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1 **Carbon gels derived from phenolic-oil for**  
2 **pollutants removal in water phase**

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15 **Abstract**

16 The gelation of a low value-added industrial waste, phenolic oil (PO), was successfully  
17 carried out for the first time in the presence of an acid catalyst and paraformaldehyde (PF),  
18 which is a by-product of the formaldehyde industry. Therefore, the use of PO and PF can be  
19 considered a win-win situation and as an attempt to valorise these 'wastes' and integrate them  
20 into a circular economy. A broad range of formulations has been explored, and the optimal  
21 preparation conditions in terms of materials' homogeneity and yield have been identified for  
22 gels dried in different ways, leading to xerogels, cryogels and aerogels, as well as to their  
23 carbonaceous counterparts after pyrolysis at 900°C. The porous textures of the latter materials  
24 were studied in depth, and the results allowed selecting one carbon xerogel for adsorption  
25 studies of a reference molecule, methylene blue (MB), in the aqueous phase. Kinetic and  
26 equilibrium measurements, as well as the calculation of associated thermodynamic  
27 parameters, allowed elucidating the detailed adsorption mechanisms of MB in this type of  
28 carbon gel.

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36 **Keywords:** Carbon gels; Water remediation; Phenolic-oil; Adsorption thermodynamics;

37 Methylene blue



## 39 **1. Introduction**

40 Pekala et al. were the first to propose the synthesis of gels based on resorcinol and  
41 formaldehyde [1-3]. The principle of gel synthesis is similar to that of resins, but uses a much  
42 higher dilution of the reactive mixture. Among the different types of phenolic resins, resoles  
43 and novolacs are the most known and synthesised [4].

44 The polycondensation of such organic precursors and the crosslinking of the resultant  
45 oligomers give, in the case of gels, nodular structures having high surface area and porosity.  
46 So far, most of the first gels were based on resorcinol or phenol, with formaldehyde as the  
47 crosslinking agent [5-7]. In this case, the gelation step is usually carried out in a closed vessel  
48 under heating (e.g. at 85°C). Before closing the system, a catalyst is added to the mix of  
49 precursor and crosslinker. The catalyst can be either acidic or basic (NaOH, Na<sub>2</sub>CO<sub>3</sub> and HCl  
50 are most commonly used) [8]. After a period varying from a few hours to several days, the  
51 heating is stopped and the system is open. The materials thus obtained are called hydrogels  
52 because their porosity is saturated by an aqueous phase. After drying, the organic gels can be  
53 pyrolysed to obtain carbonaceous materials, whose resultant surface area typically ranges  
54 from 500 to 800 m<sup>2</sup> g<sup>-1</sup>, and can reach even more than 2000 m<sup>2</sup> g<sup>-1</sup> after activation [9-11].

55 Due to the toxicity and high cost of the usual precursors, many researches focused on  
56 “greener” precursors and crosslinkers. Many new “green” precursors such as tannins or lignin  
57 were also used, in combination or not with classical precursors (e.g. phenol or resorcinol), in  
58 order to obtain gels [12-18]. Regarding the crosslinker, formaldehyde can be replaced by  
59 furfural, which can also be biosourced [19-21]. Another approach would be to use waste from  
60 the chemical industry to produce high added-value materials such as porous carbon gels.

61 Coal tar is obtained as a by-product of coal carbonisation and it is submitted to different  
62 processes for its conversion into valuable chemicals or light fuels [22-26]. Coal tar distillation

63 leads to different fractions, phenolic oil (PO) among them. To the best of our knowledge,  
64 there are only two studies dealing with gels and carbon gels based on PO in the open literature  
65 [27, 28]. A low-value PO from the company Bilbaína de Alquitrans – SA (BASA, Spain),  
66 mainly containing phenol, coumarone, o,m,p-xylene, indane, indene, o,m,p-cresol, and  
67 naphthalene, has been used in this work as carbon gel precursor. Looking at the reactivity of  
68 these different components for the synthesis of gels, one can say that the use of phenol for  
69 such application has already been well explored, and consistent results were reported [5, 19,  
70 21, 29, 30]. Several authors have also synthesised gels using cresol as precursor [31-36]. As  
71 for indene, it can react with phenol in acidic conditions to give indanylphenol. Some patents  
72 reported that indanylphenol can be used to obtain resins and thus can polymerise in acidic  
73 conditions and under heating (70-140°C) [37, 38]. Coumarone can also react with indene to  
74 form coumarone-indene resins [39, 40]. In addition, coumarone has also been used in the past  
75 to produce phenol-modified coumarone-indene resins [41, 42]. Naphthalene can also be found  
76 in phenolic oil and is known to react with epichlorohydrin to form epoxy that can eventually  
77 polymerise to epoxy resins [43, 44]. If naphthalene is alkoxyated and submitted to special  
78 conditions (multistep process, concentrated acid), it can condensate with formaldehyde [45].  
79 The reaction of part of the naphthalene in the PO used in this work is thus not excluded,  
80 although its intrinsic reactivity is probably lower than that of the other chemical species  
81 mentioned above.

82 Thus, PO should be sufficiently reactive and hence worth testing for synthesising gels. The  
83 main difficulties are the different reactivities of the various chemicals contained in the  
84 phenolic oil as well as their initial dilution state in less or even non-reactive species (indane,  
85 xylene...). Another challenge in synthesising gels based on phenolic oil is the hydrophobic  
86 nature of the latter, which prevents proper mixing with formaldehyde, generally in the form of  
87 a 37 wt. % of solution in water, stabilised by 10% of methanol. Therefore, a solvent other than

88 water should be used. Thus, many studies have proposed the use of alcohols as solvents (e.g.  
89 n-propanol, propan-1-ol or isopropanol) [7, 32, 46]. In addition, the catalyst should also have  
90 good solubility with the solvent and be preferentially organic.

91 Once porous materials are successfully prepared, some applications should be considered.  
92 Among them, water remediation is relevant and remains a hot topic. The removal of  
93 pollutants from aqueous wastewater is indeed a problem of paramount importance, whether in  
94 the event of an accidental spill or for the permanent removal of chemicals that are not  
95 eliminated using conventional water treatment technologies. The removal of these chemical  
96 species can be achieved using nanoporous materials such as activated carbons [47], zeolites  
97 [48], silica-based materials or even organic materials such as organic gels [49] or biomass  
98 materials [50-52]. Water pollutants can be inorganic, such as ions of heavy metals [53-55], or  
99 organic, such as antibiotics [56, 57] or other pharmaceutical components [58]. Despite the  
100 diversity of pollutant/sorbent systems presented in current research works, methylene blue  
101 (MB) remains a reference molecule in the case of preliminary studies of liquid phase  
102 adsorption of ionic and organic pollutants [59-61]. Even if many studies presented the  
103 characteristics of the MB adsorption on carbonaceous materials, only a few reported the use  
104 of carbon gels for that purpose [62, 63]. In addition, the thermodynamic models used to  
105 calculate enthalpy and entropy of adsorption are, according to some authors, often misused  
106 [64]. The origin of such errors in estimating thermodynamics parameters is due to the non-  
107 rigorous evaluation of the equilibrium constant [64].

108 In this study, we successfully prepared carbon gels from PO, and their application for the  
109 removal of pollutants from an aqueous phase was tested by adsorption of MB. In addition, we  
110 compared different approaches to calculate the thermodynamic adsorption parameters and we  
111 were able to elucidate the detailed adsorption mechanisms of MB in this type of carbon gel.

112 **Enthalpy and entropy of adsorption were calculated over the full range of concentration and**

113 equilibrium coverage and using two different methodologies: the isosteric method and the Van't  
114 Hoff equation.

## 115 2. Experimental

### 116 2.1. Preparation of organic gels

117 The composition of the phenolic oil (PO), provided by Bilbaína de Alquitrane, S.A.  
118 (BASA, Spain), used this work for preparing carbon gels, is given in Table S1  
119 (Supplementary material). This PO mainly contains phenol, coumarone, indene, m-p-cresols  
120 and o-cresol at the following, respective weight fractions: 14.80, 2.34, 11.54, 7.38 and 3.64  
121 %. Coumarone, indene and phenol can form resins under specific conditions [39, 41, 42]. In  
122 addition, in presence of Lewis acids (e.g. FeCl<sub>3</sub>, AlCl<sub>3</sub>) and alkyl halides (e.g. dichloroethane,  
123 trichloromethane), indene can also undergo Friedel-Crafts reaction and form hypercrosslinked  
124 networks [65, 66]. For these reasons, their respective contents are taken into account in the  
125 reactive fraction. Thus, the reactive fraction in the PO is *a priori* expected to be  
126 approximatively 40 wt. %, because naphthalene has not be taken into account (indane is also  
127 assumed not to react under the chosen synthesis conditions). The rest of the PO components  
128 are considered solvents.

129 The catalyst chosen and found suitable for our system was para-toluenesulphonic acid,  
130 PTSA (Merck®, synthesis grade, 98 %). This is mainly due to its high solubility in organic  
131 solvents and its strong acidic character. Indeed, unlike inorganic salts (i.e., NaOH or Na<sub>2</sub>CO<sub>3</sub>)  
132 or aqueous solutions containing acidic catalyst (i.e., HCl or HNO<sub>3</sub>), PTSA is highly soluble in  
133 organic solvents. In addition, PTSA is commonly used as catalyst for crosslinking reactions  
134 to produce novolac resins based on hydrophobic precursors such as cardanol [67]. Similar  
135 resins were also successfully converted into porous carbon materials [68]. Paraformaldehyde,  
136 PF (Merck®, synthesis grade, 95 %), which is soluble in isopropanol (Carlo Erba,  
137 spectroscopy grade, 99.8%), was used as crosslinker.

138 For describing the preparation of an organic gel, Job et al. suggested the use of the  
139 following molar ratios: resin-forming (possibly phenolic) monomers to catalyst (P/C), resin-  
140 forming (possibly phenolic) monomers to crosslinker (P/F), and dilution ratio ( $D = \text{total}$   
141  $\text{number of moles of solvent to number of moles of reagent}$ ) [8, 69, 70]. The P/C and P/F ratios  
142 were fixed at about 15 and 0.55, respectively, while  $D$  was taken in the range 0.5-1.8. The  
143 ratios were calculated taken into account phenol, coumarone, indene, m-p-cresols and o-cresol  
144 as resin-forming monomers. The P/C and P/F ratios were fixed in order to evaluate only the  
145 effect of the dilution on the textural properties of the gels. A representation of these ratios can  
146 be found in Figure S1 (red dashed lines), and Table 1 shows the formulations tested. Figure  
147 S1a shows the decrease of the reagent content (PF: total mass of reagents (resin-forming  
148 monomers and paraformaldehyde) to total mass of resin) while the S1d shows the linear  
149 increase of  $D$ .

150 The general preparation protocol is now described: isopropyl alcohol (IPA) was first  
151 vigorously stirred with PO during 2 min in a 50 mL beaker. Then, PTSA was added and  
152 dissolved in the blend by vigorous stirring for 2 to 5 minutes. Finally, paraformaldehyde was  
153 added and the mixture was vigorously stirred once more. At room temperature and in such a  
154 proportion, the solubilisation of paraformaldehyde is very difficult to achieve. Thus, the  
155 stirring was stopped when a large fraction was already dissolved and when the other fraction  
156 was well dispersed (no agglomerates) in the solution (5-10 min stirring). During the whole  
157 mixing step, the beaker was covered with an aluminium foil in order to minimise the  
158 evaporation of the solvent and other volatile species (the temperature of the room was also  
159 kept at 15°C for this purpose). Then, the mixtures were poured into test tubes (at 90% filling)  
160 that were hermetically sealed afterwards, and put in a ventilated oven at 85°C. After 30 min,  
161 the tubes were shaken vigorously by hand to dissolve completely the paraformaldehyde. Then  
162 the samples were left to gel at 85°C for 5 days. The gel formed after 2-3 days, but curing

163 continued for 5 days to obtain well polymerised and crosslinked material. After hardening, the  
 164 sample tubes were broken; the gels were cut into centimetre-sized cylinders and washed under  
 165 stirring with absolute ethanol (Carlo Erba®, 99.9%) for 5 days (orbital shaker, 90 rpm, 30°C).  
 166 The ethanol was renewed every day. Note that, because no water was used in the preparation  
 167 process, the resultant materials cannot be called hydrogels but are solvogels instead.

