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# KI and TEDA influences towards the retention of radiotoxic CH<sub>3</sub>I by activated carbons

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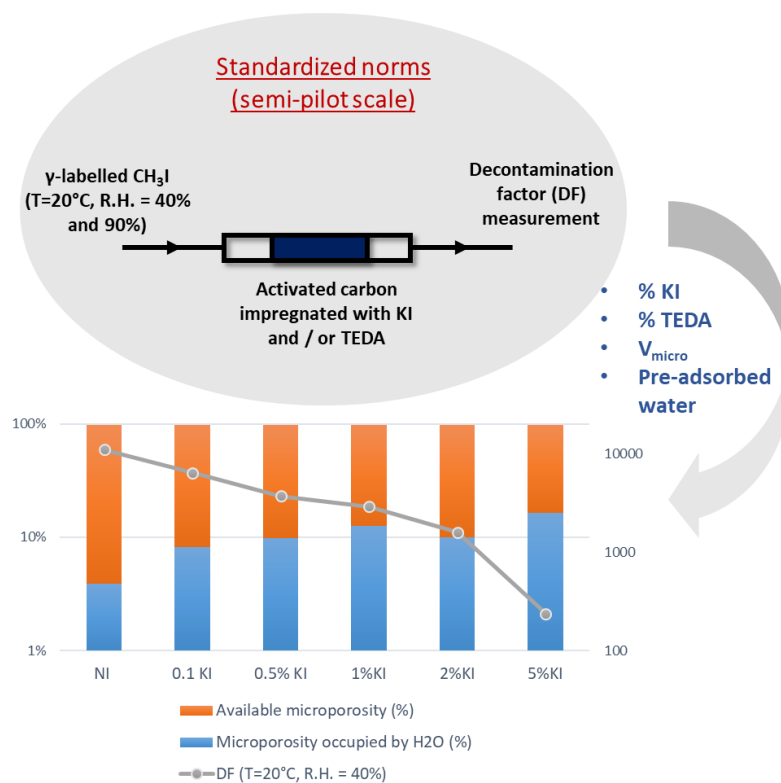
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## GRAPHICAL ABSTRACT:



## HIGHLIGHTS:

- Up to 21 AC are investigated for the capture of γ-CH<sub>3</sub>I using standardized tests.
- Micropore blocking phenomena are only observed for high molar impregnation ratio.
- TEDA/AC display the best retention performances whatever the studied condition.
- The pre-adsorbed water governs the γ-CH<sub>3</sub>I trapping for KI/AC at R.H. = 40%.

- A slight increase of DF is obtained as a function of KI content at R.H. = 90%.

## 21 **KEYWORDS:**

22 activated carbon, methyl iodide adsorption, decontamination factor, TEDA, KI

## 23 **ABSTRACT**

24 Activated carbons (AC) are widely used within the ventilation networks of nuclear facilities to  
25 trap volatile iodine species. In this paper, the performances of various commercial activated  
26 carbons towards the trapping of  $\gamma$ -labelled methyl iodide were evaluated in semi-pilot scale  
27 under different R.H. according to normalized procedures. A combination between the  
28 retention performances and the physico-chemical properties as deduced from several  
29 techniques was performed to gain insights about the AC influencing parameters on  $\gamma$ -CH<sub>3</sub>I  
30 capture. Different trends were obtained depending on the impregnant nature and the studied  
31 conditions. A high sensitivity of KI/AC towards water vapor was outlined. At R.H. = 40%. The  
32 enhancement of water uptake by KI/AC as deduced from water adsorption experiments, leads  
33 to decrease the available microporosity for CH<sub>3</sub>I physisorption, inducing therefore the  
34 reduction of performances as a function of KI content at these conditions. At R.H. = 90%, the  
35 adsorption mechanism was found to be governed by isotopic exchange reaction since 90% of  
36 the microporosity was occupied by water molecules. Therefore, a slight increase of DF was  
37 obtained in these conditions. This sensitivity was found to be of a lesser extent for TEDA/AC  
38 displaying the highest retention performances whatever the studied condition.

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## 44 **1. Introduction**

45 As the rapid increase of the nuclear industry in the 21<sup>st</sup> century, the necessity to limit the  
46 release of radioactive substances into the environment remains a major challenge for the  
47 nuclear safety [1]. Among the most hazardous radionuclides, a particular attention is devoted  
48 to iodine radioactive species owing to the presence of volatile compounds (namely I<sub>2</sub> and  
49 CH<sub>3</sub>I), their high mobility in environment and their specific affinity for the thyroid gland [2].  
50 Methyl iodide (CH<sub>3</sub>I) is resulted from reaction between I<sub>2</sub> and organic paints existing in the  
51 nuclear facilities [3][4].

52 Current filtration devices of the iodine trapping are classified into two categories [5]: wet  
53 processes using mainly scrubbing methods and dry processes through porous sorbents. Dry  
54 process is known to be more promising than wet methods, due to its high removal efficiency  
55 and low maintenance cost [5]. Depending on the context, different adsorbents are  
56 implemented at the industrial scale in order to prevent from the iodine dissemination to the  
57 environment. More particularly, activated carbons (AC) are widely used within the ventilation

58 networks of nuclear facilities to trap volatile iodine species in normal operating and degraded  
59 conditions [6]. The good performances of AC are assigned to their well-developed  
60 microporosity [7] (d pore < 2 nm) promoting therefore the capture of CH<sub>3</sub>I by physisorption  
61 phenomena. However, the AC performances for CH<sub>3</sub>I trapping are known to be drastically  
62 reduced under humid conditions due to the competitive adsorption between water vapor and  
63 methyl iodide [8]. The affinity of AC towards the CH<sub>3</sub>I must be enhanced by impregnation with  
64 organic or inorganic compounds. The most used impregnants in the nuclear field [9] are  
65 triethylenediamine (TEDA, ≤ 5 wt.%) and potassium iodide (KI, 1 wt. %) interacting with CH<sub>3</sub>I  
66 through different retention mechanisms [10][11][12][13]. On the one hand, TEDA is able to  
67 react with methyl iodide *via* different mechanisms of chemisorption depending on the R.H.,  
68 resulting in the improvement of the adsorption performance of the AC [14]. On the other  
69 hand, the trapping mechanism of the radioactive CH<sub>3</sub>I on KI impregnated AC is reported to  
70 involve an isotopic exchange reaction between the radioactive CH<sub>3</sub>I and the stable KI. It is  
71 reported that the amount of the stable KI should be in excess in order to guarantee the  
72 efficient capture of radioactive CH<sub>3</sub>I [15].

73 Despite the massive use of these adsorbents in the nuclear field, systematic studies of the  
74 intrinsic AC characteristics (textural properties, impregnants contents and speciation)  
75 towards  $\gamma$ -labelled methyl iodide retention are rarely investigated. The current investigations  
76 of the AC characteristics towards their adsorption performances remain generally at the  
77 laboratory scale through breakthrough curves or adsorption isotherms [16][17][18]. The  
78 existing publications based on the decontamination factor (DF) measurement following  
79 standardized procedures have rarely focused on the influence of the intrinsic properties of  
80 the adsorbent [19][20]. Nevertheless, recent studies of the AC performance are mainly  
81 focused on the TEDA impregnated AC with limited impregnation ratios, and no structure -  
82 activity correlation were determined [21]. Moreover, the lack of the attention for the KI  
83 impregnated AC and the associated performance comparisons with not-impregnated AC can  
84 also be noticed [12]. In that respect, the role played by KI as well as the correspondent  
85 mechanism are rarely focused in the literature.

86 In this study, we aimed therefore to gain insights on the most prominent factors towards the  
87 capture of radioactive methyl iodide in semi-pilot scale according to normalized procedures  
88 [22][23], by using different commercial formulations of activated carbons. In the first part,  
89 characterizations with different techniques (XPS, XRD, SEM-EDX, N<sub>2</sub> porosimetry...) are  
90 presented. In the second part, the decontamination factors towards  $\gamma$ -labelled methyl CH<sub>3</sub>I  
91 deduced from the standardized norms are discussed depending on the water vapor content.  
92 The main objective was to establish relationships between the adsorbent parameters and its  
93 retention properties depending on the studied condition.

## 94 2. Experimental

### 95 2.1 Presentation of the tested adsorbents

96 Different formulations of commercial AC (grain size ranging from 2 to 3 mm) are used in this  
97 study. The studied materials derived from coco-nut shells were produced in the same batch  
98 in order to limit the dispersions in the AC characteristics. Different impregnation types of KI  
99 and TEDA were made but few details were provided regarding the exact synthesis protocol

100 as well as the precise impregnation ratio. On the one hand, co-impregnated AC (KI and TEDA)  
101 were tested with the aim to compare their properties with the *nuclear grade AC* currently  
102 used in the ventilation networks. On the other hand, the KI or TEDA impregnated AC were  
103 tested separately in order to better understand the effects due both molecules on the  
104 retention performances and the involved mechanisms depending on the studied conditions.  
105 The theoretical impregnation ratio of each AC is summarized in the Table 1.

106 *Table 1 Summary of the theoretical impregnation ratio of different AC*

KI impregnation (wt.%)	TEDA impregnation (wt.%)	Co-impregnation	
		KI (wt.%)	TEDA (wt.%)
0.1	1	0.5	1, 5, 10
0.5	3	1	1, 5, 10
1	5	2	1, 5, 10
2	7		
5	10		

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## 109 2.2 Physicochemical characterizations

### 110 2.2.1 Chemical analysis

111 The experimental impregnant quantity (KI and TEDA) was determined using an extraction  
112 method [24]. Acetonitrile was used to extract the impregnants from batch experiments  
113 performed at ambient temperature. The amount of the extracted impregnants at equilibrium  
114 (overnight) was deduced from UV-Visible spectrophotometry (1900, Shimadzu). More  
115 particularly, absorbances at 247 nm and 225 nm were measured for KI and TEDA respectively  
116 using the Beer's Law.

