPA, which is a di-acid (see again Figure 1), were studied by a
450 potentiometric method by Bautista-Toledo et al (Bautista-Toledo et al. 2005). The
451 species distribution diagram showed that the first deprotonation of BPA starts at around
452 pH 8.0 and the second one at around pH 9.0. The point of zero charge, pH_{PZC} , was very
453 similar for TPC and CK.750.5 (7.2 and 7.8, respectively), while it was 10.7 for CAC.
454 BPA adsorption was carried out at pH around 6.5 – 7.5, therefore BPA should be in its
455 deprotonated form, while CK.750.5 and CAC should be positively charged, and CAC
456 even more. Thus, the higher affinity of BPA for CAC cannot be explained by higher
457 electrostatic interactions. CAC had higher heteroatom content than CK.750.5,
458 essentially for oxygen and sulphur. Carbons containing more oxygen and sulphur are
459 expected to be more hydrophilic, so the affinity for organic molecules such as BPA
460 should be lower with CAC. However, CAC had a higher ash content that might explain
461 the present results.

462 According to Foo and Hameed, (Foo & Hameed 2010), *Si* isotherm model is a
463 combined form of *La* and *Fr* equations that was deduced for predicting heterogeneous
464 adsorption. At low adsorbate concentrations, the behaviour is near that of *Fr* isotherm,

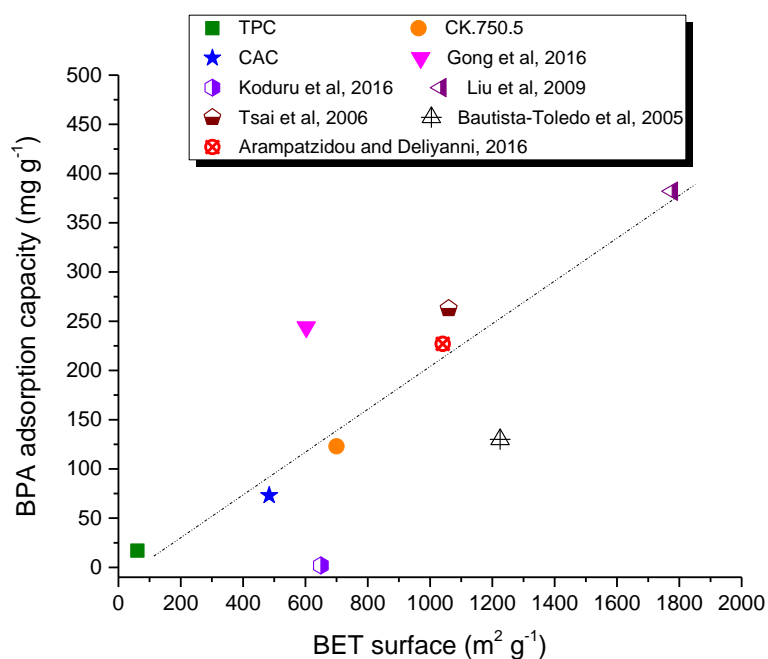
465 while at higher concentrations it predicts a monolayer adsorption characteristic of the *La*
466 isotherm. In this work, the correlation coefficients of *Si* model were close to unity,
467 allowing concluding that the maximal adsorption capacity of BPA of CK.750.5 and
468 CAC are 108 and 72 mg g⁻¹, respectively, according to this model.

469 Using *DR* and *DA* models, it was possible to determine the mean free energy,
470 which allows assigning, to a certain extent, the adsorption process to either a physical or
471 a chemical mechanism. Thus, a value of free energy in the range of 5 – 40 kJ mol⁻¹
472 suggests a physical adsorption, while a value in the range of 40 – 800 kJ mol⁻¹ indicates
473 a chemical adsorption (Liu et al. 2009). The free energy results obtained in this work for
474 CK.750.5 and CAC were 9.1 and 16.1 kJ mol⁻¹ according to *DR*, respectively, and 8.7
475 and 14.8 kJ mol⁻¹ according to *DA*, respectively. Those values suggest that the
476 adsorption of BPA onto ACs is a physisorption mechanism. Again, adsorption energies
477 were higher for CAC, as predicted by the higher affinity found by application of *La* and
478 *Fr* models.