168 **Table 1:** Composition of the formulations tested.

Formulation name	Isopropyl alcohol (g)	Para-formaldehyde (g)	PTSA (g)	PO (g)	Isopropanol fraction (wt. %)
5 g	5	3.123	0.64	15	21.04
7.5 g	7.5	3.123	0.64	15	28.56
10 g	10	3.123	0.64	15	34.77
12.5 g	12.5	3.123	0.64	15	39.98
15 g	15	3.123	0.64	15	44.43
17.5 g	17.5	3.123	0.64	15	48.26
20 g	20	3.123	0.64	15	51.60

169  
 170 2.2. Drying and pyrolysis of organic gels

171 Convective drying, leading to xerogels, was carried out in an oven for 2 days at 85°C.  
 172 Since conventional drying may induce the collapse of the pores due to capillary forces exerted  
 173 at the interface between the solid and the liquid being evaporated, the resultant materials may  
 174 be less porous than desired, and therefore not reach high specific surface areas.

175 Two other drying methods were thus investigated to minimise the collapse of the pores.  
 176 Cryodesiccation or freeze-drying, leading to cryogels, avoids the formation of the liquid  
 177 menisci but form ice crystals instead. If water is present, these crystals may increase the pore  
 178 size and therefore produce materials with a rather coarse porous texture. Moreover, cracks can  
 179 appear in the cryogel and form “megalopores” (millimetre-sized pores). Prior to the  
 180 cryodesiccation, the ethanol was thus exchanged with either ultrapure water or *tert*-butanol  
 181 (tBu) (Acros Organics®, 99.5 %, extra pure) for 3 days. The advantage of tBu is to avoid the  
 182 formation of large ice crystals in the material while the advantage of using water is its low

183 cost. The cryodesiccation was carried out in a HETO PowerDry PL6000 freeze-dryer. First,  
184 the materials, impregnated with water or tBu, were frozen at  $-90^{\circ}\text{C}$  for 24 h and evacuated at  
185 10 Pa for 3 days.

186 The last drying method involves a supercritical fluid and leads to aerogels, and  
187 supercritical  $\text{CO}_2$  (critical point  $31^{\circ}\text{C}$ , 7.3 MPa) is the most used for this application. First, the  
188 ethanol was exchanged with liquid  $\text{CO}_2$ , which was then heated up to  $40^{\circ}\text{C}$  in order to reach  
189 supercritical conditions. After this step, the pressure was slowly ( $0.04\text{ MPa min}^{-1}$ ) decreased  
190 to pass from the supercritical state to the gaseous state. In this way, no liquid/gas interface  
191 appears and drying can be theoretically achieved without causing collapse and damage to the  
192 pore structure. Thus, this method is supposed to preserve the textural properties of the gels.  
193 The process was carried out in an Autosamdri-815 Tousimis® critical point drier. The  
194 exchange of ethanol with liquid  $\text{CO}_2$  was carried out 4 times before raising the temperature to  
195  $40^{\circ}\text{C}$ . Additional details about the supercritical drying procedure can be found elsewhere [71]  
196 [13].

197 After drying, the materials were pyrolysed in a tubular furnace, using a quartz tube  
198 (diameter 25 mm) continuously flushed with nitrogen ( $100\text{ STP cm}^{-3}\text{ min}^{-1}$ ). The heating rate  
199 was set at  $2^{\circ}\text{C min}^{-1}$  up to the final temperature of  $900^{\circ}\text{C}$ , which was held for 2h. The latter  
200 temperature was selected in order to ensure a high final carbon content [12-14, 27] and a  
201 developed texture, which can be analysed by DFT models that were indeed developed for  
202 materials containing quasi-exclusively carbon [72, 73]. The carbon gels were named by a  
203 letter (A for aerogel, C for cryogel, X for xerogel), followed by the mass of phenolic oil as  
204 indicated in the formulations detailed in Table 1. For instance, X\_12.5 is the carbon xerogel  
205 obtained by convective drying of the organic xerogel called OX\_12.5 in the following,  
206 derived from the formulation 12.5 g (itself named from the initial amount of IPA that had  
207 been used), and submitted to carbonisation at  $900^{\circ}\text{C}$ .

## 208 2.3. Characterisation

### 209 2.3.1. Weight and volumes changes

210 During pyrolysis, a partial gasification of the materials takes place, and they therefore lose  
211 weight. The carbon yield  $Y_{pyr}$  of the pyrolysis is expressed as:

$$212 Y_{pyr} = \frac{m_{final\ carbon}}{m_{initial\ gel}} \times 100 \quad (1)$$

213 where  $m$  are masses measured before and after pyrolysis.

214 During drying, the material can shrink both due to pore collapse and desorption of the  
215 liquid from inside the solid matrix (un-swelling effect). During pyrolysis, gases leave the solid  
216 matrix and the network shrinks further. In both cases (drying and pyrolysis), the radial  
217 shrinkage of the samples is quantified by:

$$218 RS_{step} = \frac{\emptyset_{initial} - \emptyset_{final}}{\emptyset_{initial}} \times 100 \quad (2)$$

219 where  $RS_{step}$  represents the radial shrinkage for a synthesis step (drying or pyrolysis) and  $\emptyset$   
220 stands for the diameter of the sample (initial or final).

### 221 2.3.2 Ultimate analyses

222 Ultimate analyses of samples for the determination of their elemental composition were  
223 carried out with a CHONS elemental analyser (Vario El Cube, Elementar) as reported elsewhere  
224 [74].

### 225 2.3.3 Electron microscopy observations

226 Scanning electron microscopy was used for the determination of samples' morphology,  
227 using a FEI QUANTA600FEG microscope and a secondary electrons detector. Additional  
228 information about the model of the methodology can be found elsewhere [75].

229

#### 230 2.3.4 Gas adsorption

231 An automatic adsorption device (ASAP 2020, Micromeritics) was used for the textural  
232 characterisation of carbon gels. The samples were degassed under vacuum at 150°C until the  
233 pressure stabilised at about 0.2-0.4 mPa for more than 48 h. Further degassing was carried out  
234 at the measuring port for at least 6 h. The cold and warm volumes were determined after  
235 nitrogen or carbon dioxide adsorption to avoid helium entrapment in the narrowest pores. The  
236 analyses were carried out by nitrogen and carbon dioxide adsorption at – 196°C and 0°C,  
237 respectively. All the data were treated using the Microactive® software from Micromeritics.

238 The surface area calculated by the Brunauer-Emmett-Teller (BET) method,  $A_{BET}$ , was  
239 obtained using the BET equation in the appropriate range of relative pressures [76].  $A_{BET}$  was  
240 only determined to compare our results with those reported in the literature, and not used here  
241 for other calculations because of the corresponding well-known underestimation or  
242 overestimation of surface area by the BET equation when dealing with microporous or  
243 mesoporous materials, respectively. The micropore volumes were obtained using the Dubinin-  
244 Radushkevich ( $V_{\mu-DR}$ ) equation, and were also given for comparison with the literature [77,  
245 78]. The pore size distributions (PSDs) were obtained using the non-local density functional  
246 theory (NLDFT) from the Solution of Adsorption Integral Equation Using Splines  
247 (SAIEUS®) routine. SAIEUS® has the advantage of combining both CO<sub>2</sub> and N<sub>2</sub> adsorption  
248 data to obtain more accurate PSDs [79, 80]. The smoothing parameter  $\lambda$  was set constant and  
249 equal to 4 for all the samples in order to allow the comparison between different PSDs. This  
250 value is the most common and the lowest defined by the SAIEUS® routine for our set of  
251 samples. The average micropore ( $L_{0-NLDFT}$ ), mesopore ( $L_{meso}$ ) and total pore ( $L_{tot}$ ) sizes using  
252 NLDFT and volume ( $dV$ ) weighting were calculated using the PSD. The NLDFT method was  
253 also used to determine the surface area  $S_{NLDFT}$  by integrating the PSDs over the whole range  
254 of pore sizes. The Barrett, Joyner and Halenda method (BJH) was also used to calculate the

255 mesoporous volumes from the desorption branch of the isotherms [81]. The BJH results were  
256 refined by using the Kruk-Jaroniec and Sayari optimisation method [82, 83].

257 Finally, a comparison of the different models was made: (i) total pore volumes, according  
258 to Gurvich ( $V_{P/P0=0.98}$ ) and NLDFT; (ii) surface areas, from the BET method and the NLDFT;  
259 (iii) micropore volumes, from the DR method and the NLDFT; (iv) mesopore volumes, from  
260 NLDFT and the difference between  $V_{P/P^{\circ}=0.98}$  and the micropore volume from the NLDFT.

### 261 *2.3.5. Potentiometric titration*

262 The potentiometric titration for the determination of the surface chemistry was applied  
263 only to the carbon gel having the most developed textural properties and synthesised with the  
264 cheapest procedure. It consisted in the titration of an acidic solution (pH = 3) of 25 mL in  
265 which 1 g of carbonaceous material was dispersed. Before this initial pH adjustment with 0.1  
266 mol L<sup>-1</sup> HCl, the solution was degassed during several hours using argon bubbling in order to  
267 remove the solubilised CO<sub>2</sub>. The titration was carried out using sodium hydroxide (NaOH, 0.1  
268 mol L<sup>-1</sup>) as titration agent. In order to obtain a high number of titration data (200 points), an  
269 automatic titration system (Titrand 905, Metrohm) was used. Each point corresponds to the  
270 pH value of the solution after adding 0.01 mL of NaOH solution. The titration curve gave  
271 access to the proton-binding isotherm, which can be analysed either by using its first  
272 derivative, or by using a deconvolution model giving access to the  $pK_a$  distribution of the  
273 material [84].

274

## 275 2.4. Methylene blue adsorption

### 276 2.4.1. Kinetics studies

277 Kinetic studies of MB adsorption consisted in measuring the MB uptake by the X\_12.5  
278 carbon gel up to 25 h, using a thermostatic bath (25°C) under stirring. For that purpose, an  
279 accurately weighted amount ( $W$ ) of 12.5\_X carbon gel (5-10 mg), previously dried (24 h,  
280 105°C) ,was introduced into conical flasks containing 50 mL of an aqueous solution of MB  
281 (bi-distilled water, pH  $\approx$  5.8). The adsorption experiments were performed by considering two  
282 different initial MB concentrations ( $c_0$ ) of 10 and 90 mg L<sup>-1</sup>.

283 The temporal evolution of the concentration of MB in the solution was measured during 25  
284 h, using a UV-Vis spectrophotometer (Lambda 35, Perkin Elmer) at a wavelength of 554 nm,  
285 corresponding to the maximum absorbance of MB. This optimal wavelength was previously  
286 evaluated by measuring the absorption spectrum of an aqueous solution of MB at 10 mg L<sup>-1</sup>.  
287 The absorbance data were then converted into concentration using a calibration plot, built for  
288 the MB concentration range from 0 to 10 mg L<sup>-1</sup>.

289 During the whole adsorption process, the conical flasks were totally covered by aluminium  
290 foil to avoid MB photo-degradation under UV light. After adsorption, appropriate dilutions of  
291 MB solutions were performed for respecting the linearity of Beer-Lambert's law. The absence  
292 of pH drift during the experiment was checked by measuring the pH with a glass electrode  
293 before and after the adsorption process. The adsorbed amounts at time  $t$  and at equilibrium,  $q_t$   
294 and  $q_e$ , respectively, were calculated as follows:

$$295 \quad q_t = \frac{(c_i - c_t)V}{W} \quad (3)$$

$$296 \quad q_e = \frac{(c_i - c_e)V}{W} \quad (4)$$

297 where  $c_i$ ,  $c_t$  and  $c_e$  are the initial concentration, the concentration at a given time  $t$ , and the  
298 concentrations at equilibrium, respectively.  $V$  is the volume of the MB solution, and  $W$  is the  
299 dry weight of carbon gel.

300 The modelling of the adsorption kinetics was carried out using the pseudo-first (equation  
301 (5)) and pseudo-second (equation (6)) order models [85]:

$$302 \quad \log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{\ln(10)} \quad (5)$$

$$303 \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

304 where  $k_1$  and  $k_2$  are the rate constants of the pseudo-first or pseudo-second order kinetic  
305 models, respectively.