117 Particular precautions were taken for the impregnants analysis. On the one hand, an excess  
118 of  $\text{Na}_2\text{S}_2\text{O}_3$  was added during extraction in order to avoid the oxidation phenomena of iodine  
119 for KI impregnated AC. On the other hand, the subtraction of each molecule spectral  
120 contribution was required for co-impregnated materials due to KI and TEDA spectra  
121 interferences.

122 X-ray photoelectron spectroscopy (XPS) analysis were performed for some AC to gain insights  
123 on the chemical surface groups of the tested sorbents. Details about experimental acquisition  
124 and spectra deconvolution are reported in the supplementary (see S1, in ESI).

### 125 2.2.2 Textural properties

126 The porous structure of the investigated AC were derived from  $\text{N}_2$  isotherms at 77 K (3FLEX,  
127 Micromeritics). Prior to each adsorption/desorption experiment, samples were preheated at  
128  $120^\circ\text{C}$  overnight followed by an *in-situ* degassing at  $120^\circ\text{C}$  ( $10^{-6}$  mbar) for 12 h to remove most  
129 of the adsorbed impurities. Once the temperature was cooled down to 77 K,  $\text{N}_2$  adsorption  
130 phase was started for increasing relative pressures ( $P/P_0$ ) from  $10^{-7}$  to 0.99. The desorption  
131 phase was then achieved for decreasing  $P/P_0$  until 0.35. Specific surface areas ( $S_{\text{BET}}$ ) were  
132 based on the BET calculation [25] and optimized by the Rouquerol's method [26]. The  
133 micropore volume and the micropore size distribution were deduced from the HK (Horwath-

134 Kawazoe) method for pore widths until 2 nm [27]. Finally, the total pore volume was  
135 measured from N<sub>2</sub> adsorption isotherms at relative pressure of 0.99 [28].

136 Additional information on the morphology of some AC were deduced from SEM/EDX  
137 characterizations. Details about the used instrument and the analysis conditions are reported  
138 in the supplementary (see S2, in ESI).

### 139 2.2.3 Water adsorption isotherms

140 H<sub>2</sub>O adsorption isotherms were performed for some AC using a dynamic vapor sorption (DVS)  
141 Vacuum microbalance (Surface Measurement Systems, SMS). Prior to each sorption test, AC  
142 samples (mass = 60-70 mg) were outgassed at mild conditions (60 °C, 15 hours, vacuum of 10<sup>-5</sup>  
143 Torr) to eliminate the residual humidity without inducing a significant modification of their  
144 surface chemistry according to recent works of Velasco et al [29]. Then, gravimetric  
145 measurements are carried out for R.H. ranging from 0% to 95% at 25°C. The thermodynamic  
146 equilibration for each tested R.H. was assumed when a water mass change of less than 0.0004 %  
147 per minute was obtained.

### 148 2.3 CH<sub>3</sub><sup>131</sup>I gas phase dynamic adsorption experiments

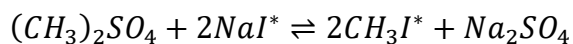
149 The retention of the CH<sub>3</sub><sup>131</sup>I was investigated within the PERSEE Facility [30], using a specific  
150 setup denoted as “low flow rates bench” (Fig. 1) to evaluate the performance of AC towards  
151 the capture of radioactive methyl iodide at semi-pilot scale. This experimental setup can be  
152 divided schematically into three main parts: (i) the generation of γ – labelled CH<sub>3</sub>I and water  
153 vapor, (ii) the adsorbent to be tested (upstream stage) and (iii) the referenced AC  
154 (downstream stage) devoted to trap the fraction of methyl iodide not retained by the tested  
155 adsorbent. This adsorbent was the same for all the presented retention tests for comparison  
156 purposes.

157 Up to four AC can be tested simultaneously thanks to this test bench. Different sensors were  
158 placed in order to monitor the different test parameters, especially temperature, relative  
159 humidity and face velocity of the flowing gas. The experimental protocol developed for this  
160 setup was adapted from the ASTM3803 [22] and NFM62-206 standards [23] devoted to  
161 characterize the retention performances of commercial nuclear grade AC towards γ – labelled  
162 CH<sub>3</sub>I.

163 The AC samples to be tested as well as the reference AC were prepared through the same  
164 geometry, according to a specific procedure summarized in the supplementary (see S3, in ESI).  
165 For all retention testes, a bed depth of 5 cm and bed density of 0.5 g/cm<sup>3</sup> were employed.  
166 Such conditions allow an AC loading in agreement with the normalized test procedures [22,  
167 23].

168 Once the AC are prepared, a pre-equilibration under humidity (R.H. = 40% and 90% at 20°C)  
169 of at least 16h is made under flowing mode (gas flow rate of 17.5 L/min (NTP) corresponding  
170 to a face velocity of 25 cm/s and residence time of 0.2 s at 20°C) for both upstream and  
171 downstream sections. The objective is to achieve the equilibrium between the tested samples  
172 and the desired R.H. before the adsorption test. Then, the retention test was carried out using  
173 these same conditions. More particularly, a pulse (duration of 30 min) of γ-labelled CH<sub>3</sub>I (C<sub>0</sub> =  
174 0.15 ppmv) was generated from the following reaction:

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After 30 mins of the  $\gamma$  – labelled  $CH_3I$  generation, an elution phase of 60 min with air flow in the same conditions is carried out in order to take into account the desorption of physiosorbed  $CH_3I$  [23]. Finally, *ex-situ*  $\gamma$ -spectrometry measurements (*Cryo-Pulse 5 Plus, Canberra*) were carried out for both the upstream and downstream AC. DF can be therefore deduced from the following expression:

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$$DF = \frac{A_{upstream} + A_{downstream}}{A_{downstream}}$$

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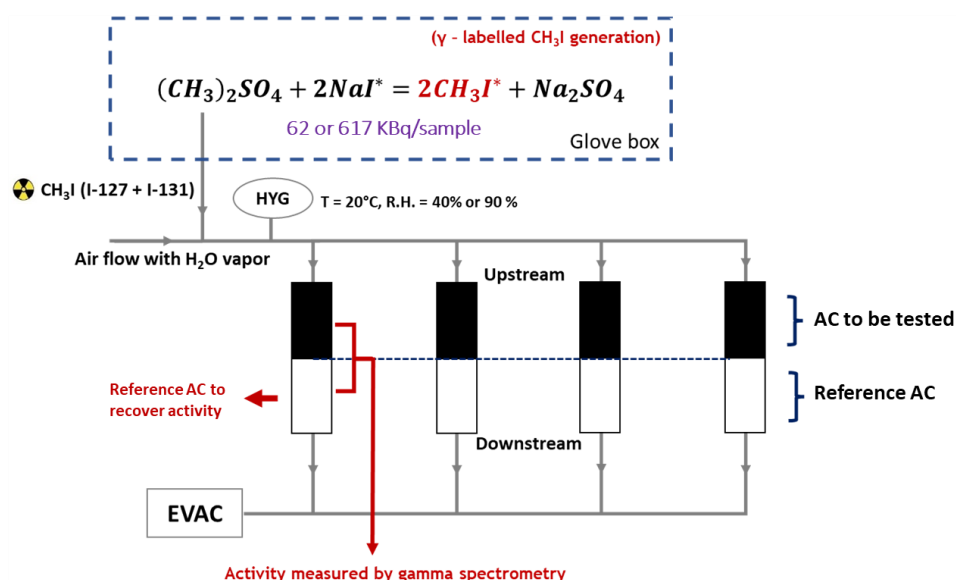
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Where  $A_{upstream}$  and  $A_{downstream}$  denote the measured  $^{131}I$  activities by  $\gamma$ -spectrometry in the upstream and downstream stages (Figure 1) respectively. Due to the expected difference in the retention behavior as a function of the relative humidity, the injected activity of radioactive methyl iodide was adapted especially for moderately humid conditions, to increase the expected activity in the downstream section (generally close to the detection limit at R.H. = 40%). More precisely, initial  $^{131}I$  activities per section equal to 62 and 617 KBq were targeted for R.H. of 40 and 90% respectively.



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Figure 1 Schematic representation of the “low flow rates” test bench of PERSEE

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### 192 3. Results and discussions

#### 193 3.1 Physicochemical characterizations of impregnated AC

##### 194 3.1.1. Chemical composition

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The determined impregnant quantities of KI and TEDA are presented in the Figure 2 (a). Firstly, the absence of KI and TEDA molecules was checked for the not-impregnated AC. In addition, a quasi-linear relationship can be noticed when comparing experimental and theoretical contents. Nevertheless, a deviation of 23%, 15% and 27% from the theoretical amount was found for the tested TEDA, KI and co impregnated AC respectively (Figure 2 (a)). For example, contents of 0.69 wt. % and 3.85 wt. % were measured for KI and TEDA respectively for

201 theoretical contents of 1 wt. % (KI) and 5 wt. % (TEDA). These results were compared with  
202 CHNS analysis in some TEDA AC. The TEDA contents deduced from nitrogen quantity, were  
203 found to be close to the theoretical loadings despite some observed variabilities (Table S1).  
204 This discrepancy may be related to the presence of more bonded (*i.e.* chemisorbed)  
205 molecules that cannot be evidenced by the reported extraction method. Indeed, the  
206 molecular diameter of the acetonitrile (0.652 nm [31]) is found to be slightly higher than the  
207 expected pore width of the tested AC, indicating that the accessibility of the acetonitrile  
208 towards certain KI or TEDA sites may be hindered. These strongly bonded or inaccessible  
209 molecules can be nevertheless measured by CHNS technique based on a combustion step  
210 followed by chromatographic measurements. According to the further exchanges with the AC  
211 supplier, all the tested AC were impregnated using specific impregnation protocols [32]  
212 leading possibly to inaccessible fraction in TEDA and KI molecules using an acetonitrile  
213 extraction method. In the following parts, only theoretical contents will be presented since  
214 the deviation of experimental amounts from the indicated values was linear.