479 Finally, *Re-Pe* and *Ra-Pr* models are hybrid isotherms featuring both *La* and *Fr*
480 equations (Foo & Hameed 2010). For these models, the determination coefficients were
481 the highest, i.e., close to one (see [Table 5](#)). The models have linear and power law
482 dependences of concentration in the numerator and in the denominator, respectively.
483 According to *Ra-Pr* equation, the calculated maximal adsorption capacities were always
484 higher than those determined from the kinetic models and other isotherm models.
485 Despite the good coefficients of determination (> 0.99), the maximum adsorption
486 capacity determined by this model was very high and could not describe correctly the
487 experimental equilibrium data. While in all cases the *Re-Pe* model reduced to the
488 Langmuir equation ($\beta = 1$), and a_R was thus similar to the Langmuir adsorption constant
489 (k_L).

490 [Figure 7](#) shows the BPA adsorption capacities of the sorbents used in this work,
491 as well as those reported in the open literature (Koduru et al. 2016; Bautista-Toledo et
492 al. 2005; Tsai et al. 2006; Liu et al. 2009; Gong et al. 2016; Arampatzidou & Deliyanni
493 2016). A roughly linear correlation between S_{BET} and the maximum BPA adsorption
494 capacity of the different ACs was observed. Discrepancies observed for a few data, seen
495 to be out of trend, are most probably due to different moieties present at the surface of
496 those ACs, as explained below for a few cases. However, this cannot be discussed much
497 further due to the absence of information in most of the corresponding literature, or due
498 to the use of different determination techniques preventing any straightforward
499 comparison of adsorbents with each other. Moreover, our results showed the same trend
500 with the surface area as those already presented by [Arampatzidou and Deliyanni](#),
501 ([Arampatzidou & Deliyanni 2016](#)), [Tsai et al](#) (Tsai et al. 2006) and [Liu et al](#) (Liu et al.
502 2009), dealing with ACs of higher surface area. [Gong et al](#) (Gong et al. 2016) obtained
503 higher capacities than those reported here, due to the modification of the carbon surface
504 through acidification with hydrochloric acid and subsequent functionalisation with
505 addition of amino groups. Such a treatment can indeed shift the pH_{PZC} value and
506 therefore may favour the adsorption of this type of compounds. On the contrary, [Koduru](#)
507 [et al](#) (Koduru et al. 2016) and [Bautista-Toledo et al](#) (Bautista-Toledo et al. 2005)
508 reported lower performances, possibly due to a lack of chemical interaction at the
509 surface of the material, and due to the high pH_{PZC} value. In conclusion, tailoring the
510 surface of the ACs for increasing electrostatic interactions between BPA and the sorbent
511 is crucial to enhance the adsorption of BPA. Treatments such as acidification and
512 functionalisation can improve the surface chemistry number of ACs, leading to higher
513 interaction with the adsorbate. These assumptions are supported by the materials
514 investigated here: coming back to [Figure 3b](#)) and to [Table 2](#), the AC presenting the

515 highest BPA adsorption, CK.750.5, is the one both having the highest S_{BET} and bearing
516 the highest number of acidic groups. The opposite is observed for TPC, exhibiting the
517 lowest amount of acidic groups, the lowest surface area, and hence the lowest BPA
518 uptake. CAC is in-between.
519



520

521 [Figure 7](#). Literature review of BPA adsorption capacity of activated carbons
522 produced in different conditions, as a function of their BET surface area. The
523 straight line is just a guide for the eye.

524

525 3.5 Thermodynamic studies

526 The thermodynamic parameters of BPA adsorption onto CK.750.5 were
527 evaluated by analysing the adsorption isotherms at different temperatures (15, 25 and
528 35°C), and using different initial concentrations. The results are gathered in [Table 6](#).

529

530

531 **Table 6.** Thermodynamic parameters for BPA adsorption onto CK.750.5 calculated as a
 532 function of temperature and BPA initial concentration.

C_0 (mg L ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)		
			15°C	25°C	35°C
31.52	-40.46	-128.76	-3.45	-2.09	-0.88
63.04	-16.11	-49.31	-1.95	-1.33	-0.97
86.68	-16.65	-53.41	-1.26	-0.73	-0.24
118.20	-10.53	-33.54	-1.22	-0.82	-0.20
157.60	-8.57	-27.43	-0.67	-0.42	-0.12
196.99	-8.71	-28.19	-0.67	-0.31	-0.12