306 The quality of the fit was assessed by the determination coefficient ( $R^2$ ) and the chi-square  
307 ( $\chi^2$ ) value of the associated linear plots. In addition, the classical intra-particle diffusion  
308 model was also applied [86]. The corresponding equation reads:

$$309 \quad q_t = K_{id} t^{0.5} + R_i \quad (7)$$

310 where  $K_{id}$  is the intra-particle diffusion constant and  $R_i$  is the diffusion resistance [86].

#### 311 *2.4.2. Equilibrium adsorption studies*

312 The equilibrium points were obtained using 10 mL of MB solution with concentrations of  
313 10 to 180 mg L<sup>-1</sup> while the amounts of carbon were in the range of 0.3 to 0.6 g L<sup>-1</sup>. The  
314 equilibration time was set at five days, at least. The adsorption experiments were carried out  
315 at three different temperatures (15°C, 25°C and 45°C) and a constant pH (5.8-6). The glass  
316 vials containing the suspensions of carbon gel in MB aqueous solution were kept hermetically  
317 sealed and protected from light during the whole adsorption process.

318 Three different adsorption models were selected: Freundlich, Langmuir and Sips. The  
319 Freundlich (equation (8)) and the Langmuir (equation (9)) adsorption models read as follows:

$$320 \quad n_{ads} = N_F (c_e)^b \quad (8)$$

$$321 \quad n_{ads} = N_L \frac{K_L c_e}{1 + K_L c_e} \quad (9)$$

322 where  $n_{ads}$  is the adsorbed amount at equilibrium, and  $N_F$ ,  $b$ ,  $N_L$  and  $K_L$  are constants.  $N_L$   
323 represents the maximum adsorption capacity and  $K_L$  is the Langmuirian equilibrium constant.

324 The Sips model, also called Langmuir-Freundlich model, is defined as follows:

$$325 \quad n_{ads} = N_S \frac{K_S (c_e)^{1/n}}{1 + K_S (c_e)^{1/n}} \quad (10)$$

326 where  $N_S$ ,  $1/n$ , and  $K_S$  are constants. The isotherms were directly fitted using the Levenberg-  
327 Marquardt algorithm implemented in the Matlab® software. The relevance of a specific  
328 model was evaluated by observing the values of determination coefficient ( $R^2$ ) and Chi-square  
329 ( $\chi^2$ ) of the fits.

### 330 *2.4.3. Thermodynamic studies*

331 The free energy of adsorption is defined by the following equation:

$$332 \quad \Delta G_{ads} = -RT \ln (K) \quad (11)$$

333 where  $K$  is the equilibrium constant while  $R$  and  $T$  are the universal gas constant and the  
334 absolute temperature, respectively. Sometimes the equilibrium constant is defined using a  
335 distribution constant (equations (12) and (13)). In this case, the distribution constant is defined  
336 as the ratio of the adsorbed amount ( $q_e$ , in  $\text{mg g}^{-1}$ ) to the equilibrium concentration ( $c_e$ , in  $\text{mg}$   
337  $\text{L}^{-1}$ ). Another definition of the distribution constant uses the adsorbed amount ( $c_{ads}$ , in  $\text{mg L}^{-1}$ )  
338 (equation (13)). Some authors suggest that the most rigorous method consists in using  $c_{ads}$

339 instead of  $q_e$  [64]. Consequently, the definition of the distribution constant given by equation  
340 (13) is the only one used here for further investigation.

$$341 \quad K = \frac{q_e}{c_e} \quad (12)$$

$$342 \quad K = \frac{c_{ads}}{c_e} \quad (13)$$

343 The free energy of adsorption is also equal to:

$$344 \quad \Delta G_{ads} = \Delta H_{ads} - T \Delta S_{ads} \quad (14)$$

345 Thus, plotting  $\Delta G_{ads}$  as a function of temperature gives access to the enthalpy through the  
346 intercept ( $H_{ads}$ ) of the linear regression, and the entropy of adsorption through the slope  
347 ( $\Delta S_{ads}$ ).

348 These results were compared to those obtained using the isosteric method, based on the  
349 assumption of thermodynamic equilibrium:

$$350 \quad \Delta G_{ads} = 0 \quad (15)$$

351 This condition guarantees the validity of the Clausius-Clapeyron equation. Once derived,  
352  $\Delta H_{ads}$  is obtained [74, 87]:

$$353 \quad \Delta H_{ads} = -R \left( \frac{\partial \ln(c_e)}{\partial T^{-1}} \right) \quad (16)$$

354 The isosteric heat is defined by:

$$355 \quad q_{st} = -\Delta H_{ads} \quad (17)$$

356 The isosteric heat of adsorption was obtained by plotting the quantity  $\ln(c_e)$  as a function of  
357  $1/T$ . The equilibrium condition also gives access to the isosteric entropy of adsorption:

$$358 \quad \Delta S_{ads} = \frac{\Delta H_{ads}}{T} \quad (18)$$

359 Such an assumption is only valid at equilibrium and is the expression of the well-known  
 360 entropy-enthalpy compensation principle [88]. As the range of temperature is likely to be  
 361 considered small (i.e., 15 – 45°C), the adsorption temperature will be considered to be equal  
 362 to the average of the three temperatures used for the adsorption isotherms. The isosteric heat  
 363 and the entropy of adsorption were both estimated, after assessment of the quality of the fit,  
 364 using the most relevant adsorption model presented above (Langmuir, Freundlich or Sips).

365 Some authors report  $\Delta H_{ads}$  as the enthalpy of displacement. Indeed, it refers both to  
 366 desorption of solvent molecules (i.e., water) from the adsorbent surface and to adsorption of  
 367 the solute (i.e., MB) [89]. In this case, the thermodynamic quantities result from both a  
 368 dilution effect (the solvent being desorbed from the sorbent surface) and an adsorption effect  
 369 (the solute being desolvated and adsorbed on the sorbent surface). Johnson et al. used similar  
 370 terminology to present an equation similar to that used for the isosteric method [90]:

$$371 \quad \Delta_{dpl}h_{st} = -\frac{RT^2}{\phi_1^1} \left( \frac{\partial \ln(a_2^1)}{\partial T} \right)_{x_2^a} \quad (19)$$

372 where  $\Delta_{dpl}h_{st}$  is the displacement enthalpy of compound 1 (solvent) by compound 2 (solute)  
 373 obtained using the isosteric method,  $\phi_1^1$  is the volume fraction of compound 1 in the bulk  
 374 phase and  $a_2^1$  is the activity of the compound 2 in the bulk phase at constant molar fraction  $x_2^a$   
 375 of solute in the adsorbed phase. In the assumption of “infinite dilution”, such equation can be  
 376 reorganised and reduced to the following equation, which is similar to equation (16) [91].

$$377 \quad \Delta_{dpl}h_{st} = -RT^2 \left( \frac{\partial \ln(C_e)}{\partial T} \right)_{q_e} \quad (20)$$

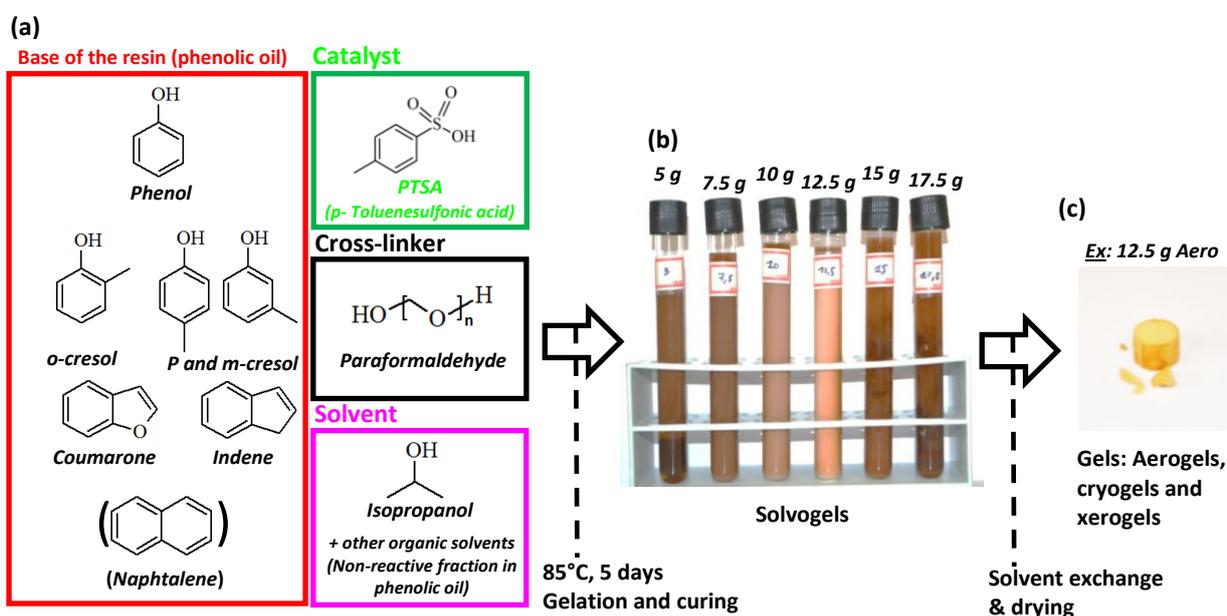
378 Thus, the isosteric method must have the characteristic of a displacement enthalpy.  
 379 Therefore, the thermodynamic parameters calculated here are only apparent. Such apparent  
 380 thermodynamic parameters are supposed to include both adsorption of solute and desorption  
 381 of solvent. Thus, the terms displacement or adsorption will be interchangeably used here.

### 382 3. Results and discussion

#### 383 3.1. Main characteristics of solvogels and carbon gels

##### 384 3.1.1. Colour and homogeneity of solvogels

385 The gel synthesis method is summarised in Figure 1. The gels had a colour going from  
386 dark brown to almost white (Figure 1b), depending on the amount of solvent. Below 5 to 7.5 g  
387 of isopropanol (21-29 wt. % of the formulation), demixing occurred during gelation, leading  
388 to two different phases in the formulation 5 g (see Figures S2 and 1b). Above 15 g of IPA, the  
389 obtained material was also heterogeneous. The concentrations of the precursors of the resin  
390 indeed became too low to reach the gel point. As a result, the gel was heterogeneous with  
391 some parts resembling agglomerated flakes (see formulations 15 g and 17.5 g in Figures S2  
392 and 1b). Between 7.5 and 15 g of isopropanol ( $\approx$  29-44 wt. %), the gels had a homogeneous



393 appearance and a light brown to orange colour.

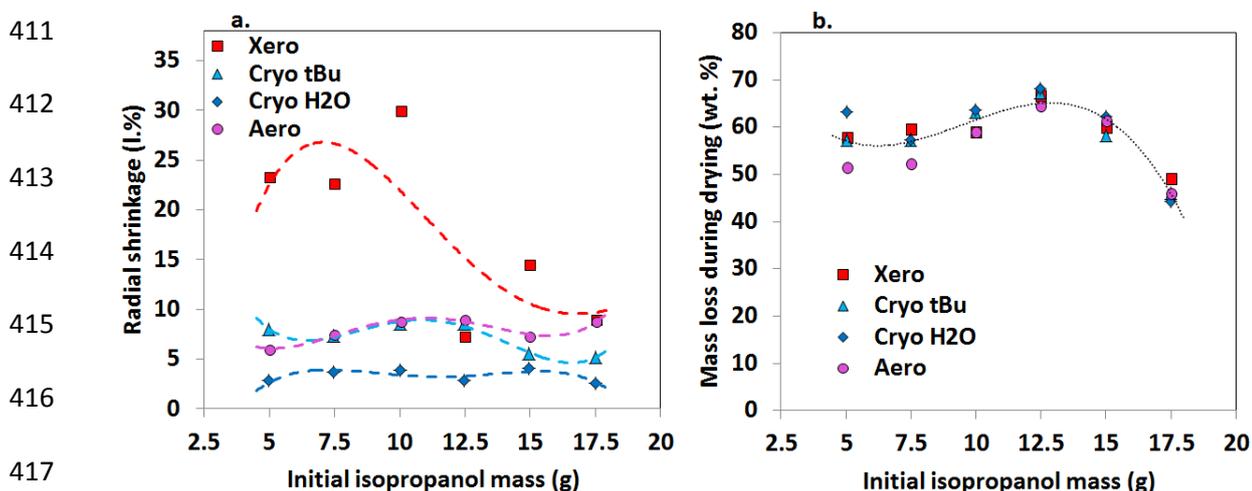
394 **Figure 1.** Scheme of the gel synthesis: (a) main compounds of phenolic oil; (b) photograph of  
395 the solvogels in their tests tubes, and (c) photograph of the 12.5 g organic aerogel.