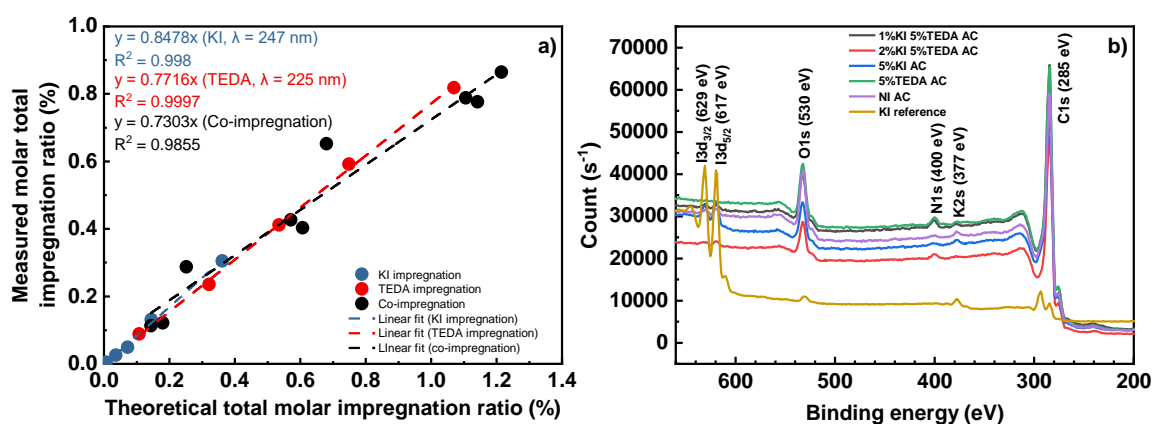
215 Additional information regarding the AC sample surface can be deduced from the XPS spectra  
216 presented in the Figure 2 (b). As expected, the considered samples are mainly carbonaceous  
217 (88-90 at. % in carbon) in agreement with the CHNS analysis (Table S1). Other elements  
218 resulting from the raw material and the further production steps can be also evidenced  
219 (Figure S1). We notice namely the presence of oxygen (8-10 at. %), nitrogen (0.5-2 at. %),  
220 potassium (0.2-1.1 at. %) and iodine (0.1-0.5 at. %). The semi-quantitative analysis using XPS  
221 gives also evidence for KI and TEDA impregnations by comparing the chemical composition of  
222 both starting and impregnated AC. An increase of the iodine surface contents has been  
223 observed without linear correlation for the tested materials. The discrepancy compared to  
224 the theoretical amount of KI is probably related to the XPS sensibility to AC surface (depth of  
225 about 1 nm) as comparison with the global characterizations by extraction and UV-Visible  
226 measurements. Moreover, potassium contents were analyzed in order to make sure from the  
227 stoichiometric K/I ratios. In the case of reference KI, a K/I ratio close of unity ( $\sim 0.9$ ) was found.  
228 However, a very large deviation from 1:1 stoichiometry was observed at the expense of iodine  
229 for 5%KI AC (K/I  $\sim 2$ ), 1%KI5%TEDA (K/I  $\sim 5$ ) and 2%KI5%TEDA AC (K/I  $\sim 4$ ). This discrepancy may  
230 be attributed to the presence of significant amount of potassium in the starting material (%K  
231 = 1.11 at. %, Figure S1), making it difficult to distinguish the native potassium (raw material)  
232 from additional potassium due to the KI impregnation. For TEDA, no correlation between the  
233 surface nitrogen concentrations with TEDA contents was possibly due to the volatility of this  
234 molecule under vacuum. Nevertheless, a quasi-similar amount of nitrogen (1.56 – 1.97 at. %)  
235 related to the strongly bonded TEDA species, was found for three adsorbents with 5 wt. % in  
236 TEDA as indicated in the Figure S1.

237 The deconvolution of XPS spectra allowed us to gain insights on the element speciation. It can  
238 be mentioned firstly that the tested AC display rather similar C1s (285 eV) and O1s (530 eV)  
239 speciation (Figure S2), in agreement with the use of the same batch and substrate for their  
240 production. On the one hand, the carbon speciation is mainly dominated by the  $sp^2$  graphitic  
241 contribution (Figure S3) [33], consistently with the amorphous graphitic structures of these  
242 materials, as depicted from XRD characterizations (two broad peaks located at  $22^\circ$  and  $43.5^\circ$ ,  
243 see Figure S4). Other contributions assigned to oxidized carbon species can also be identified



244 (alcohols, carbonyls, quinones, Figure S3). On the other hand, the O1s line is found to be  
 245 composed of 5 contributions, consistent with the carbon oxidized species observed at the  
 246 C1s line [34] (Figure S5).

247 Information about KI and TEDA speciation can be deduced from nitrogen and iodine peaks  
 248 deconvolution. In the case of nitrogen (N1s), two peaks located at 398 eV (N1) and 400 eV  
 249 (N2) are observed (Figure S6). The N1 peak corresponds to three-coordinated nitrogen N  
 250 sigma-bonded to carbons (with  $sp^3$  bonds), as in amines (N-H<sub>3</sub>) and in TEDA (N-C<sub>3</sub>) [35]. The  
 251 N2 peak is rather associated with N-Csp<sup>2</sup> bonds, as for quaternary amines, that may be  
 252 attributed to a nitrogen interaction with a carbon atom in the graphitic structure [36]. It is  
 253 difficult to relate the TEDA quantity to the N1 speciation since N1 is already present on the  
 254 not-impregnated AC and 5%KI AC. Then, the N1 speciation is not only contributed by the TEDA  
 255 but also by other potential nitrogen functional groups on the AC surface. In general, it is  
 256 observed that the speciation of the N1 and N2 remains the same for all the tested AC sample,  
 257 indicating their similar surface characteristics. For iodine (I3d), two different components can  
 258 be also displayed: 619 eV (I1) and 621 eV (I2) (Figure S7). The dominant contribution I1 is due  
 259 to ionic I<sup>-</sup> characteristic of the KI signature. While, the small one I2 is associated to less  
 260 negative iodine (I<sup>δ-</sup>). A ratio between I1 and I2 of about 80/20 was found for all the tested  
 261 samples, as a comparison with the reference KI product mostly made from the I1 peak (94%).  
 262 The presence of the peak I2 for the tested AC sample may indicate the potential interaction  
 263 of iodine with surface defects of the AC, leading to the formation of more covalent iodine  
 264 species. The presence of this contribution may explain also the observed deviation from  
 265 acetonitrile extraction, since the developed analytical method was only sensitive to I-  
 266 component. Finally, a rather similar speciation of nitrogen and iodine can be observed when  
 267 comparing the studied singly impregnated or co-impregnated AC. Therefore, it can be  
 268 proposed that there is no interaction between TEDA and KI molecules within the AC. The  
 269 absence of interaction could be explained by two factors: (i) different molecules localizations  
 270 within the AC surface; (ii) a large excess of TEDA as a comparison with KI in the studied  
 271 adsorbents (TEDA/KI molar ratios of 3.7 and 7.4 for 2%KI+5%TEDA and 1%KI+5%TEDA AC  
 272 respectively).