533

534 These parameters indicate the sensitivity to temperature of BPA adsorption.
 535 BPA adsorption on CK.750.5 is an exothermic process, having a negative enthalpy
 536 (ΔH°) that produces a decrease in the adsorption capacity when the temperature
 537 increases. The absolute value of ΔH° increased considerably, from -8.71 to -40.46 kJ
 538 mol⁻¹, when the initial BPA concentration decreased from 197 to 31.5 mg L⁻¹. At low
 539 BPA concentrations, the most energetic sites are indeed occupied first and ΔH° indeed
 540 had a value close to what is considered to be the limit of chemical adsorption, but it
 541 steadily tended towards -10 kJ mol⁻¹, on average, at concentrations higher than 100 mg
 542 L⁻¹. These adsorption enthalpies are of the same order of magnitude as those reported in
 543 the literature for the adsorption on ACs of ceftazidime (19 kJ mol⁻¹) (Hu et al. 2017),
 544 dichromate (10 kJ mol⁻¹) (Maneechakr & Karnjanakom 2017), methylene green 5 (18 kJ
 545 mol⁻¹) (Tran et al. 2017) and mercury (25 kJ mol⁻¹) (Saleh et al. 2017).

546 The negative values obtained for the entropy (ΔS°) correspond to a decrease of
 547 disorder at the adsorbent–solution interface. Finally, the negative values for the Gibbs
 548 free energy (ΔG°) indicate that adsorption of BPA onto CK.750.5 is spontaneous and
 549 thermodynamically favourable in the limits of the experimental conditions used here.
 550 Moreover, when the temperature increased from 15 to 35°C, ΔG° decreased for all

551 initial concentrations employed, suggesting that adsorption is more spontaneous at
552 lower temperature. The inversion temperature was calculated for all concentrations and
553 varied from 41°C at 31.5 mg L⁻¹ to 36°C at 197 mg L⁻¹.

554

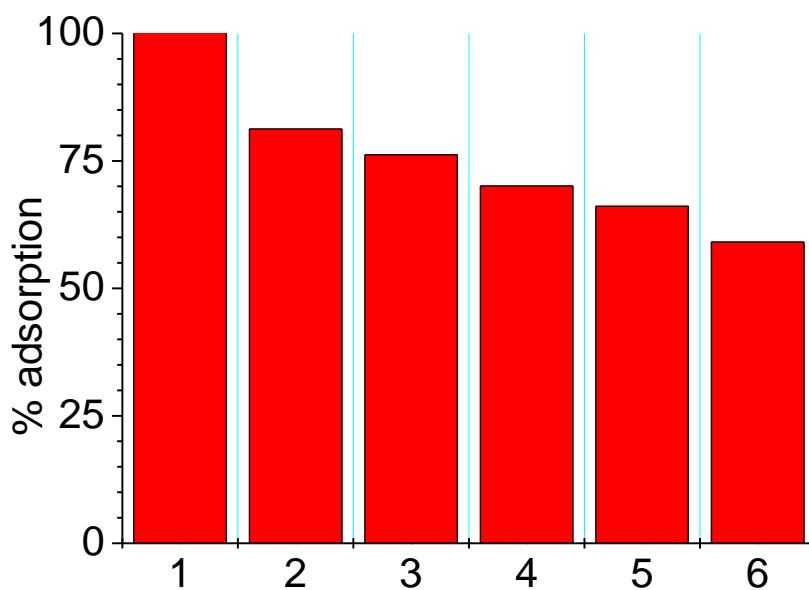
555 3.6 Regeneration and reuse study

556 Figure 8 shows the decrease of BPA adsorption performances of CK.750.5 after 5
557 consecutive cycles of regeneration and reuse. After the first adsorption-regeneration
558 cycle, the BPA adsorption capacities decreased by 19%. Further adsorption-
559 regeneration cycles had a lower effect as the adsorption capacity decreased by 5% at
560 each new cycle, on average. Therefore, the initial BPA adsorption capacity was reduced
561 by 41% after 5 adsorption-regeneration cycles. Such decrease might be due either to the
562 irreversible adsorption of BPA on the sorbent that would limit further uptake, or to the
563 modification of the surface functionalities related to washing with acid. BPA desorption
564 might be improved by sonication in methanol or other organic solvents, as reported
565 elsewhere (Sun & Weavers, 2006; Kwon et al, 2017).