396

397 After drying, the aerogels retained colours and homogeneity similar to their wet  
398 counterparts. Due to the formation of ice crystals and stresses induced by capillary forces, the  
399 cryogels and xerogels suffered shrinkage and cracks, respectively. After pyrolysis, the gels  
400 were black and had the usual glassy appearance of conventional carbon gels of phenolic  
401 origin.

### 402 3.1.2. Yield and shrinkage

403 The shrinkage of the gels during drying is due to both the collapse of the pores and the  
404 evaporation of the solvent. Figure 2a shows the shrinkage of the different solvogels during  
405 drying. As expected, the shrinkage was higher for convective drying (xerogels) than for  
406 cryodesiccation (cryogels) and supercritical drying (aerogels). However, when using more  
407 than 12.5 g of isopropanol, the shrinkage was similar for all gels, which could be explained by  
408 the higher rigidity of the partly phase-separated (flake-like) structure obtained (see again  
409 Figure S2). The shrinkage of the gels during the supercritical drying was slightly higher than  
410 during cryodesiccation with water as solvent, about 7.5 %.



418 **Figure 2.** (a) Radial shrinkage, and (b) weight loss during drying of organic gels, depending  
419 on the amount of isopropyl alcohol in the formulation.

420 The shrinkage that occurs during the cryodesiccation depended on the solvent (Figure 2a).  
421 The use of water instead of tBu decreased the shrinkage by almost 5%. This can be explained

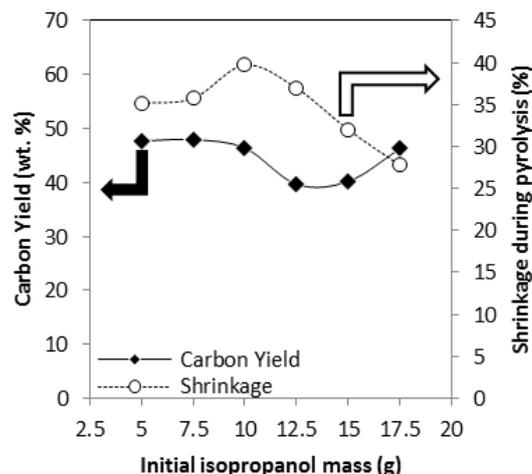
422 by the size of the water ice crystals, which are the largest and burst the material structure, and  
423 which somewhat compensates the shrinkage occurring during drying due to solvent  
424 desorption. For cryodesiccation, the shrinkages of the two sets of materials (Cryo\_tBu and  
425 Cryo\_H<sub>2</sub>O in Figure 2a) were similar when using more than 15 g of isopropanol in the  
426 formulation, probably due to the higher rigidity of the separated phase, as mentioned above.

427 The weight loss during drying gives information on the porosity. Despite the different  
428 solvents used in the different drying methods, the weight losses were remarkably similar and  
429 independent of the drying mode (Figure 2b). The weight loss increased from 50 to 65 % when  
430 the amount of isopropanol increased from 5 to 12.5 g. As the shrinkage varied a little in this  
431 range for aerogels and cryogels, it can be concluded that the porosity increased in this range  
432 of isopropanol amounts. Above 12.5 g of isopropanol in the formulation, the weight loss  
433 decreased. However, this indicates that, due to phase separation and at least for cryogels and  
434 aerogels, the porosity decreased when the amount of solvent increased too much. At this  
435 point, an assumption can already be made: the materials synthesised with an amount of  
436 isopropanol close to 12.5 g should have the most developed porous texture due to their  
437 combined highest weight loss and lowest shrinkage.

438 Figure 3 shows both the carbon yield and the radial shrinkage when the organic aerogels  
439 have been subjected to pyrolysis. A minimum carbon yield was obtained when using 12.5 g of  
440 isopropanol while the shrinkage showed opposite behaviour. Maximum shrinkage was  
441 obtained when using 10 g of isopropanol.

442

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450



451 **Figure 3.** Carbon yield ( $Y_{carb}$ ) and shrinkage during pyrolysis.

452 *3.1.3. Elemental composition*

453 The elemental composition of one the carbon aerogels, as well as that of two cryogels and  
454 one xerogel based on the formulation using 12.5 g of IPA are presented in Table 2.  
455 Concerning the latter formulation, the composition of one organic xerogel is also given.

456 **Table 2:** Elemental composition the gels and of the 12.5 g organic xerogel.

	H (wt.%)	C (wt.%)	N (wt.%)	O (wt.%)	S (wt.%)
<b>OX_12.5 (organic xerogel)</b>	6.2	78.4	0.6	13.6	1.1
<b>After carbonisation</b>					
A_7.5	0.7	95.5	0.7	3.1	0.0
A_10	0.7	95.0	0.8	3.4	0.0
A_12.5	0.6	95.0	0.5	4.0	0.0
A_15	0.6	94.5	0.8	4.1	0.0
A_17.5	0.7	94.3	0.8	4.2	0.0
C_H <sub>2</sub> O_12.5	0.6	94.7	0.5	4.2	0.0
C_tBu_12.5	0.5	95.5	0.5	3.5	0.0
X_12.5	0.6	94.7	0.5	4.3	0.0

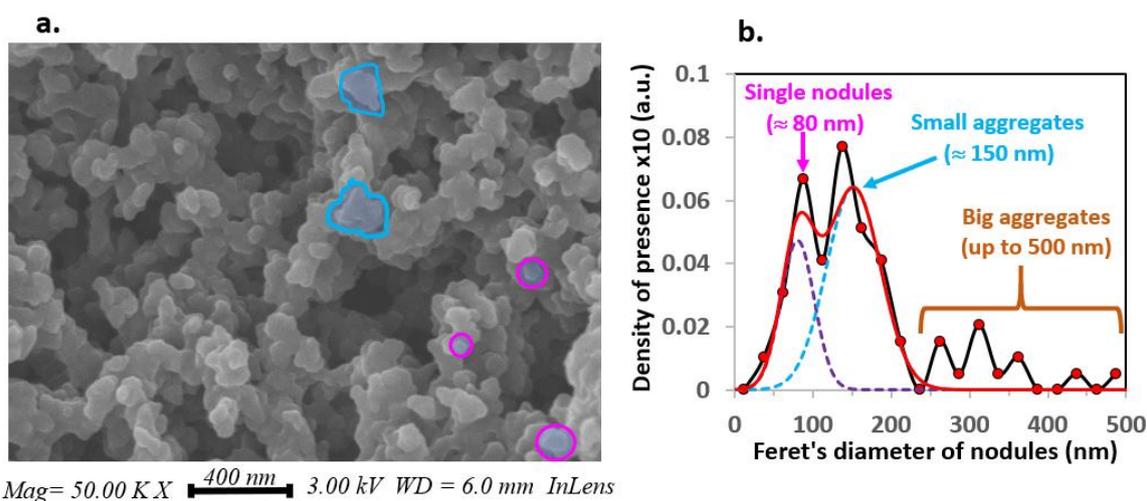
457  
458 The organic xerogel OX\_12.5 already contains a high percentage of carbon (78.4 wt. %),  
459 comparable to that of the PO. Indeed, if we consider only phenol, o-m-p cresols and

460 coumarone as reactive species in the PO, the elemental composition of the reactive fraction  
461 would be C: 77.45 wt. %, H: 6.68 wt. %, and O: 15.87 wt. %. These percentages are thus very  
462 similar to those of the organic xerogel OX\_12.5 presented in Table 2. However, the  
463 percentage of carbon in OX\_12.5 is slightly higher than the last calculated, suggesting that a  
464 small fraction of indene could still react. In addition, the presence of sulphur suggests that the  
465 catalyst (PTSA) could partly be reacted with, or at least, be trapped in, the solid matrix.

466 The carbon content in all the other gels, around 95 wt. %, indicates that the materials  
467 obtained after pyrolysis really deserve being named “carbons”.

#### 468 3.1.4. Samples' morphology

469 SEM images (Figure 4a) revealed the expected nodular structure, very typical of phenolic  
470 gels, with nodule sizes far below the micrometre. After digital filtering, binarisation and  
471 application of a particle detection routine (ImageJ software), the size distribution of nodules  
472 could be obtained (Figure 4b). While large carbon aggregates (up to 500 nm) can be noticed,  
473 the smallest ones have an average Feret diameter close to 150 nm.

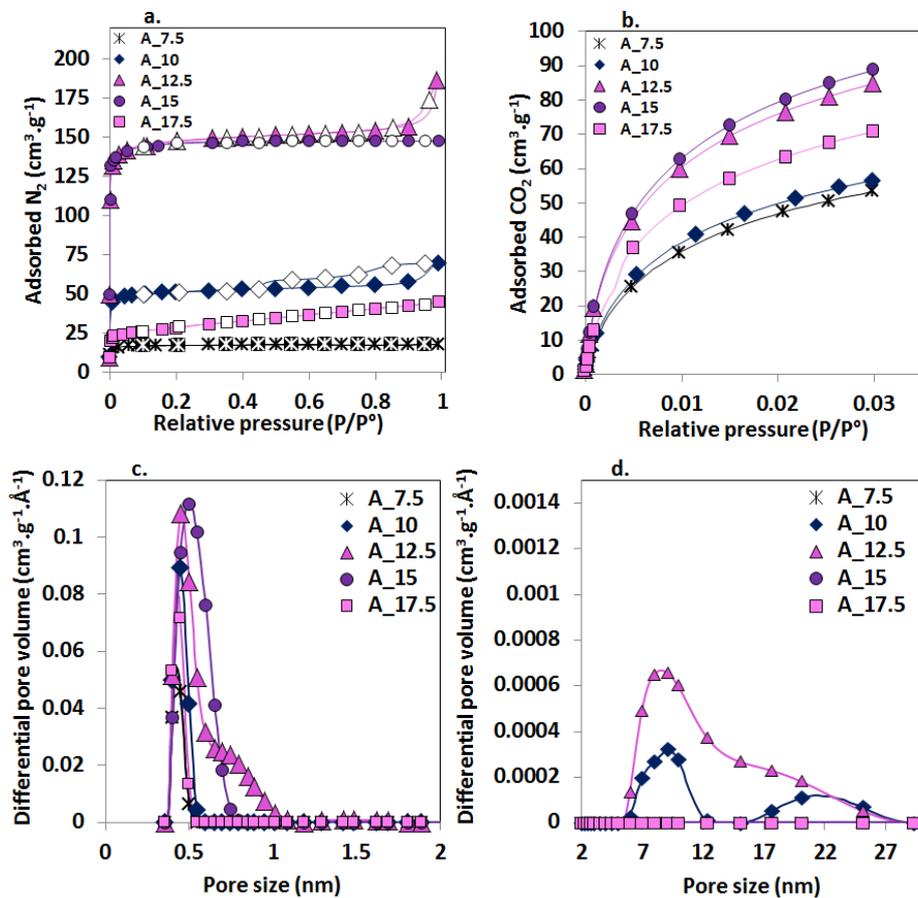


474  
475 **Figure 4.** (a) SEM imaging of the X\_12.5 carbon xerogel, and (b) size distribution of its  
476 carbon nodules.

477 The smallest observable structures are the individual carbon nodules. Their average Feret  
 478 diameter is close to 80 nm and is similar to what is observed in other carbon gels derived from  
 479 resorcinol-formaldehyde [92] or tannins-formaldehyde resins [13].

### 480 3.1.5. Textural properties

481 Figure 5a shows the nitrogen adsorption-desorption isotherms (at  $-196^{\circ}\text{C}$ ) made on carbon  
 482 aerogels. The final adsorbed amount, at  $P/P_0 = 0.98$ , increased from 18 to  $187\text{ cm}^3\text{ STP g}^{-1}$   
 483 when the amount of isopropanol increased from 7.5 to 12.5 g, and decreased to  $44\text{ cm}^3\text{ STP g}^{-1}$   
 484 <sup>1</sup> when 17.5 g of isopropanol have been used.