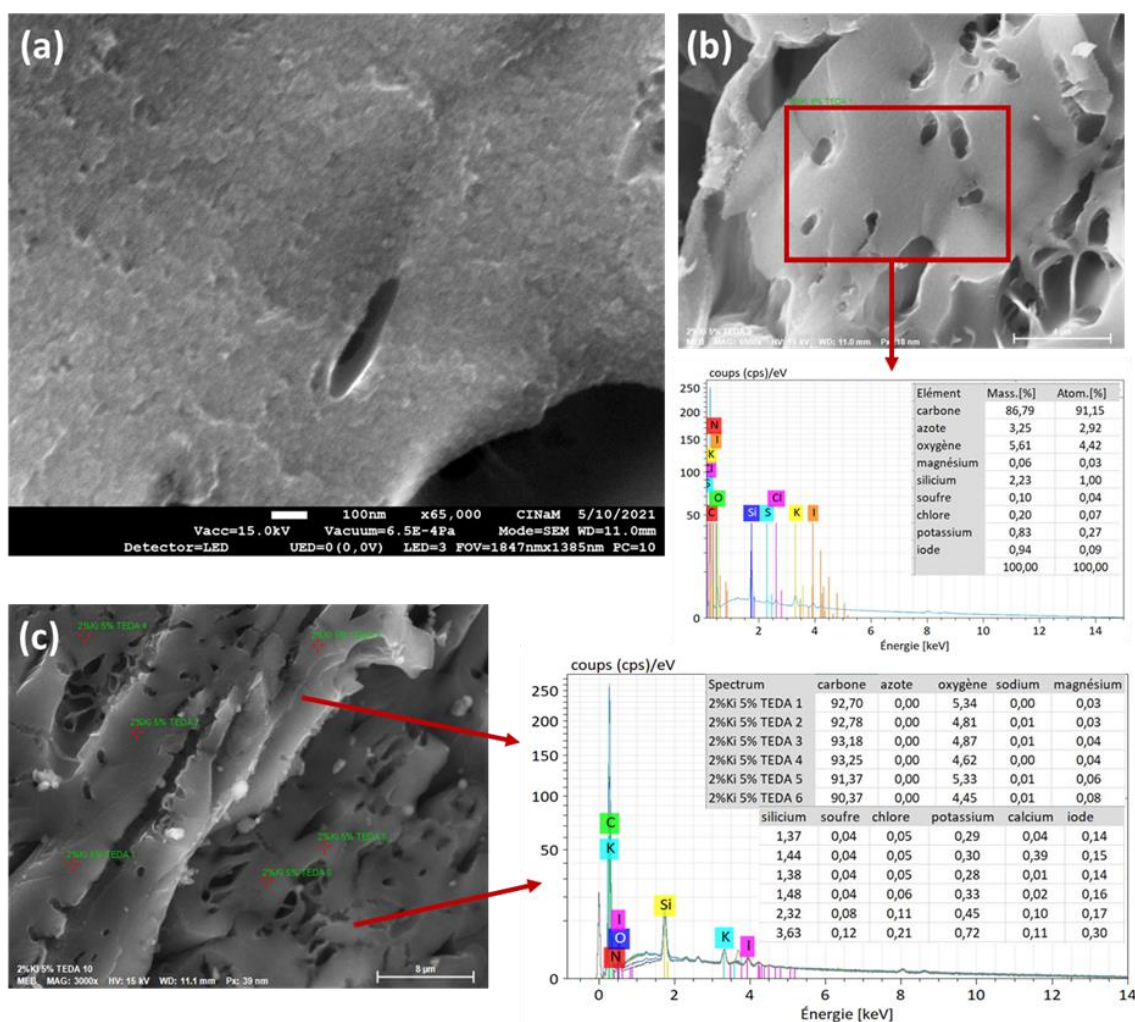
273

274 *Figure 2 (a) Determined impregnation ratio; (b) XPS spectra for some of the tested AC*

### 275 3.1.2. XRD and SEM/EDX analysis

276 Additional elements regarding KI and TEDA localizations within the investigated AC can be

277 deduced from XRD and SEM/EDX analysis. On the one hand, no new X-ray diffraction peaks  
 278 typical of KI and TEDA lines were observed, indicating the absence of agglomeration of the  
 279 impregnants on the external surface (Figure S4). Therefore, it can be proposed that these  
 280 agents are well-dispersed within the internal porosity in molecular way. This observation was  
 281 also confirmed by SEM/EDX investigations. Indeed, no substantial change before and after  
 282 impregnation was noticed according to the different recorded SEM images. An example for  
 283 the 2%KI and 5%TEDA AC is presented in the Figure 3 with increasing magnifications. More  
 284 particularly, the 65000 magnification (Figure 3 (a)) reveals the presence of macropores  
 285 presenting a typical geometry of the coconut shell based AC [21]. Other magnifications  
 286 (Figures 3 (b) and (c)) show the existence of some particles heterogeneously distributed on  
 287 the carbon surface. According to their EDX analysis, neither KI nor TEDA are identified.  
 288 However, other elements can be depicted (such as magnesium, sodium, chlorine, silicon...) which  
 289 are reported to be inherent to the raw material and the further fabrication steps [21].  
 290 Hence, KI and TEDA seem to be well dispersed within the internal porosity of the studied  
 291 materials.



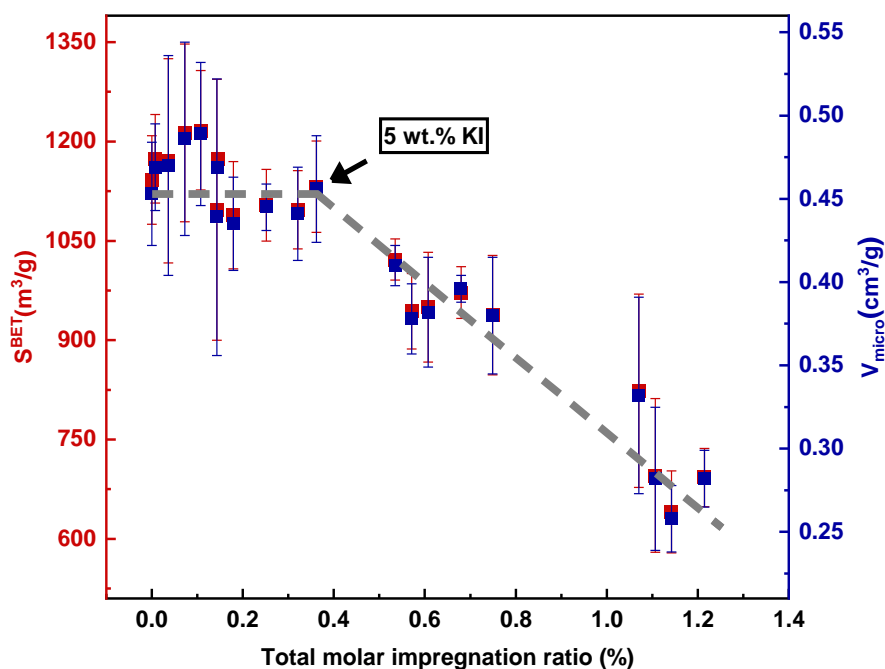
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293 *Figure 3 Selected SEM images of the 2%KI 5%TEDA AC: (a) magnification × 65000;(b) magnification ×*  
 294 *6500 and EDX analysis in the rectangular area; (c) magnification × 3000 and EDX analysis at six*  
 295 *locations*

296 3.1.3. Porous structure

297 The effect of impregnants presence within the internal porosity of the tested AC is now  
298 discussed in terms of porosimetric characteristics as deduced from N<sub>2</sub> adsorption/desorption  
299 isotherms at 77 K. The obtained N<sub>2</sub> adsorption isotherms exhibit a type I, typical of  
300 microporous materials [37] (Figure S8 in ESI). A very small hysteresis can be also depicted  
301 indicating the presence of narrow mesopores [38], whose contribution was found to be  
302 negligible (< 6 %). The associated porosimetric data ( $S_{BET}$  and  $V_{micro}$ ) are summarized in the  
303 Table 2. These parameters are expressed as average values from at least two measurements.  
304 The related uncertainties are calculated using the standard error of the mean expressed at  
305 coverage factor  $k=2$  (*i.e.* confidence level of 95%). The tested AC exhibit in general high  
306 specific surface area around 1000 m<sup>2</sup>/g, with an important contribution due to the  
307 microporous volume ( $V_{micro} / V_{pore} > 94\%$ ). The observed microporous characteristics of the  
308 tested AC sample are in agreement with the AC made from coconut shell in the nuclear field.  
309 This raw material is reported to be able to develop high microporosity for the AC [21][39].  
310 Besides, the mean pore diameter deduced from the HK method is around 0.5 nm, making it  
311 suitable for the CH<sub>3</sub>I trapping (kinetic diameter of 0.5-0.6 nm [40]) by physisorption  
312 phenomena.

313 The evolution of determined  $S_{BET}$  and  $V_{micro}$  as a function of the total molar impregnation ratio  
314 is presented in the Figure 4. Two distinct zones can be depicted as function with the  
315 impregnant content. For total molar impregnation lower than 0.4% (around 3 wt.% TEDA or  
316 5 wt.% KI), a quasi-similar microporosity can be stated. Nevertheless, a closer look for low  
317 impregnations contents (< 0.1 at. %) shows a slight increase of the  $S_{BET}$  and  $V_{micro}$  as a  
318 comparison with the not impregnated AC. This unexpected increase is also reported in the  
319 literature [41][42][43]. It can be postulated that a small amount of impregnation may create  
320 more heterogeneity on the surface, inducing a slight overestimation of the microporosity. For  
321 total molar impregnation ratio exceeding 0.4 %, a linear decreasing evolution can be observed  
322 (Figure 4). For example, the  $S_{BET}$  decreases from 1097 m<sup>2</sup>/g (3%TEDA, Table 2) until 715 m<sup>2</sup>/g  
323 (2% KI + 10% TEDA, Table 2). Indeed, the impregnation is known to induce partial blocking of  
324 the porosity on the AC surface (especially the micropores)[44][45]. The observed  
325 microporosity decrease may be assigned to the presence of KI and TEDA mainly within or in  
326 the micropores openings. This observation seems to be in line with the previous XRD and  
327 SEM/EDX analysis indicating the presence of such agents within the internal porosity without  
328 agglomeration on the external surface. Moreover, the linear decrease of the textural  
329 properties ( $S_{BET}$  and  $V_{micro}$ ) as function of the global molar amount of impregnants, seems to  
330 follow the same trend whatever the type of impregnation (TEDA, or co-impregnated). This  
331 observed evolution is governed mainly by the TEDA contribution due to its large excess on  
332 the detriment of KI (except for 2%KI+1%TEDA) for the studied co-impregnated AC. Such a  
333 linear decreasing was also observed in the literature after TEDA impregnation [21][46][47].  
334 This behavior was attributed to specific interaction between the nucleophile amine of TEDA  
335 and  $\pi$ -electrons of the graphene [47][48].