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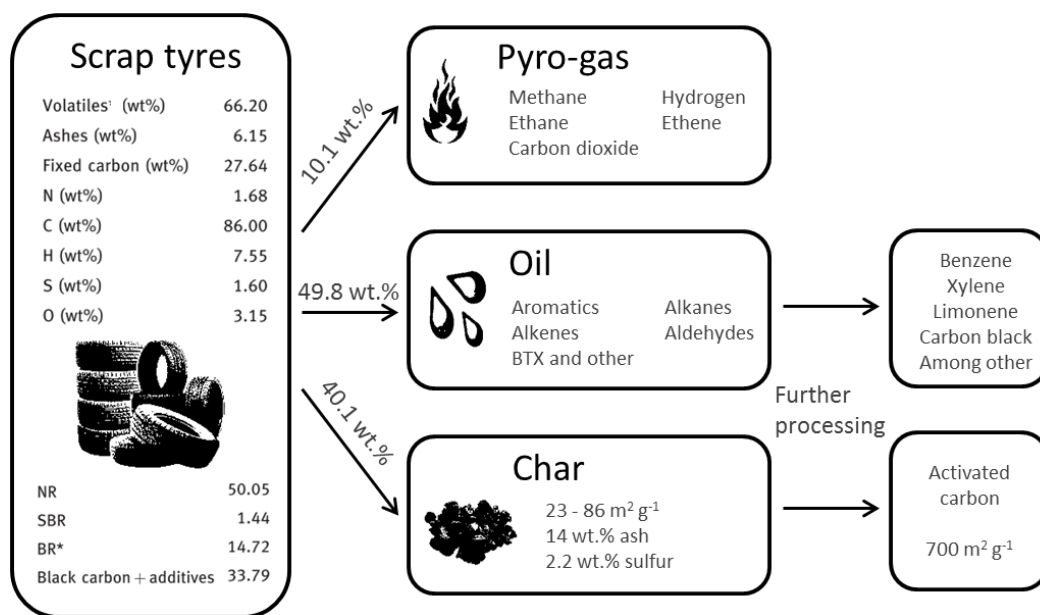
570 **Figure 8.** Changes of BPA adsorption after use and 5 additional regeneration-reuse
 571 cycles.

572

573 3.7 Economic considerations

574 About one billion units of scrap tyres per year are produced in the world,
 575 200,000 units per year only in Colombia (Marin. 2012). Tyre manufacturing includes
 576 using different types of materials, such as natural rubber (NR) (22 -30 wt. %), synthetic
 577 rubber (styrene or butadiene rubber, SBR) (15 – 23 wt. %), carbon black (20 – 28 wt.
 578 %), steel (13 – 20 wt. %) an others (10 – 14 wt. %) (Sienkiewicz et al. 2012), depending
 579 on the future use of the tyre. The pyrolysis of rubber tyres leads to a range of valuable
 580 chemicals in solid (39 wt. %), liquid (53 wt. %) or gaseous form (8 wt. %), which can
 581 be used in petrochemical, energy or iron/steel industries after suitable processing. The
 582 pyrolysis gas is mainly composed of carbon dioxide, methane, hydrogen, ethane and
 583 ethylene, and the corresponding calorific values range from 29.9 to 42 MJ m⁻³,
 584 depending on the tyre brand (Kyari et al. 2005). These gases can be used to provide part
 585 of the energy requirements for the pyrolysis plant.

586 Otherwise, the calorific value of the tyre oil is approximately 43 MJ kg⁻¹, so the
587 price of pyrolytic tyre oil could have similar a market value as the fuel oil, US\$ 45 per
588 barrel (BP 2016) (\approx US\$ 0.3 kg⁻¹). Economic viability is only obtained when pyrolysis
589 processes are not limited to primary products but also induce higher value-added
590 products: chemicals such as benzene, xylene and limonene, and/or high-quality carbon
591 black and AC. For example, according to [Danon et al](#) (Danon et al. 2015), at least 2.5
592 wt. % of a steel-free tyre can be converted into dipentene (dl-limonene), which has a
593 mean commercial value of US\$ 2 kg⁻¹. 56 wt. % of activated carbon was obtained from
594 pyrolytic char in this study; currently, the selling price of activated carbon from scrap
595 tyre is set at US\$ 2 kg⁻¹ (Alibaba 2016). CK.750.5, produced from tyres, has a moderate
596 surface area and BPA adsorption capacity. However, it might be far cheaper than
597 commercial ACs. From a practical point of view, one might indeed reasonably consider
598 using twice as much activated carbon if it is four times cheaper. This choice would be
599 rather dependent on adsorption reactors for existing industries, but it would not be
600 limiting for new industries or rural communities. An ideal concept of pyrolytic tyre
601 reprocessing into value-added products is presented in [Figure 9](#).