485  
 486 **Figure 5.** (a) Nitrogen and (b) carbon dioxide adsorption isotherms of carbon aerogels, and  
 487 corresponding (c) micropore and (d) mesopore size distributions calculated by NLDFT.

488 The  $\text{N}_2$  adsorption isotherms of A\_7.5 and A\_15 carbon aerogels are pure type Ia [93],  
 489 with a narrow knee at low pressure and a perfectly horizontal plateau, which is characteristic

490 of microporous solids. The isotherm of A\_17.5 is a combination of types Ia and II [93] and  
491 shows a sharp knee and a non-horizontal plateau, which is characteristic of solids with a  
492 narrow microporosity and mesoporosity. The isotherms of A\_10 and A\_12.5 are of mixed  
493 types Ia and IV [93]. Indeed, they both exhibit a sharp knee and a hysteresis at relatively high  
494 relative pressures, indicating the development of wide mesopores. Carbon dioxide adsorption  
495 isotherms (Figure 5b) give access to the amount of ultramicropores and so thus show that the  
496 ultramicroporous volume increased when the amount of isopropanol in the formulation  
497 increased to 15g. Higher amounts of isopropanol resulted in a reduction in the  
498 ultramicroporous volume.

499 Table 3 shows the BET area ( $A_{BET}$ ) of the carbon aerogels. An optimum of  $A_{BET}$  is located  
500 between formulations 12.5 and 15 g, with similar areas 593 and 594  $\text{m}^2 \text{g}^{-1}$ , respectively. This  
501 observation of an optimum is consistent with the previous analysis of the isotherms (Figures  
502 5a and 5b).

503 Figure 5c presents the micropore size distributions of the carbon aerogels obtained using  
504 the NLDFT model applied to both nitrogen and carbon dioxide adsorption isotherms. The  
505 texture is in good agreement with the basic analysis of the isotherms, predominantly  
506 microporous for most materials. In the microporous range, the pore size distributions (PSDs)  
507 are unimodal with a single peak in the pore size range of 0.4-0.6 nm, which changes only  
508 slightly with the amount of solvent in the formulation. However, the PSDs became broader  
509 when the amount of isopropanol increased from 7.5 to 12.5 g and narrower again above 12.5 g  
510 of isopropanol. Only the carbon aerogels derived from the 10 g and 12.5 g formulations had a  
511 slightly mesoporous texture with some peaks between 6 and 30 nm but with a very low  
512 amplitude (Figure 5d). These very low amplitudes confirm the predominantly microporous  
513 nature of the carbon gel texture.

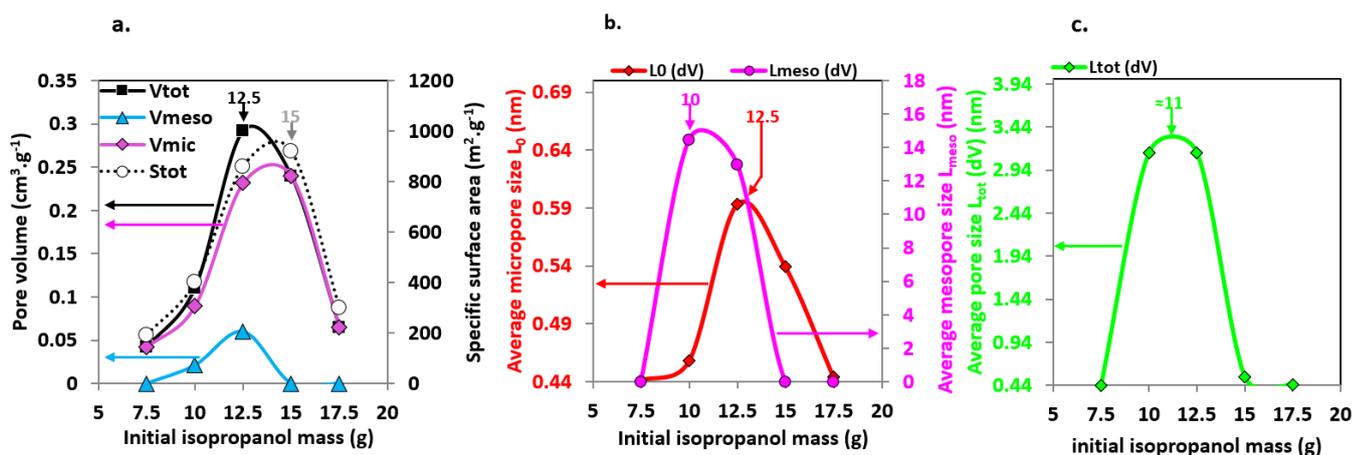
514 Table 3 shows that  $A_{BET}$  is much lower (68-649  $\text{m}^2 \text{g}^{-1}$ ) than  $S_{NLDFT}$  (192-948  $\text{m}^2 \text{g}^{-1}$ ) due to  
515 the limitations of the BET method together with the limitations of nitrogen diffusion at –  
516 196°C. Thus, the combined use of  $\text{CO}_2$  and  $\text{N}_2$  adsorption isotherms in the NLDFT model  
517 allows a more accurate description of the texture, and is more likely to take into account the  
518 smallest pores. The total pore volumes obtained according to the Gurvich method ( $V_{tot\_98}$ ) and  
519 those obtained using the 2D-NLDFT-HS ( $V_{tot}$ ) were similar, but the DR method, applied only  
520 to  $\text{N}_2$  adsorption, leads to an underestimation of the microporous volume (0.03-0.25  $\text{cm}^3 \text{g}^{-1}$ )  
521 compared to the NLDFT method (0.04-0.25  $\text{cm}^3 \text{g}^{-1}$ ) that takes also into account the fraction  
522 of micropore volume only accessible to  $\text{CO}_2$ . Logically this underestimation of the  
523 microporous volume by the DR method leads to an overestimation of the mesoporous volume  
524 (calculated as  $V_{meso} = V_{tot\_98} - V_{\mu\_DR}$ ) compared to that obtained using the NLDFT ( $V_{meso}$ ).  
525 Therefore, the average micropore size  $L_0$  obtained using the NLDFT model was considered  
526 the most reliable.

527 **Table 3.** Textural parameters of the carbon gels calculated by different methods.

Materials	Textural parameters (classical / <b>NLDFT</b> )				
	$A_{BET} / S_{NLDFT}$ ( $\text{m}^2 \text{g}^{-1}$ )	$V_{tot\_98} / V_{tot\_NLDFT}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$V_{\mu\_DR} / V_{\mu\_NLDFT}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$V_{meso} / V_{meso\_NLDFT}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$L_{0\_DR} / L_0$ ( $dV$ ) (nm)
<b>A_7.5</b>	68 / <b>192</b>	0.04 / <b>0.04</b>	0.03 / <b>0.04</b>	0.01 / <b>0.00</b>	0.52 / <b>0.44</b>
<b>A_10</b>	200 / <b>401</b>	0.11 / <b>0.11</b>	0.08 / <b>0.09</b>	0.03 / <b>0.02</b>	0.50 / <b>0.46</b>
<b>A_12.5</b>	593 / <b>860</b>	0.29 / <b>0.29</b>	0.23 / <b>0.23</b>	0.06 / <b>0.06</b>	0.47 / <b>0.59</b>
<b>A_15</b>	595 / <b>921</b>	0.24 / <b>0.24</b>	0.23 / <b>0.24</b>	0.01 / <b>0.00</b>	0.46 / <b>0.54</b>
<b>A_17.5</b>	102 / <b>299</b>	0.07 / <b>0.07</b>	0.04 / <b>0.07</b>	0.03 / <b>0.00</b>	0.47 / <b>0.44</b>
<b>C_tBu_12.5</b>	649 / <b>948</b>	0.32 / <b>0.32</b>	0.25 / <b>0.25</b>	0.07 / <b>0.07</b>	0.48 / <b>0.58</b>
<b>C_H<sub>2</sub>O_12.5</b>	629 / <b>908</b>	0.31 / <b>0.31</b>	0.24 / <b>0.24</b>	0.07 / <b>0.07</b>	0.48 / <b>0.60</b>
<b>X_12.5</b>	620 / <b>891</b>	0.34 / <b>0.34</b>	0.25 / <b>0.24</b>	0.09 / <b>0.10</b>	0.89 / <b>0.62</b>

528  
529 The PSDs of the materials in the mesopore range were also estimated by applying the BJH  
530 method with the KJS correction to the data of the nitrogen desorption branches of the  
531 isotherms (Figure S3). Due to the inaccuracy of the BJH method, only the carbon aerogels

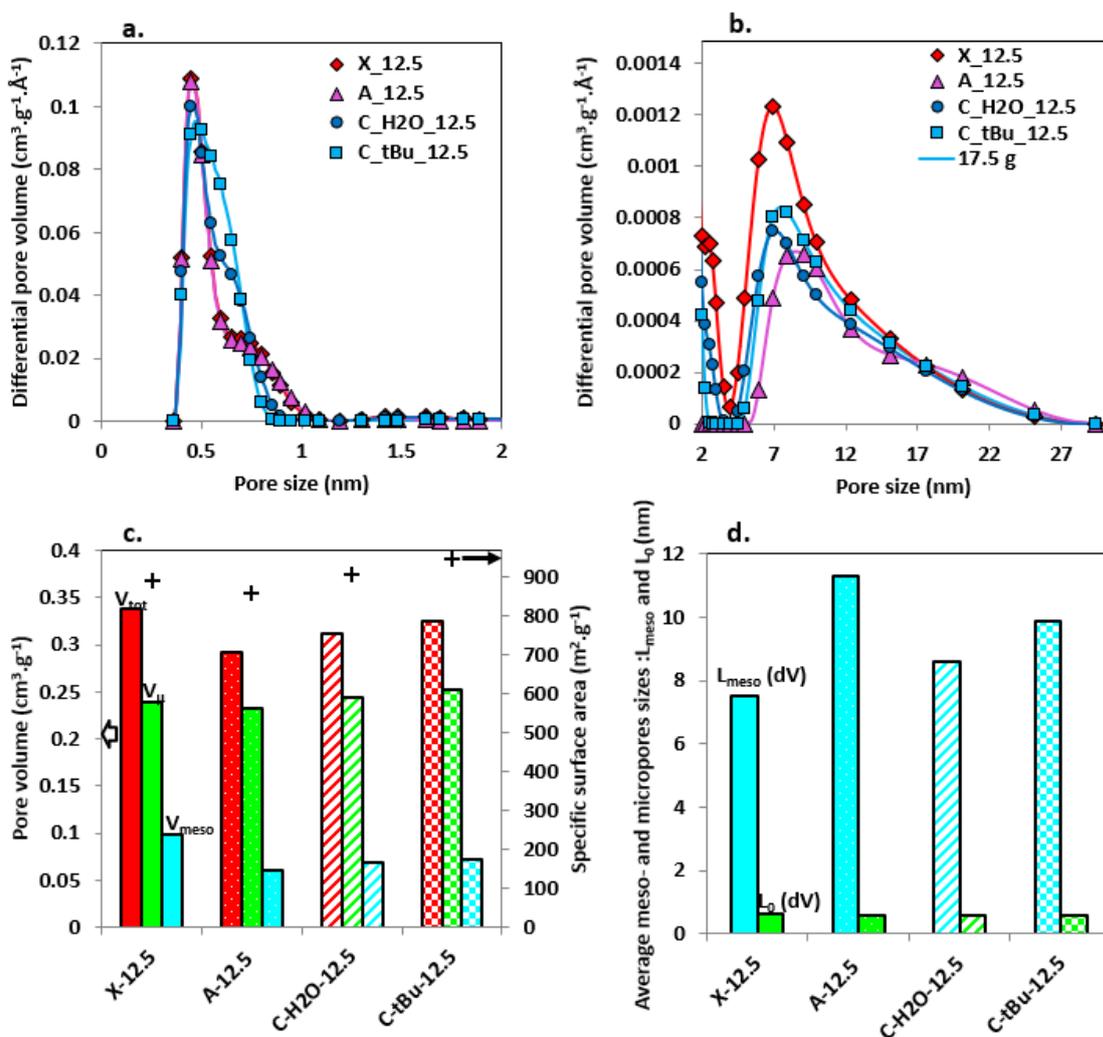
532 derived from the 10 g formulation gave results that were consistent with the 2D-NLDFT-HS  
 533 method. Indeed, the material A\_10 is the only one having a narrow PSD in the mesopores  
 534 range (with peaks well located in Figure 5d). For all the other materials, the low volumes of  
 535 mesopores as well as their very broad and dispersed character in terms of PSD make the  
 536 application of the BJH method unsuitable and inconsistent with the results obtained with the  
 537 NLDFT method.