336

337

Figure 4 Evolution of  $S_{BET}$  and  $V_{micro}$  towards total impregnation ratio

338

339

Table 2 Textural properties of the investigated AC from  $N_2$  porosimetry

Impregnation type	Total molar impregnation (%)	$S_{BET}$ ( $m^2/g$ )	$V_{micro}$ ( $cm^3/g$ )	$d_{micro}$ (nm)	$V_{pore}$ ( $cm^3/g$ )
NI	0.000	$1142 \pm 67$	$0.453 \pm 0.031$	$0.473 \pm 0.003$	$0.472 \pm 0.032$
0.1% KI	0.007	$1174 \pm 67$	$0.469 \pm 0.026$	$0.474 \pm 0.001$	$0.492 \pm 0.030$
0.5% KI	0.036	$1171 \pm 154$	$0.470 \pm 0.066$	$0.480 \pm 0.009$	$0.496 \pm 0.075$
1% KI	0.072	$1213 \pm 134$	$0.486 \pm 0.058$	$0.482 \pm 0.017$	$0.513 \pm 0.061$
1% TEDA	0.107	$1217 \pm 90$	$0.489 \pm 0.043$	$0.485 \pm 0.016$	$0.513 \pm 0.051$
0.5%KI + 1%TEDA	0.143	$1097 \pm 197$	$0.439 \pm 0.083$	$0.478 \pm 0.018$	$0.458 \pm 0.086$
2% KI	0.145	$1174 \pm 0$	$0.469 \pm 0.002$	$0.479 \pm 0.003$	$0.493 \pm 0.003$
1%KI + 1%TEDA	0.179	$1089 \pm 81$	$0.435 \pm 0.028$	$0.479 \pm 0.003$	$0.454 \pm 0.029$
2% KI + 1% TEDA	0.252	$1104 \pm 54$	$0.445 \pm 0.014$	$0.487 \pm 0.009$	$0.472 \pm 0.011$
3% TEDA	0.321	$1097 \pm 59$	$0.441 \pm 0.028$	$0.488 \pm 0.006$	$0.464 \pm 0.029$
5% KI	0.361	$1132 \pm 69$	$0.456 \pm 0.032$	$0.484 \pm 0.014$	$0.483 \pm 0.034$
5% TEDA	0.535	$1022 \pm 31$	$0.410 \pm 0.012$	$0.492 \pm 0.002$	$0.433 \pm 0.009$
0.5%KI + 5%TEDA	0.571	$944 \pm 57$	$0.378 \pm 0.021$	$0.492 \pm 0.012$	$0.394 \pm 0.020$
1%KI + 5%TEDA	0.607	$950 \pm 83$	$0.382 \pm 0.033$	$0.492 \pm 0.004$	$0.403 \pm 0.035$
2%KI + 5%TEDA	0.679	$972 \pm 39$	$0.396 \pm 0.008$	$0.508 \pm 0.020$	$0.420 \pm 0.013$
7% TEDA	0.749	$938 \pm 90$	$0.380 \pm 0.035$	$0.501 \pm 0.008$	$0.401 \pm 0.035$
10% TEDA	1.070	$824 \pm 146$	$0.332 \pm 0.059$	$0.515 \pm 0.003$	$0.343 \pm 0.076$
0.5%KI + 10%TEDA	1.106	$696 \pm 116$	$0.282 \pm 0.043$	$0.518 \pm 0.024$	$0.298 \pm 0.014$

1%KI + 10%TEDA	1.142	641 ± 62	0.258 ± 0.020	0.519 ± 0.010	0.268 ± 0.002
2%KI + 10%TEDA	1.214	693 ± 44	0.282 ± 0.017	0.526 ± 0.003	0.293 ± 0.003

340

341 3.2  $\gamma$ -labelled CH<sub>3</sub>I retention performances by impregnated activated carbons at semi pilot  
342 scale

### 343 3.2.1 Performances of co-impregnated AC

344 The DF of the tested AC at RH = 40% and 90% were summarized in the Table 3 and shown in  
345 the Figure 5. The reported DF are expressed as average values from at least 3 replicates. The  
346 associated uncertainties are calculated using the standard error of the mean expressed at  
347 coverage factor k=2. The co-impregnated AC exhibit separate retention performances  
348 depending on the investigated condition. On the one hand, excellent filtering properties are  
349 highlighted at RH = 40% with DF order of magnitude ranging from 10<sup>4</sup> to 10<sup>5</sup> (Table 3).  
350 Therefore, the DF determined at this condition are found to be in agreement with the  
351 required performances for AC currently implemented in the French nuclear industry [49]. A  
352 closer look to the results displayed by co-impregnated materials indicates a different behavior  
353 depending on the impregnation nature. Indeed, a decrease of DF values can be reported as a  
354 function of KI content when fixing the TEDA quantity. For example, a reduction in  
355 performances is noticed from (91958 ± 19879) to (12575 ± 2046) when varying KI contents  
356 from 0.5 to 2 wt.% for a fixed TEDA quantity of 1 wt.% (Table 3). In contrast, progressive TEDA  
357 impregnation from 1 to 5 wt.% (whatever the fixed loading of KI, Figure 5 (a)) contributes to  
358 the enhancement of methyl iodide retention performances. For higher TEDA contents, a  
359 rather similar DF is reported. Thus, it seems that the best retention performances at this  
360 condition (T=20°C, RH = 40%) are obtained for the AC co-impregnated with 0.5 and 5 wt.% in  
361 KI and TEDA respectively with a DF value of (173182 ± 4347). This composition seems to agree  
362 well with the reported composition of nuclear grade activated carbons (%KI < 1 wt.%, TEDA  
363 content of 5 wt.% [49]). Nevertheless, an uncertainty is still remaining concerning the role  
364 played by KI in the removal of CH<sub>3</sub>I through the tested methodology. In fact, higher DF value  
365 was obtained without KI and for TEDA content of 5 wt.% (220228 ± 40203, Table 3).

366 On the other hand, a drastic decrease of DF for the studied co-impregnated AC is observed at  
367 this second set of conditions, with corresponding DF around 1000 times lower than those  
368 obtained at the previous conditions {T=20°C, RH = 40%}. This performances decrease is  
369 consistent with the adverse effect related to the water vapor adsorption by AC [45]. The DF  
370 of the tested co-impregnated AC are ranging from (31 ± 2.6) to (109 ± 25) in humid conditions.  
371 As a comparison, a DF of about 100 is required for nuclear grade AC at this conditions, *i.e.* in  
372 the presence of large excess of water vapor [49]. This order of magnitude is also reported in  
373 several studies in the literature [19][21]. More particularly, a greater beneficial effect due to  
374 TEDA impregnation as a comparison with KI can be observed. Indeed, TEDA contents of 5 or  
375 10 wt.% are required to guarantee satisfactory retention performances towards CH<sub>3</sub>I (DF  
376 about 100, for KI content lower than 2 wt.%, Table 3). However, a negligible contribution due  
377 to KI for CH<sub>3</sub>I removal can be reported considering these tests. An even detrimental effect is  
378 highlighted when increasing KI contents from 1 to 2 wt.% for fixed TEDA loadings of 5 or 10  
379 wt.% (curves in red and blue, Figure 5 (b)). Indeed, the correspondent DF are only about (53  
380 ± 14) and (60 ± 5.4) for (2%KI + 5%TEDA) AC and (2%KI + 10%TEDA) AC respectively (Table 3).

381 In addition, just a slight increase in DF performances was observed from ( $91 \pm 6.5$ ) to ( $106 \pm$   
 382  $20$ ) when increasing KI content from 0.5 to 1 wt.% and a for a fixed TEDA quantity of 5 wt.%  
 383 (Table 3). For the other co-impregnated AC, quasi-similar DF values are reported when  
 384 modifying the KI content (Table 3 and Figure 5 (b)). Considering the tested co-impregnated  
 385 AC, the best retention performances are corresponding to 1 wt.% KI and 5 wt.% TEDA. The  
 386 same impregnation combination is also reported for the commonly used nuclear grade AC [9].  
 387 This AC displays also a slightly higher performance than TEDA only impregnated AC ( $DF = 88$   
 388  $\pm 15$  for 5 wt.% TEDA, Table 3). Despite this enhancement, the contribution due to KI for  $CH_3I$   
 389 removal at this set of conditions is still negligible as a comparison with TEDA.

390 Overall, satisfying performances of the tested co-impregnated AC towards  $CH_3^{131}I$  trapping  
 391 are observed at different RH, with similar DF as the nuclear grade AC. Using this test  
 392 methodology, the KI contribution may be masked because of the simultaneous presence of  
 393 TEDA, presenting higher affinity for methyl iodide capture in moderately or highly humid  
 394 conditions [44][46].