602

603

[Figure 9](#). Summary of possible valorisation ways of waste tyres by pyrolysis.

604 According to the above, 100 kg of steel-free tyre would yield 22 kg of activated
605 carbon, 50 kg of pyrolytic oil and 2.5 kg of limonene, taken as main value-added
606 products. These products are estimated at about US\$ 44, US\$ 15 and US\$ 5,
607 respectively, which mean an average appraisal of US\$ 6.4 per processed tyre, or US\$
608 0.6 kg⁻¹, demonstrating the possibility of generating a profitable and environment-
609 friendly environment process.

610

611 4. Conclusion

612 Activated carbons (ACs) with high BET surface area, 700 m² g⁻¹, can be
613 produced from pyrolysis followed by chemical activation of scrap tyres and using KOH
614 as activating agent. The as-obtained AC can be used as a potential adsorbent for the
615 removal of pollutants such as Bisphenol A (BPA), showing a maximal BPA adsorption
616 capacity of 123 mg g⁻¹, higher than the commercial activated carbon used as reference.
617 Furthermore, the adsorption kinetics of BPA onto the investigated AC was well
618 described by a pseudo-second order model. The isotherm adsorption parameters
619 obtained from the fits of different models allowed determining the maximal adsorption
620 capacity and describing the adsorption as a physical process, according to values of free
621 energies. Finally, BPA adsorption onto tyre-derived AC was an exothermic process, i.e.,
622 favoured by the decrease of temperature. The utilisation of pyrolytic char as precursor
623 of ACs would allow improving the economic balance of scrap tyres recycling to
624 produce pyrolysis oils.

625 Supplementary information

626 FTIR spectra and SEM images are given as supplementary information.

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636

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865

866 **Figure captions**

867 Figure 1. Molecular structure of Bisphenol A (BPA).

868 Figure 2. Ultimate analysis of tyre pyrolysis char and of the two activated carbons
869 investigated here.

870 Figure 3. (a) N₂ adsorption/desorption isotherms of TPC, CK.750.5 and CAC at -
871 196°C. For emphasising their differences in the range of low relative pressures,
872 corresponding to microporosity, the scale of P/P₀ is logarithmic below 0.1 and linear
873 above. (b) Textural characterisation of the same materials: V_{MIC} = micropore
874 volume, V_{MES} = mesopore volume, and surface area (blue stars).

875 Figure 4. Density of functional groups as a function of pK_a, for TPC, CAC and
876 CK.750.5

877 Figure 5. a) Adsorbed amounts of BPA at 25°C as a function of time, on TPC,
878 CK.750.5 and CAC. Continuous and dotted lines represent the pseudo-first and
879 pseudo-second order models, respectively. b) BPA removal at 25°C as a function of
880 time, on TPC, CK.750.5 and CAC. Discontinuous lines are just guides for the eye.
881 Experimental conditions were: C₀ = 100 mg L⁻¹ and 200 mg L⁻¹ for TPC and ACs,
882 respectively; stirring speed 170 rpm, temperature 25°C, and pH 6.5 – 7.5. The data
883 of TPC correspond to the top horizontal axis and the right vertical axis.

884 Figure 6. (a) BPA adsorption isotherm and b) BPA removal (%) on TPC.
885 Experimental conditions were: C₀ = 5 – 80 mg L⁻¹, stirring speed 170 rpm for 8 h,
886 temperature 25°C, and pH 6.5 – 7.5. (c) BPA adsorption isotherms and d) BPA
887 removal (%) on CK.750.5 and CAC. Experimental conditions were: C₀ = 30 – 200
888 mg L⁻¹, stirring speed 170 rpm for 50 h, temperature 25°C, and pH 6.5 – 7.5.
889 Continuous and dotted lines represent Langmuir (*La*) and Radke-Prausnitz (*Ra-Pr*)
890 adsorption isotherm models, respectively.

891 Figure 7. Literature review of BPA adsorption capacity of activated carbons
892 produced in different conditions, as a function of their BET surface area. The
893 straight line is just a guide for the eye.

894 Figure 8. Changes of BPA adsorption after use and 5 additional regeneration-reuse
895 cycles.

896 Figure 9. Summary of possible valorisation ways of waste tyres by pyrolysis.

897