538  
 539 **Figure 6.** Pore texture of carbon aerogels as a function of the amount of isopropanol in the  
 540 formulation: (a) total pore volume ( $V_{tot}$ ), mesopore volume ( $V_{meso}$ ), micropore volume ( $V_{\mu}$ )  
 541 and total specific area ( $S_{tot}$ ); (b) average micropore ( $L_0$ ) and mesopore ( $L_{meso}$ ) sizes; and (c)  
 542 total average pore size ( $L_{tot}$ ). All the values were obtained using data from the PSD obtained  
 543 by application of the NLDFT model. The pore sizes were calculated using volume ( $dV$ )  
 544 ponderations.

545 Figure 6a shows that the maximum pore volume is reached for A\_12.5 while the maximum  
 546 of NLDFT surface area is reached for the A\_15 material. Indeed, A\_12.5 has a lower  
 547 microporous volume than A\_15, but the latter does not present any mesoporosity. Figure 6b  
 548 shows that the largest average micropore size (0.59 nm) was obtained with A\_12.5, while the  
 549 maximum average mesopores size (15.5 nm) was for A\_10. The optimum of average total  
 550 pore size  $L_{tot}$  (around 3.4 nm, see Figure 6c) corresponds to A\_10 and A\_12.5. Therefore, the

551 material chosen as the most desirable for liquid-phase adsorption of organic molecules was  
 552 the carbon aerogel A\_12.5. This material indeed has the best balance between pore volume,  
 553 surface area and pore size.



554  
 555 **Figure 7.** Pore textures of carbon xerogel, cryogel and aerogel derived from the formulation  
 556 12.5 g. Pore size distributions: (a) in the micropore range, and (b) in the mesopore range,  
 557 according to NLDFT; (c) Total pore volumes ( $V_{tot}$ ), microporous ( $V_{\mu}$ ), mesoporous volumes  
 558 ( $V_{meso}$ ) and NLDFT surface areas; (d) average mesopores ( $L_{meso}$ ), micropore ( $L_0$ ) and total  
 559 average ( $L_{tot}$ ) pore sizes.

560 When comparing the impact of the drying method for the same formulation 12.5 g, it can  
 561 be noted that all the isotherms are type Ia-IV (Figure S4a). Even if the isotherms exhibit

562 similar adsorbed amounts for the different carbon gels, some differences can be seen.  
563 Surprisingly, the carbon aerogel had the lowest adsorbed volumes of all these carbon gels.  
564 According to the CO<sub>2</sub> adsorption isotherms (Figure S4b), the volumes of ultramicropores  
565 were similar whatever the drying mode. Figures 7a and 7b show that the PSDs of the carbon  
566 gels derived from the 12.5 g formulation are comparable despite the different ways of drying  
567 used for their organic precursors. These PSDs are indeed unimodal in the range of micropore  
568 sizes, have similar amplitudes, and the position of their peaks is located at 0.45-0.46 nm.

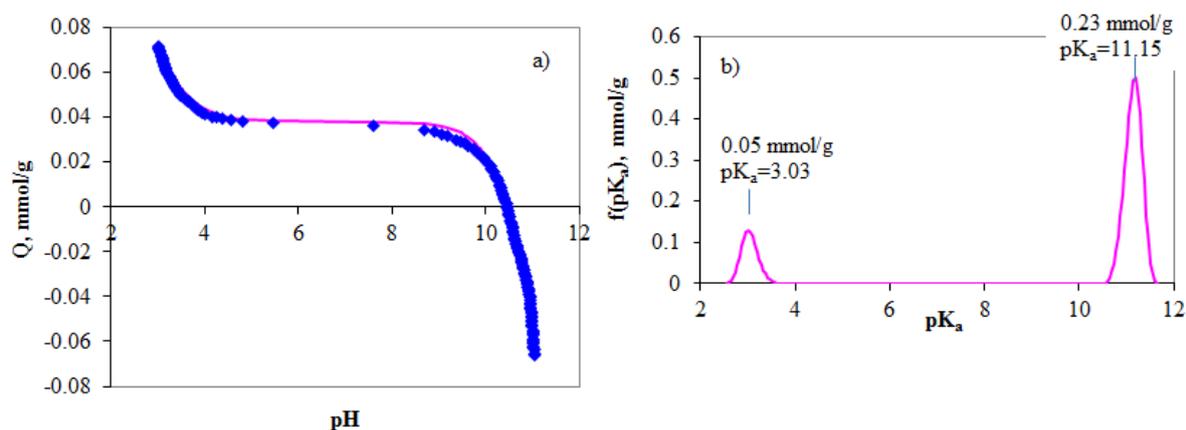
569 As for the aerogels (Figure 5c), the PSDs were narrow and very similar in shape, position  
570 and amplitude. The comparison of the main textural characteristics (total pore volume and  
571 specific surface area) of carbon aero-, xero-, and cryogels can be found in Figure 7c and in  
572 Table 3. First, the specific surface areas are similar and in the range of 860 to 950 m<sup>2</sup> g<sup>-1</sup>. The  
573 same observation can be made on the total pore volumes, which are between 0.29 and 0.34  
574 cm<sup>3</sup> g<sup>-1</sup>. Therefore, the drying method had a moderate effect on the textural properties of the  
575 final carbon materials. This is due to the essentially ultramicroporous nature of the texture of  
576 the gels. Indeed, in such a range of pore sizes, no menisci are formed during the drying step  
577 and, therefore, it is unlikely that a pore collapse mechanism could occur in such small pores.  
578 Figure 7d and Table 3 show the average pore size in the micro- and mesopores ranges. The  
579 carbon aerogel is the material that exhibited the highest average mesopores size.

580 Given the small differences in texture and considering the drying cost, the X\_12.5 material  
581 was thus chosen to perform the MB adsorption tests.

### 582 *3.1.6. Surface chemistry*

583 Figure 8a shows the proton-binding curve, expressed in mmol of NaOH per gram of  
584 carbon gel,  $Q$ , obtained by treating the titration curve of X\_12.5. The excellent fit obtained  
585 after application of the Saieus-pK-Dist software is also shown. Figure 8b presents the  
586 distribution of acidity constants  $f(pK_a)$  giving access to the  $pK_a$  and the quantification of the

587 acidic and basic functionalities. The curve  $f(pK_a)$  presents only two peaks with  $pK_a$  maxima at  
 588 3.03 and 11.15. The  $pK_a$  distribution shows the predominance of strongly basic species: 0.23  
 589 mmol/g at  $pK_a = 11.5$ , compared to 0.05 mmol/g of strong acidic surface groups, at  $pK_a =$   
 590 3.03.



591  
 592 **Figure 8.** Results of potentiometric titration of the carbon xerogel X\_12.5: (a) proton-binding  
 593 curve and (b) distribution of acidity constants.

594 Some surface groups, having a  $pK_a$  beyond 10 ( $pK_a = 11.15$ ) can be noticed on the  $pK_a$   
 595 distribution. Such groups can be assimilated to phenol groups [94]. In a lesser extent, other  
 596 groups having  $pK_a$  between 3 and 7, can also be noticed and are assimilated to carboxylic or  
 597 carboxylic anhydride groups ( $pK_a = 3.03$ ) [94].

## 598 3.2. MB adsorption properties

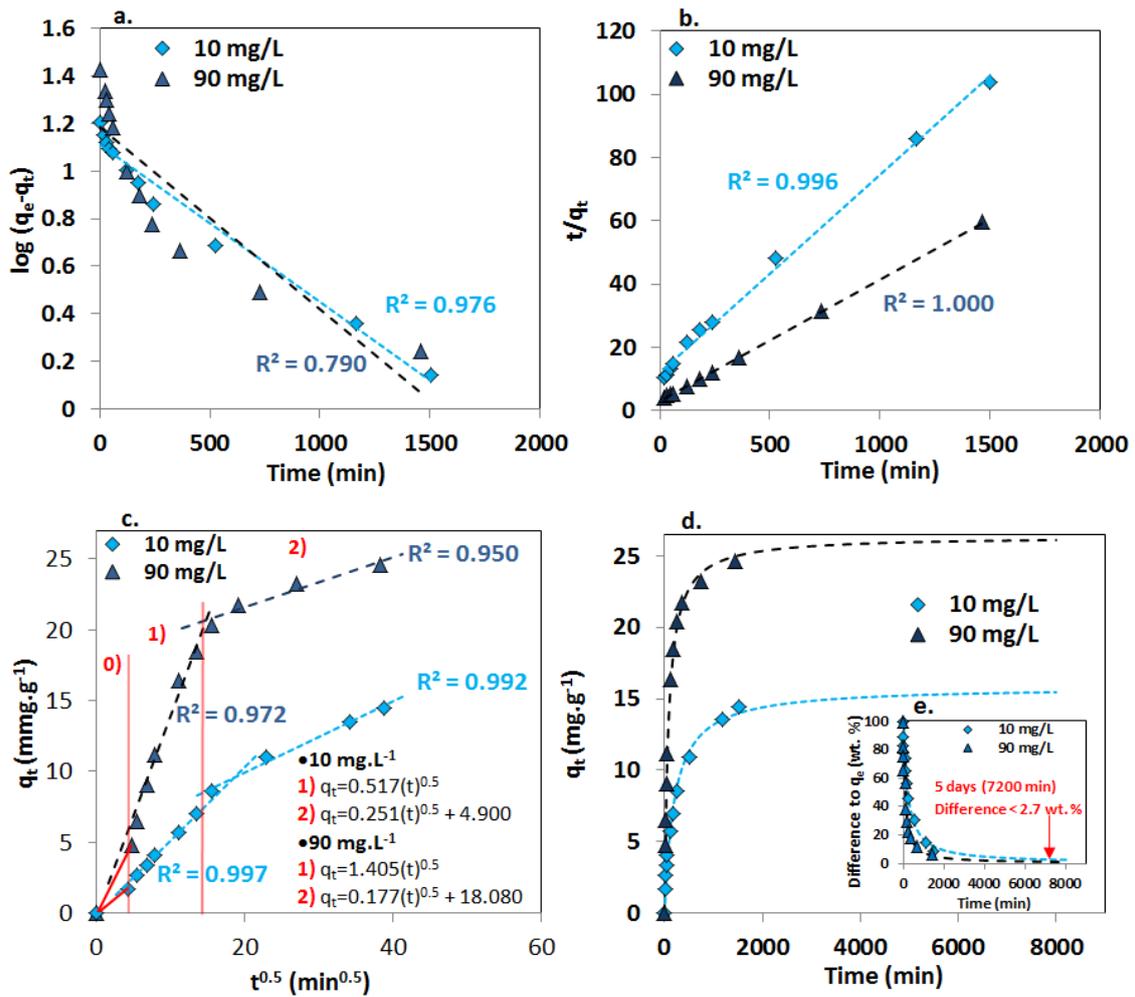
### 599 3.2.1. Adsorption kinetics

600 The pseudo-first and pseudo second order kinetic plots for the solutions containing initially  
 601 10 and 90 mg L<sup>-1</sup> of MB (25°C) are presented in Figures 9a and 9b. The linear fit of the  
 602 pseudo-second order kinetic model led to a poor to fair correlation ( $R^2$  in the 0.79-0.98 range)  
 603 while the pseudo-second order gave a much better determination coefficient ( $R^2$  very close to  
 604 1). This allows concluding that the adsorption kinetics of MB on the X\_12.5 carbon gel  
 605 follows a pseudo-second order. The low adsorption rates (presented in Table S2) are due to

606 the very small pore size of the material ( $L_0$  around 0.62 nm and  $L_{tot}$  around 3 nm). Such  
607 narrow pore sizes slow down the diffusion of MB molecules to their final adsorption site. The  
608 initial rates,  $h_0$ , are respectively equal to 0.084 and 0.329 mg g<sup>-1</sup> min<sup>-1</sup> for the solutions  
609 containing 10 and 90 mg L<sup>-1</sup> of MB.