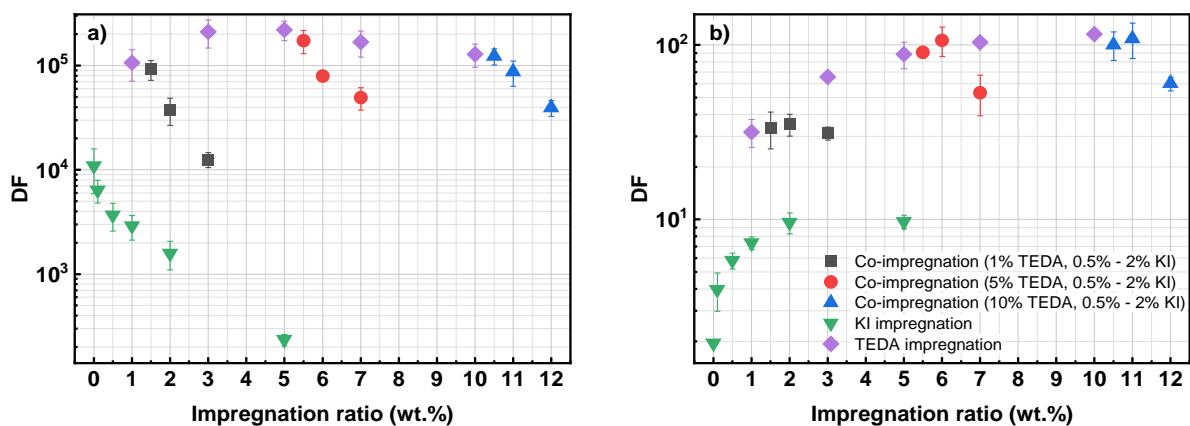
395 Therefore, the KI and TEDA impregnations will be separately investigated in the following  
 396 parts. This will allow also us to better assess the role played by AC parameters towards their  
 397 ability for radiotoxic  $CH_3I$  retention.

398

399 *Table 3 Summary of DF for different AC at RH = 40% and 90%: T = 20°C, linear velocity = 25 cm/s,*  
 400 *residence time = 0.2 s, initial  $^{131}I$  activity per AC = 62 KBq (RH = 90%) and 617 KBq (RH = 40%)*

KI-impregnated AC			TEDA-impregnated AC		
KI%	DF (RH = 40%)	DF (RH = 90%)	TEDA%	DF (RH = 40%)	DF (RH = 90%)
0	$10917 \pm 4981$	$1.96 \pm 0.08$	1	$106286 \pm 35606$	$32 \pm 5.8$
0.1	$6378 \pm 1557$	$3.96 \pm 0.98$	3	$210578 \pm 62883$	$66 \pm 2.4$
0.5	$3689 \pm 1097$	$5.82 \pm 0.61$	5	$220228 \pm 46423$	$88 \pm 15$
1	$2895 \pm 769$	$7.33 \pm 0.60$	7	$167621 \pm 46755$	$103 \pm 4.6$
2	$1587 \pm 486$	$9.60 \pm 1.32$	10	$128365 \pm 32189$	$115 \pm 5.9$
5	$236 \pm 29$	$9.71 \pm 0.87$			
Co-impregnated AC					
KI%	TEDA%	DF (RH = 40%)	DF (RH = 90%)		
0.5	1	$91958 \pm 19879$	$33 \pm 8.0$		
0.5	5	$173182 \pm 43473$	$91 \pm 6.5$		
0.5	10	$123006 \pm 21794$	$100 \pm 19$		
1	1	$37772 \pm 10984$	$35 \pm 5.0$		
1	5	$79281 \pm 7743$	$106 \pm 20$		
1	10	$86905 \pm 23751$	$109 \pm 25$		
2	1	$12575 \pm 2046$	$31 \pm 2.6$		
2	5	$49410 \pm 11971$	$53 \pm 14$		
2	10	$39445 \pm 6884$	$60 \pm 5.4$		

401



402

403 *Figure 5 DF evolution for the tested AC towards the capture of  $\gamma$ -labelled  $CH_3I$  ( $T = 20^\circ C$ , linear*  
 404 *velocity = 25 cm/s, residence time = 0.2 s): a) RH = 40%, initial  $^{131}I$  activity per AC = 617 KBq; b) RH =*  
 405 *90%, initial  $^{131}I$  activity per AC = 62 KBq*  
 406

### 407 3.2.2 Behavior of singly impregnated AC

#### 408 3.2.2.1. T = 20°C, RH = 40%

409 The specific behaviors of the impregnants are now discussed using singly impregnated AC. On  
 410 the one hand, the TEDA impregnated AC present the highest DF among all the investigated  
 411 adsorbents. Besides, similar DF evolution towards TEDA impregnation as the co-impregnated  
 412 materials is observed (Figure 5 (a), curve in purple). Indeed, an enhancement of methyl iodide  
 413 decontamination factors is observed from  $(106286 \pm 35606)$  to  $(220228 \pm 46423)$  for  
 414 increasing TEDA contents from 1 to 5 wt.% (Table 3). For higher TEDA contents, a slight DF  
 415 decrease is however observed until reaching a value of  $(128365 \pm 32189)$  when TEDA amount  
 416 is about 10 wt.% (Table 3).

417 On the other hand, the DF displayed by KI impregnated AC are found to be lower than that of  
 418 the co-impregnated and TEDA impregnated AC (Table 3). More particularly, a paradoxical  
 419 decrease of DF (Figure 5 (a), curve in green) is observed with the increase of KI content from  
 420  $(10917 \pm 4981)$  for non-impregnated AC to only  $(236 \pm 29)$  for 5 wt.% KI AC (Table 3). The  
 421 obtained DF magnitude is in agreement with the literature under similar conditions [8][49].  
 422 This decreasing feature is also found to be consistent with the behavior displayed by co-  
 423 impregnated AC when fixing the TEDA quantity, confirming the absence of any interaction  
 424 between KI and TEDA molecules as observed in the previous chapter. Same orders of  
 425 magnitude of DF for KI impregnated AC were also reported in the literature with RH ranging  
 426 from 30% to 40% ( $T = 20 - 30^\circ C$ ) [8][50]. However, no attempt was performed before to better  
 427 assess the role played by KI by comparing for instance with the non-impregnated AC.

#### 428 3.2.2.2. T = 20°C, RH = 90%

##### 429 TEDA impregnated AC

430 An increasing relationship can be evidenced between DF and TEDA content until 7 wt.%  
 431 (Figure 5 (b), curve in purple). More particularly, a DF increase from  $(32 \pm 5.8)$  to  $(103 \pm 4.6)$   
 432 can be highlighted for TEDA loadings of 1 wt.% and 7 wt.% respectively (Table 3). A less



433 pronounced increase in DF can be outlined for TEDA content of 10 wt.% (DF = (115 ± 5.9)).  
434 The observed DF are in the same order of magnitude of that reported in the literature under  
435 similar conditions for TEDA impregnated AC [8][20].

#### 436 KI impregnated AC

437 Similar to the TEDA impregnated AC, the DF are also observed to increase with KI  
438 impregnation at {T=20°C, RH = 90%}, but with a less important extent. When varying KI  
439 content from 0 to 5 wt%, a slight increase of DF from (1.96 ± 0.08) to (9.71 ± 0.87) can be  
440 highlighted (Table 3 and Figure 5 (b), curve in green), indicating the inability of KI-impregnated  
441 AC to retain methyl iodide at the considered conditions compared to TEDA impregnation.  
442 Besides, the DF for a KI content of 2 wt.% and 5 wt.% are found to be similar ((9.60 ± 1.32)  
443 and (9.71 ± 0.87) respectively, Table 3), indicating a potential saturation of the AC  
444 performances for KI impregnation under current conditions. The inability of KI-impregnated  
445 AC to retain  $\gamma$ -labelled CH<sub>3</sub>I seems to be consistent with the literature, where a magnitude of  
446 more than 600 of the DF decrease are outlined for RH ranging from 40 to 98% (residence time  
447 = 0.2 s) [8].

448 In general, singly impregnated AC present nearly the same DF evolutions as that of the co-  
449 impregnated AC. The absence of any interaction between TEDA and KI molecules can be  
450 therefore proposed, consistently with characterization results in the chapter II. An attempt to  
451 explain these observed trends will be presented in the next part.

#### 452 *3.2.2 Discussions about the role played by KI and TEDA*

##### 453 **3.2.2.1 T = 20°C, RH = 40%**

454 In order to explain the obtained DF evolutions (Figure 5), it is necessary to evaluate all the  
455 potential involved mechanisms. More precisely, three mechanisms are distinguished: the  
456 physisorption phenomena (controlled by the microporosity and the micropore filling of H<sub>2</sub>O),  
457 the chemisorption *via* TEDA and the isotopic exchange reaction due to KI impregnation. Under  
458 moderately humid conditions (T = 20°C, RH = 40%), the physisorption mechanism was  
459 generally reported to be dominant compared to chemisorption phenomena or the potential  
460 isotopic exchange [46]. Therefore, a specific attention is devoted to assess the influencing  
461 parameters towards physisorption in this first set of condition.

462 On the one hand, the microporosity of the KI and TEDA impregnated AC present different  
463 features depending on the impregnation ratio. According to the previous characterization of  
464 the porous structure, the decreasing evolution of the microporosity cannot be observed for  
465 low impregnation ratio (< 0.4 % in molar, Figure 4), which corresponds to the studied KI  
466 impregnated AC and 3% TEDA AC (Table 2). In contrast, a more significant reduction in the  
467 microporosity was obtained for other TEDA AC because of a higher impregnation molar ratio  
468 (up to 10 wt.% corresponding to molar fraction of 1.07 %). The extent of the reduction in  
469 microporosity can reach more particularly about 27 % for a TEDA content of 10 wt.% (Table  
470 2). To sum-up, the starting microporosity (*i.e.* before the pre-equilibration step) can be  
471 considered to be similar for KI impregnated AC but decreasing for TEDA impregnated AC  
472 especially after 3 wt.% in TEDA.



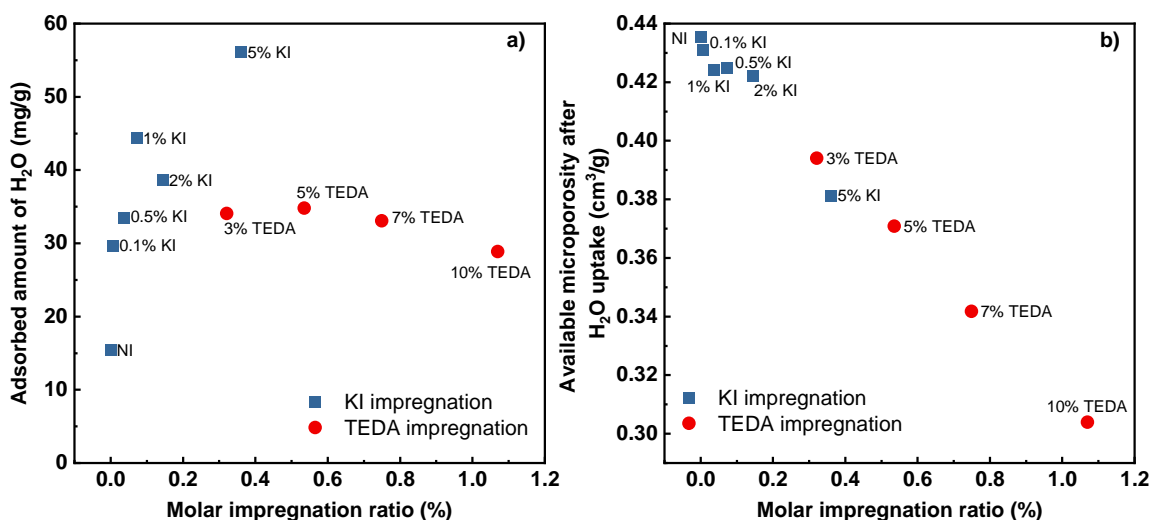
473 On the other hand, the available microporosity for CH<sub>3</sub>I trapping can be influenced by the pre-  
474 adsorbed H<sub>2</sub>O during the pre-equilibration step performed before retention test. Therefore,  
475 H<sub>2</sub>O adsorption isotherms were determined at T=25°C for the studied singly-impregnated AC.  
476 The obtained curves are presented in the supplementary (see Figures S9 and S10). The  
477 obtained isotherms are of type V according to IUPAC classifications [51]. In the low-pressure  
478 range, adsorbent/adsorbate interactions are weak due to the hydrophobic character of AC  
479 surface. At Higher relative humidity, the water uptake is mainly controlled by the AC  
480 microporosity due to the micropore filling phenomena [52][53].

481 For this first studied condition (T=20°C, RH = 40%), the attention was focused on the water  
482 uptake at 30 and 95% (T =25°C). The correspondent results for different AC are reported in  
483 the Table 4. Different behaviors can be highlighted depending on the investigated impregnant.  
484 On the one hand, a significant increase of the adsorbed amount of H<sub>2</sub>O was observed with KI  
485 impregnation (Figure 6 (a)). For example, an increase of water uptake from about 15 mg·g<sup>-1</sup>  
486 to about 56 mg·g<sup>-1</sup> was obtained when moving from non-impregnated AC to 5%KI AC (Table  
487 4). Indeed, KI molecules may play primary clustering or nucleation sites towards water vapor  
488 adsorption at low RH, allowing therefore to reduce the hydrophobic character of AC [44][53].  
489 On the other hand, the adsorbed amount of H<sub>2</sub>O using the same conditions {T=25°C, RH =  
490 30%} seems to be quasi-similar for the different tested TEDA AC (Figure 6 (a)), indicating a less  
491 effect due to nucleation for TEDA as a comparison with KI. Moreover, a lower water uptake  
492 was generally obtained for TEDA impregnated materials (a value ranging from 29 to 35 mg·g<sup>-1</sup>,  
493 Table 4).

494 *Table 4 Summary of the adsorbed amount of H<sub>2</sub>O at 25°C for different AC for DF at (T = 20°C, RH =*

Impregnation	$V_{micro}$ ( $\text{cm}^3/\text{g}$ )	Adsorbed $\text{H}_2\text{O}$ at RH = 30%* ( $\text{mg}/\text{g}$ )	Adsorbed $\text{H}_2\text{O}$ at RH = 95% ( $\text{mg}/\text{g}$ )	$\text{H}_2\text{O}$ filling fraction at RH = 30% (%)	Available $V_{micro}$ ( $\text{cm}^3/\text{g}$ )	DF
Non impregnated	0.453	15.4	397.4	4	0.435	10917
0.1 wt.% KI	0.469	29.7	364.8	8	0.431	6378
0.5 wt.% KI	0.470	33.4	343.1	10	0.424	3689
1 wt.% KI	0.486	44.4	353.9	13	0.425	2895
2 wt.% KI	0.469	38.6	385.4	10	0.422	1587
5 wt.% KI	0.456	56.1	342.4	16	0.381	236
3 wt.% TEDA	0.441	34.1	320.4	11	0.394	210578
5 wt.% TEDA	0.410	34.8	364.3	10	0.371	220228
7 wt.% TEDA	0.380	33.1	329.5	10	0.342	167621
10 wt.% TEDA	0.332	28.9	342.4	8	0.304	128365

496 \* The conditions of the adsorption isotherms of  $\text{H}_2\text{O}$  ( $T=25^\circ\text{C}$ ,  $\text{RH} = 30\%$ ) are equivalent to the conditions of the  
497 retention test ( $T=20^\circ\text{C}$ ,  $\text{RH} = 40\%$ ) in terms of absolute humidity.

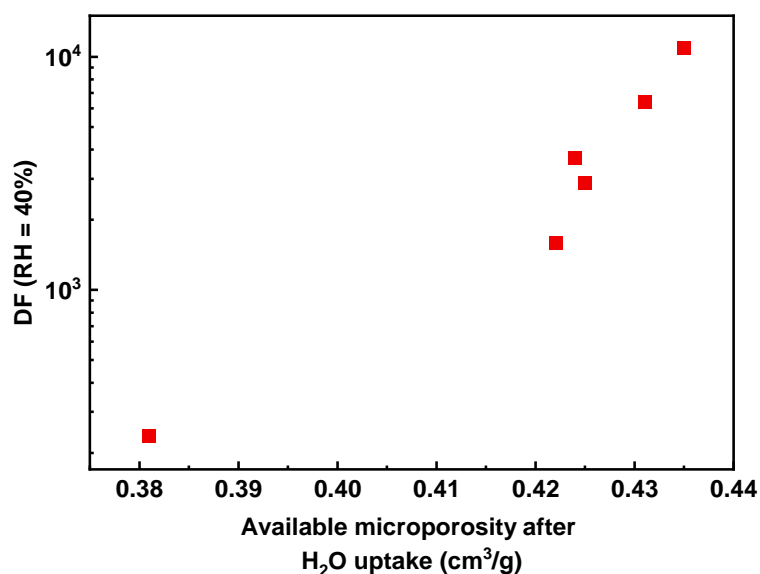


498  
499 *Figure 6 a) Pre-adsorbed  $\text{H}_2\text{O}$  versus the molar impregnation ratio at  $T = 25^\circ\text{C}$ ,  $\text{RH} = 30\%$ ; b) Available*  
500 *microporous volume after water uptake at  $T = 25^\circ\text{C}$ ,  $\text{RH} = 30\%$  versus molar impregnation ratio*

501 Regarding these considerations, it is necessary to determine the available microporous  
502 volume by multiplying the starting  $V_{micro}$  (as deduced from HK model) and the fraction of  
503 residual pores ( $1-\text{H}_2\text{O}$  filling fraction). As depicted in the Figure 6 (b), the available  
504 microporosity after water uptake decreases for both KI and TEDA impregnation. This  
505 reduction is attributed to different reasons depending on the molecule nature. For KI, this  
506 decrease is related to the enhancement of adsorbed  $\text{H}_2\text{O}$  at low RH after KI progressive  
507 loading. For TEDA, this trend is assigned to the decrease of microporosity because of the  
508 presence of TEDA within or in the openings of AC pores (Table 2). Therefore, the contribution  
509 of physisorption in all cases is expected to decrease after KI and TEDA impregnation.

510 For TEDA impregnated AC, the contribution of the physisorption is proved to be decreased.  
511 In the meantime, the contribution of the chemisorption is expected to increase with TEDA  
512 content. More precisely, the reactivity of TEDA at such moderately humid conditions { $T = 20^{\circ}\text{C}$ ,  
513  $\text{RH} = 40\%$ } is reported to be dominated by an alkylation mechanism based on  $\text{CH}_3\text{I}$  dissociation  
514 followed by the formation of stable ammonium [48]. Hence, The DF evolution for TEDA  
515 impregnation at  $\text{RH} = 40\%$  can be considered as a compromise between these two opposite  
516 mechanisms. According to the obtained results, the optimum TEDA impregnation  
517 corresponding to these two mechanisms seems to be 5 wt.%, where the accessible  
518 microporosity is decreased only by 15% against 23% with 7wt.% of TEDA, for instance.