610 The diffusion of MB molecules follows three regimes, represented by 0), 1) and 2) in  
611 Figure 9c. The first regime 0) is quite slow (slope slightly less than that given by regime 1)),  
612 and might be due to the progressive impregnation of the carbon particles by the solution.  
613 Indeed, it can be assumed that the penetration of the solvent (i.e., water) containing the MB  
614 molecules is quite slow due the narrowness of the pores. The diffusion regime 1) is slightly  
615 faster ( $K_D$  in the range of 0.517-1.405 mg g<sup>-1</sup> min<sup>-1/2</sup>) and the intercept of its linear equation is  
616 equal to zero. A zero intercept means that the diffusional resistance ( $R_f$ ) during this period is  
617 almost inexistent. Thus, during this period, the molecules already adsorbed still do not slow  
618 down the diffusion of the MB molecules in the liquid phase. In addition, during this second  
619 period, the system is still very far from the equilibrium condition, and the MB concentration  
620 remains quite high, which leads to this fast rate, compared to the next, adsorption, step  
621 (regime 2)) [86].

622 After approximatively 200 min of adsorption, the diffusion rate decreased and switched  
623 from regime 1) to regime 2). This transition occurred earlier (around 200 min) in the case of  
624 the 90 mg L<sup>-1</sup> MB solution than for the 10 mg L<sup>-1</sup> MB solution (around 300 min). This is due  
625 to a more important steric hindrance induced by the more important adsorbed amount in the  
626 case of the 90 mg L<sup>-1</sup> solution when compared to the 10 mg L<sup>-1</sup>, and to a rarefaction of MB  
627 molecules in the solution. Consequently, the diffusion rates decreased from 0.517 to 0.251 mg  
628 g<sup>-1</sup> min<sup>-0.5</sup> in the case of the 10 mg L<sup>-1</sup> MB solution, and from 1.405 to 0.177 mg g<sup>-1</sup> min<sup>-0.5</sup> in  
629 the case of the 90 mg L<sup>-1</sup> MB solution. A diffusion resistance (non-zero intercept) also  
630 appeared in both cases.



631

632 **Figure 9.** Adsorption kinetics of MB on X<sub>12.5</sub> carbon xerogel: (a) pseudo-first order plot,  
 633 (b) pseudo-second order plot, (c) intra-particle diffusion plot, and (d) fit of the pseudo-  
 634 second order to the adsorbed amount as a function of time for initial MB concentrations of 10  
 635 and 90 mg L<sup>-1</sup> at 25°C; the inset (e) shows the difference between the two curves.

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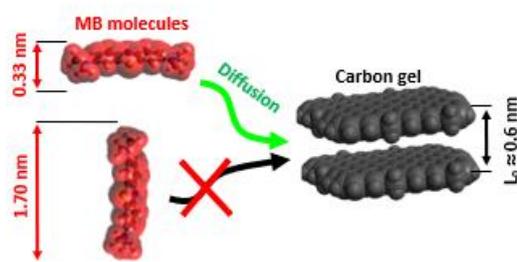
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642

This diffusion resistance was higher when the initial concentration increased due to the faster initial adsorption rate and the higher adsorbed amount when the initial concentration was higher. The plot of adsorbed amount as a function of time and its modelling according to a pseudo second order kinetics show that, after 1500 min (25 h), the equilibrium was reached at least at 90 % (Figure 9d). Thus, in order to minimise the error on the equilibrium points, the duration of the adsorption experiment was fixed at 5 days. Such duration corresponds to an error of 2.7% on the equilibrium condition, which is acceptable compared to the combined

643 experimental errors on the dilutions, initial concentrations and sample weights. The  
644 parameters of the pseudo-first and pseudo-second order are given in Table S2.

645 The very narrow micropore size of the X\_12.5 carbon gel explains the slow diffusion of  
646 MB molecules. Indeed, taking into account the molecular size of MB ( $\approx 1.70 \times 0.74 \times 0.33$   
647 nm), after rapid filling of the biggest pores, the MB molecules can only slide laterally in the  
648 smallest pores (ultramicropores) (Figure 10). In addition, and as explained before, the  
649 previously adsorbed molecules induce a steric hindrance effect and slow down the adsorption  
650 and diffusion process. Moreover, the methylene blue molecules should desolvate upon  
651 entering the narrowest pores. This necessary desolvation step hinders adsorption [95], and is  
652 this likely to slow down the adsorption process.



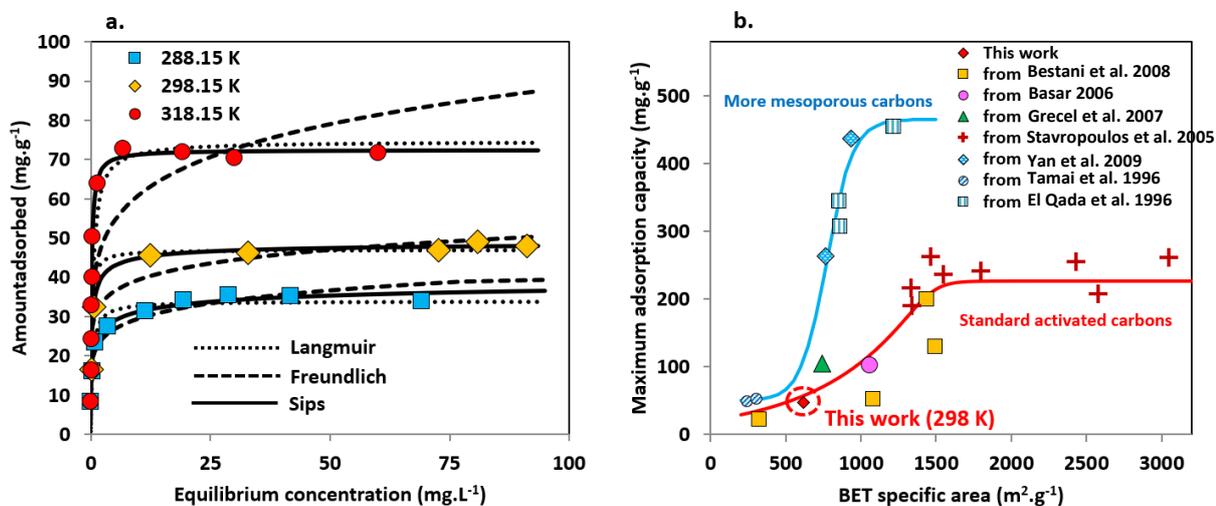
653  
654 **Figure 10.** Schematic diffusion of methylene blue molecules within ultramicropores.

655

### 656 3.2.2. Adsorption at equilibrium

657 Figure 11a shows the MB adsorption isotherms on the X\_12.5 carbon gel. A maximum  
658 adsorption capacity of  $72.50 \text{ mg g}^{-1}$  was measured at  $45^\circ\text{C}$ , and it decreased to  $47.00$  and  
659  $34.00 \text{ mg L}^{-1}$  when the temperature decreased to  $25^\circ\text{C}$  and  $15^\circ\text{C}$ , respectively. When the  
660 adsorption is thermodynamically favourable (the free enthalpy of displacement is negative  
661 [96]), this type of behaviour possibly indicates an endothermal process associated with  
662 entropy-driven adsorption and displacement [96, 97]. Table S3 shows the Langmuir,

663 Freundlich and Sips parameters. Sips model best fitted the experimental data ( $R^2$  in the range  
 664 of 0.979-0.997).



665  
 666 **Figure 11.** (a) Methylene blue adsorption isotherms of the X\_12.5 carbon xerogel carried out  
 667 at different temperatures. (b) Methylene blue adsorption capacities (15°C – 45°C) of various  
 668 carbons from the literature [98-104] as a function of BET area, where the solid lines are  
 669 sigmoid functions.

670 As the temperature increased, the quality of the fit (both through  $R^2$  and  $\chi^2$  values) of the  
 671 Langmuir model increased while that of the Freundlich model got worse (Table S3). This  
 672 transition from Freundlich to Langmuir model is explained by the fact that at higher  
 673 temperatures, the maximum capacity of the material is reached for lower equilibrium  
 674 concentration. Therefore, the higher the temperature, the narrower the knee of the adsorption  
 675 isotherm is. Typically, the Freundlich isotherm model gives poor results when the material is  
 676 close to the saturation capacity and when the filling of adsorption sites increases very fast  
 677 with the equilibrium concentration. The fitting parameters of the three models are given in  
 678 Table S3.

679 The comparison of the adsorption capacity of X\_12.5 with other carbonaceous materials is  
 680 presented in Figure 11b. The X\_12.5 carbon gel fits well the trend of classic activated

681 carbons. Unlike most of the materials presented in this Figure, X\_12.5 was synthesised  
 682 without any activation or doping. In addition, the precursor consisted of a low-value product  
 683 (phenolic oil) that may be considered as waste. Materials with mesoporosity exhibit higher  
 684 capacities than usual microporous carbons. Wider pores could allow a better organisation of  
 685 the adsorbed MB molecules and, consequently, better packing on the adsorbent surface. In  
 686 addition, the average pore size (around 0.62 nm) allows the adsorption of a single MB  
 687 molecule ( $1.70 \times 0.74 \times 0.33$  nm) between the two walls of a slit-shaped ultramicropore. Such  
 688 an adsorption mechanism, due to the possible permanent pore blocking, decreases the  
 689 potential maximum adsorption capacity of the material.

### 690 3.2.3. Adsorption thermodynamics

691 The use of equation (13) gives access to the equilibrium constant. We chose an equilibrium  
 692 concentration equal to  $1 \text{ mg L}^{-1}$  MB ( $c_e \approx 3.13 \cdot 10^{-3} \text{ mol L}^{-1}$ ) and we used the Sips model to obtain  
 693 the adsorbed concentration,  $c_{ads}$ , for the three isotherms.  $c_{ads}$  was simply obtained by dividing  
 694 the number of moles of adsorbed MB by the volume of the solution. Table 4 shows the free  
 695 enthalpies of adsorption as well as the estimated equilibrium constants calculated using  
 696 equation 13.

697 **Table 4.** Equilibrium constants from different estimations and their associated free enthalpies.

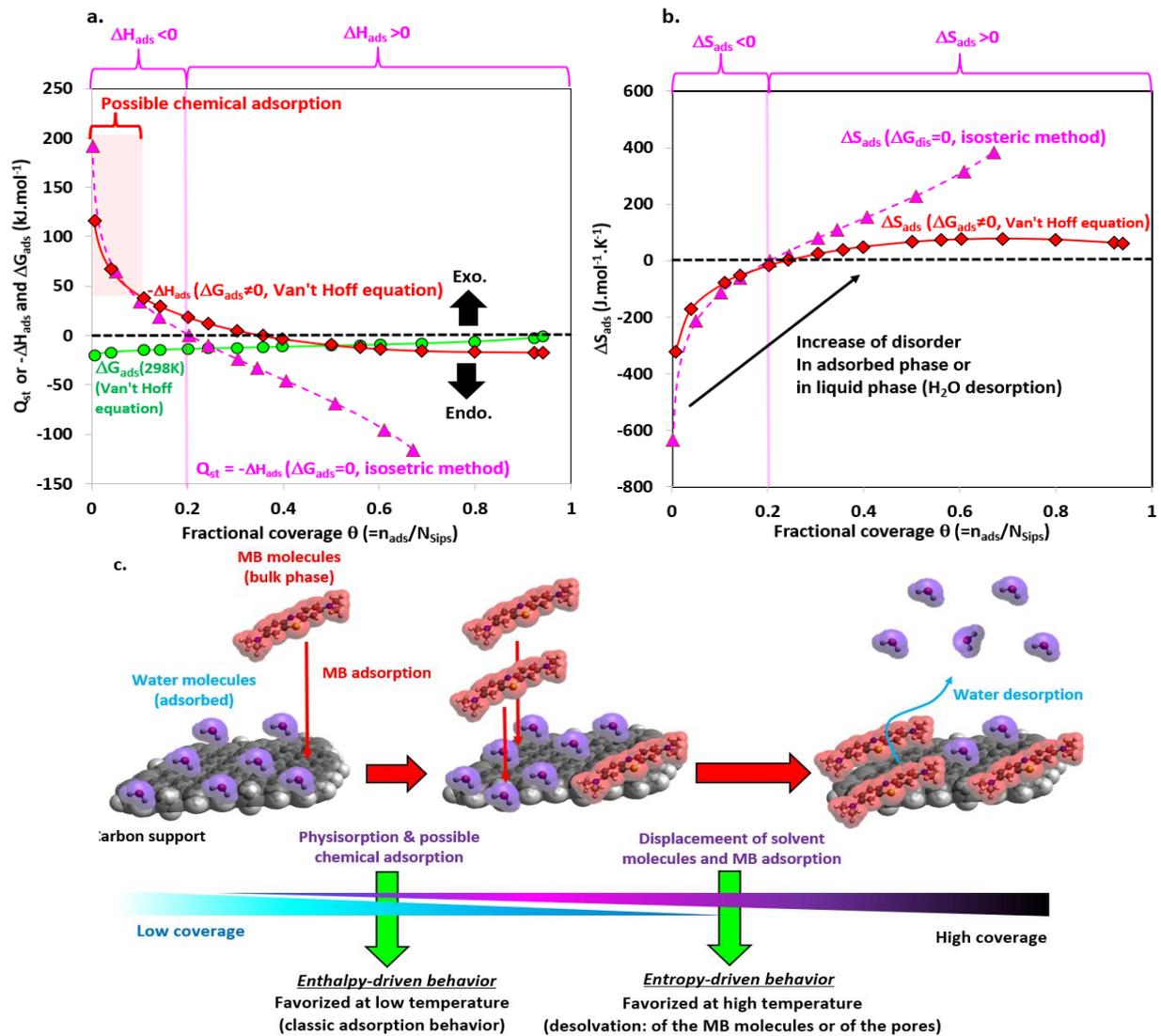
	Temperature		
	15°C	25°C	45°C
$K = c_{ads}/c_e$ (dimensionless)	14.95	24.10	30.89
$\Delta G_{ads}$ (kJ mol <sup>-1</sup> )	-6.5	-7.9	-9.1

698

699 The good quality of the linear regression allows calculating the changes of enthalpy  
 700 ( $\Delta H_{ads}$ ) and entropy ( $\Delta S_{ads}$ ) during the adsorption process (equation (14)). The value of  $\Delta H_{ads}$   
 701 was close to  $17 \text{ kJ mol}^{-1}$ , while that of  $\Delta S_{ads}$  was equal to  $83 \text{ J mol}^{-1} \text{ K}^{-1}$ . The use of the

702 isosteric method (equation (16)) on Sips isotherms (equation (10)), combined to the  
703 enthalpy/entropy compensation principle (equation (18)), led to similar values. The latter were  
704 indeed close to  $25 \text{ kJ mol}^{-1}$  when considering the adsorption enthalpy while the adsorption  
705 entropy was close to  $83 \text{ J mol}^{-1} \text{ K}^{-1}$ . The positive values of entropy can be analysed as an  
706 increase in the disorder of the solvent phase due to desorption of water molecules from the  
707 carbon surface or to desolvation of MB molecules. However, the observation of a single value  
708 of adsorption enthalpy or entropy, at a given equilibrium concentration, is not enough to fully  
709 understand the adsorption process. The assessment of the thermodynamic parameters should  
710 be carried out over the entire range of coverage.

711 Figure 12a presents the adsorption (or displacement) enthalpies (at 298 k) from both the  
712 isosteric method and the Van't Hoff equation. Above the range of low fractional coverage  
713 (i.e., at  $\theta > 0.2$ ), the isosteric heat becomes negative (and therefore  $\Delta H_{ads}$  becomes positive).  
714 Thus, it can be assumed that the overall displacement process (water desorption and MB  
715 adsorption) is exothermic within the range of low coverage while at high coverage, the  
716 aforementioned process is endothermic.



717

718 **Figure 12.** (a) Enthalpy and Gibbs free energy; (b) entropy; and (c) supposed mechanism of  
 719 methylene blue adsorption at 24°C on the X\_12.5 carbon gel (results obtained using either the  
 720 isosteric method or the Van't Hoff equation).

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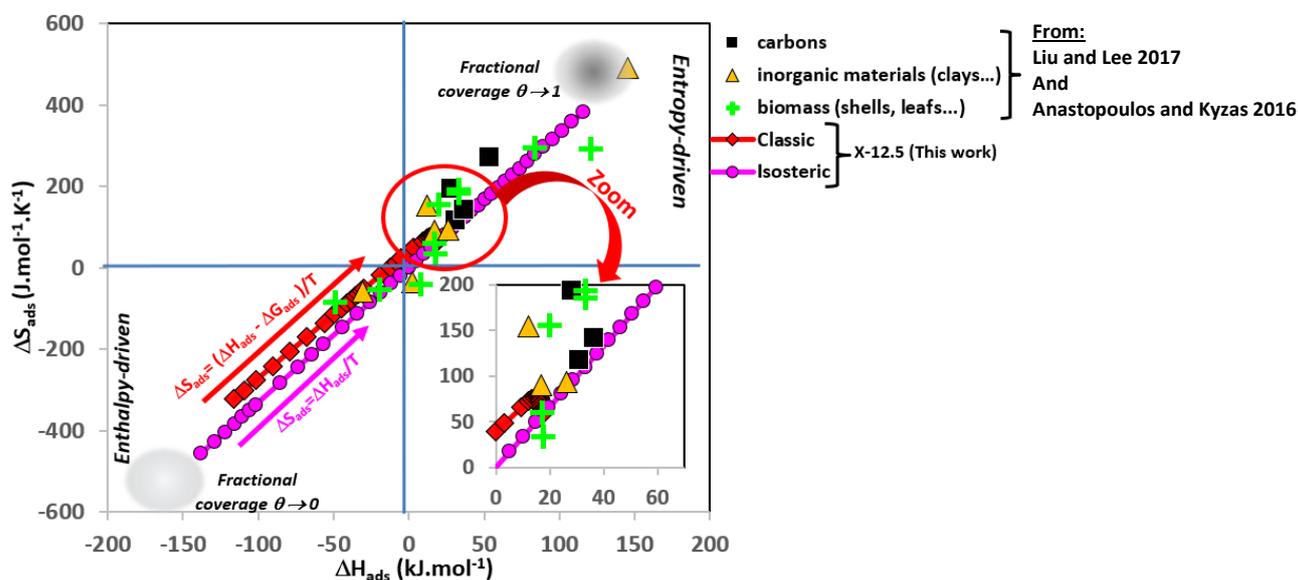
722 As expected from the enthalpy/entropy compensation principle (isosteric method only), an  
 723 opposite behaviour is observed for isosteric adsorption entropies. The gradual increase in  
 724 isosteric entropy of adsorption (or displacement) could be analysed as an increase in water  
 725 desorption from the carbon surface as the adsorption proceeds. Thus, the higher the coverage  
 726 by MB, the higher water desorption, which initially covers the entire carbon surface.

727 Consequently, the MB adsorption and packing, which should make adsorption improbable, do  
728 not balance the increase in entropy, induced by water desorption and the possible desolvation  
729 of MB molecules. Therefore, at low coverage, MB adsorption follows a classic enthalpy-  
730 driven process, which is possibly due to strong physisorption or even chemical adsorption on  
731 specific sites. Above the low coverage region ( $\theta > 0.2$ ), the adsorption of MB on X\_12.5  
732 becomes an entropy-driven process, in which the desolvation of MB molecules and water  
733 desorption from the carbon surface are favoured at high temperature. Such a transition from  
734 enthalpy-driven process to entropy-driven process has been evidenced by other authors for the  
735 adsorption of n-butanol/water and benzene/n-heptane on carbon black and silica gel,  
736 respectively [96, 105].

737 At low coverage, thermodynamic parameters thus obtained, either by the isosteric method  
738 or by the Van't Hoff equation ( $\Delta H_{ads}$  and  $\Delta S_{ads}$ ), follow the same evolution depending on  
739 coverage (Figure 12a and 12b). At high coverage, the quantities obtained from the isosteric  
740 method seem to diverge towards infinite values while those obtained from the Van't Hoff  
741 equation seem to converge to 0. The aforementioned specific adsorption sites are, most likely,  
742 the heteroatoms that are present in the surface groups like phenols (i.e.,  $pK_a = 11.15$ ) or  
743 carboxylic and carboxylic anhydride groups (i.e.  $pK_a = 3.03$ ). On these specific sites, chemical  
744 adsorption and highly polarised physisorption can take place. Indeed, the MB molecule has a  
745 permanent dipole like the aforementioned surface groups. Consequently, Keesom forces,  
746 complementary to chemisorption, might play a major role in adsorption in this low range of  
747 coverage. A possible adsorption mechanism of the MB molecules on this carbon surface is  
748 proposed in Figure 12c.

749 In order to verify the validity of the estimation of the thermodynamic parameters, a  
750 comparison was made with different materials (Figure 13). The calculated values, using the

751 isosteric method or the Van't Hoff equation, are similar to those found in the literature. Such  
 752 similarities show the robustness of the two methods to compare thermodynamic data.



753  
 754

755 **Figure 13.** Entropies versus enthalpies of adsorption of methylene blue on the X\_12.5 carbon  
 756 gel, obtained by the isosteric method (●) or the Van't Hoff equation (■) compared with some  
 757 data from the literature [106, 107].

758

#### 759 4. Conclusion

760 The use of phenolic oil (PO) combined with para-toluenesulphonic-acid (PTSA),  
 761 paraformaldehyde (PF) and isopropanol (IPA) as a solvent, allowed synthesising organic  
 762 solvogels. The investigations were carried out using a formulation containing 3.123 g of PF,  
 763 0.64 g of PTSA, 10 g of PO and different amounts of IPA. The almost exclusively  
 764 ultramicroporous texture allowed obtaining similar textural properties whatever the drying  
 765 mode (supercritical drying, cryodesiccation, or classical convective drying). The formulation  
 766 with 12.5 g of IPA was selected as the best, and a carbon xerogel was selected to test and  
 767 investigate methylene blue (MB) adsorption.

768 This carbon xerogel had a BET area of  $620 \text{ m}^2 \text{ g}^{-1}$  while its NLDFT surface area was 891  
769  $\text{m}^2 \text{ g}^{-1}$ . MB adsorption was slow due to the very narrow pores ( $L_0 = 0.62 \text{ nm}$ ), and the  
770 adsorption capacity of the carbon at  $25^\circ\text{C}$  was estimated at  $47.00 \text{ mg g}^{-1}$ , in good agreement  
771 with the literature. The Sips model was the best to fit the MB adsorption isotherms, and the  
772 calculation of the thermodynamic parameters using both conventional and isosteric methods  
773 led to positive values of the change of entropy (at  $c_e = 1 \text{ mg L}^{-1}$ :  $83 \text{ J mol}^{-1} \text{ K}^{-1}$ ), suggesting  
774 that the adsorption of MB in these materials is driven by entropy above a 20% of coverage.  
775 Such entropy-driven behaviour can be explained either by the desolvation of the MB  
776 molecules when they enter the smallest pores or by water desorption from the carbon surface.  
777 Below such limit coverage, the analysis of the thermodynamic parameters suggests that the  
778 adsorption process is driven by enthalpy. Such phenomenon is probably due to specific  
779 adsorption sites, as heteroatoms or defects, on the carbon surface.

780 This study thus reported the first successful acid-catalysed synthesis of gel based on PO  
781 published so far, the only previous work on a similar topic concerning base-catalysed gels,  
782 hence with different characteristics. The crosslinking agent, PF, can also be considered as a  
783 by-product of the formaldehyde industry. Therefore, the use of PO and PF can be seen as a  
784 win-win situation and as an attempt to recover these 'wastes' and integrate them into a circular  
785 economy. The adsorption capacities and the kinetics of the materials synthesised here might  
786 be improved further by tuning their textural properties. For instance, an activation step or a  
787 preliminary mesostructuration would probably increase the porous volume as well as the  
788 accessibility of the pores. As the precursor is PO, an industrial by-product, such steps could  
789 be affordable from an environmental and energy perspective.

790

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