519 It is reasonable to think that the DF evolution for KI impregnated AC at the studied conditions  
520 should be the same as displayed by TEDA impregnated AC. Indeed, there are also two  
521 mechanisms that work oppositely with KI content: the physisorption and the isotopic  
522 exchange led by the KI. However, it seems that the DF evolution for KI AC at { $T = 20^{\circ}\text{C}$ ,  $\text{RH} =$   
523  $40\%$ } is dominated by physisorption and more particularly by the pre-adsorbed amount of  
524 water vapor during the equilibration step. This unusual observation is evidenced in the Figure  
525 7 which shows the increasing evolution of DF versus the available microporosity for  $\text{CH}_3^{131}\text{I}$   
526 retention. Finally, it can be proposed that the trapping performance of the  $\gamma$ -labelled  $\text{CH}_3\text{I}$  for  
527 KI impregnated AC at moderately humid conditions is only dominated by the physisorption  
528 influenced itself by the water pre-adsorption. Therefore, this trend may indicate in other  
529 words the absence of the isotopic exchange under the first set of conditions.



530  
531 *Figure 7 DF evolution (logarithmic scale) versus the available microporosity for KI impregnated AC*  
532 *(RH = 40%)*

533 The role played by TEDA and KI towards the capture of  $\text{CH}_3\text{I}$  under more humid conditions will  
534 be discussed in the next section.

### 535 3.2.2.2 $T = 20^{\circ}\text{C}$ , $\text{RH} = 90\%$

536 In these conditions, the significant changes in DF evolution compared to  $\text{RH} = 40\%$  indicates  
537 the change of each trapping mechanism contribution (physisorption, chemisorption and the  
538 isotopic exchange). Using the same strategy, the physisorption contribution can be firstly

539 investigated using the adsorption isotherms of H<sub>2</sub>O (T=25°C, Figures S9 et S10). As  
540 summarized in the Table 5, all the tested AC present significant amount of pre-adsorbed H<sub>2</sub>O  
541 regardless the impregnation type (adsorbed amount higher than 300 mg·g<sup>-1</sup>). The water  
542 molecules are reported to be firstly adsorbed on the AC surface due to the strong  
543 chemisorption of the water molecules with functional groups as mentioned in the previous  
544 section [54][55]. Then, water clusters are progressively formed on the AC surface through the  
545 formation of hydrogen bonds [54][55], corresponding to the micropore filling of the water  
546 molecules. The increase of the pre-adsorbed amount of H<sub>2</sub>O compared to RH = 40% induces  
547 a huge increase of the micropore filling fraction to about 90% (Table 5), indicating a strong  
548 competitive adsorption between CH<sub>3</sub>I and H<sub>2</sub>O. Consequently, the deduced available  
549 microporous volume for the impregnated AC is found to be less than 0.08 cm<sup>3</sup>·g<sup>-1</sup> (Figure 8),  
550 which is almost negligible compared to the first set of conditions. To sum up, it can be  
551 concluded that the contribution of the physisorption is significantly reduced at RH = 90% since  
552 the accessibility to the active sites for physisorption is largely hindered by H<sub>2</sub>O [10]. The  
553 significant reduction of the physisorption for all the tested AC under current conditions  
554 explains the drastic diminution of DF compared to RH = 40%.

555 Apart from the significant decrease of DF at RH = 90% compared to RH = 40%, the DF were  
556 found to increase with both TEDA and KI impregnations (Figure 5), which is clearly assigned  
557 to the chemisorption and the isotopic exchange respectively, since there is no other  
558 mechanism responsible for such increase of the AC performance in these conditions. Taking  
559 into account the low available microporosity that still remains at RH = 90%, it can also be  
560 proposed that as a preliminary step for the adsorption phenomena [15][56], the physisorption  
561 is no longer dominant for the CH<sub>3</sub>I removal under current conditions. Nevertheless, the extent  
562 of DF increase due to the KI impregnation is less important as a comparison with TEDA, which  
563 is due to its high reactivity. Unlike the CH<sub>3</sub>I dissociation mechanism for TEDA at RH = 40%, a  
564 protonation mechanism between CH<sub>3</sub>I, H<sub>2</sub>O and TEDA results to the formation of a molecular  
565 complex of TEDA/CH<sub>3</sub>I under humid conditions, enhancing the chemical interaction of TEDA  
566 with CH<sub>3</sub>I [46][47]. Besides, the saturation of the DF increase between 2 wt.% and 5 wt.% in  
567 KI may be assigned to the increase of the diffusion resistance by pre-adsorbed H<sub>2</sub>O and  
568 deposited KI [46].

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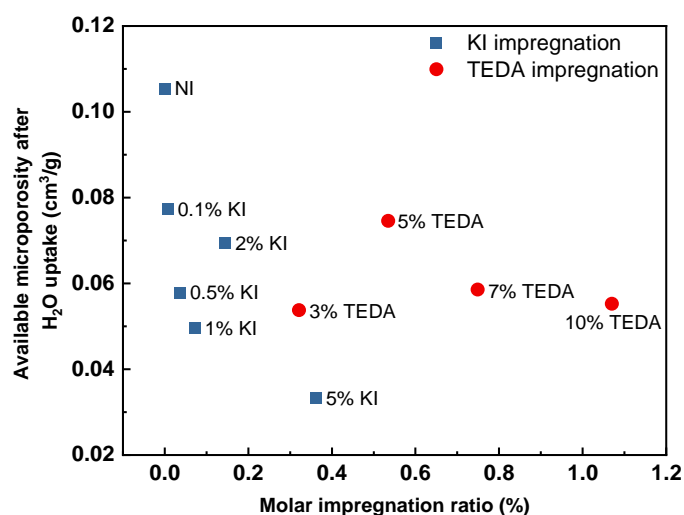
574

575 *Table 5 Summary of the adsorbed amount of H<sub>2</sub>O at 25°C for different AC for DF at (T = 20°C, RH =*

Impregnation	$V_{micro}$ ( $\text{cm}^3/\text{g}$ )	Adsorbed $\text{H}_2\text{O}$ at RH = 70%* ( $\text{mg}/\text{g}$ )	Adsorbed $\text{H}_2\text{O}$ at RH = 95% ( $\text{mg}/\text{g}$ )	$\text{H}_2\text{O}$ filling fraction at RH = 70% (%)	Available $V_{micro}$ ( $\text{cm}^3/\text{g}$ )	DF
Non impregnated	0.453	305.0	397.4	77	0.11	2.0
0.1 wt.% KI	0.469	304.7	364.8	84	0.08	4.0
0.5 wt.% KI	0.470	300.9	343.1	88	0.06	5.8
1 wt.% KI	0.486	317.8	353.9	90	0.05	7.3
2 wt.% KI	0.469	328.4	385.4	85	0.07	9.6
5 wt.% KI	0.456	317.4	342.4	93	0.03	9.7
3 wt.% TEDA	0.441	281.3	320.4	88	0.05	66
5 wt.% TEDA	0.410	298.0	364.3	82	0.07	88
7 wt.% TEDA	0.380	278.7	329.5	85	0.06	103
10 wt.% TEDA	0.332	285.4	342.4	83	0.06	115

577 \* The conditions of the adsorption isotherms of  $\text{H}_2\text{O}$  ( $T = 25^\circ\text{C}$ ,  $\text{RH} = 70\%$ ) are equivalent to the conditions of the  
578 retention test ( $T = 20^\circ\text{C}$ ,  $\text{RH} = 90\%$ ) in terms of absolute humidity.

579



580

581 *Figure 8 Available microporous volume after water uptake at  $T = 25^\circ\text{C}$ ,  $\text{RH} = 70\%$  versus molar*  
582 *impregnation ratio*

583 It can be noticed that the isotopic exchange *via* KI seems to be observed only under humid  
584 conditions. Similar tendencies were reported in the literature using the breakthrough curves  
585 measurements for 5%KI<sub>3</sub> impregnated AC (equal amount of KI and I<sub>2</sub>) [57]. Despite the  
586 different experimental conditions (4625 Bq/m<sup>3</sup> of CH<sub>3</sub><sup>131</sup>I,  $\text{RH} = 86\%$ ), it is observed that the  
587 penetration of radioactive CH<sub>3</sub>I is less than that of stable CH<sub>3</sub>I, which justifies the presence of  
588 the isotopic exchange during the fix-bed adsorption experiment [57]. More particularly, the  
589 effect of the isotopic exchange becomes more significant during the breakthrough phase, and  
590 no specific effect was observed at the beginning of the breakthrough curve (retention phase).

591 Hence, it is assumed that the effect of the isotopic exchange can only be observed when the  
592 KI impregnated AC are in the breakthrough phase. At RH = 40% in the current study, the  
593 conversion of DF to trapping efficiency indicates that the tested KI impregnated AC are still in  
594 the retention phase. However, the low value of DF at RH = 90% indicates the breakthrough of  
595 the AC. Hence, the effect of the isotopic exchange was only observed at RH = 90%.  
596 Nevertheless, a slight contribution from this mechanism can be highlighted using the  
597 normalized protocol test.

598

#### 599 4. Conclusion

600 In this paper, the behaviors of KI and/or TEDA impregnated AC towards the capture of  $\text{CH}_3^{131}\text{I}$   
601 are investigated at different RH. First, a characterization of chemical, textural and structural  
602 properties of the investigated AC was performed. The presence of KI or TEDA has been  
603 evidenced for all the tested AC, but a slight and linear difference was observed between the  
604 theoretical and the experimental content of such molecules. SEM/EDX and XRD  
605 characterizations for some AC have shown that these entities are well dispersed within the  
606 internal porosity without clusters formation on the external surface of the tested materials.  
607 The absence of any interaction between KI and TEDA is further confirmed by the DF evolution  
608 for the co-impregnated AC, as they share similar tendencies with the singly impregnated AC.  
609 The tested AC present similar carbon and oxygen speciation as deduced from XPS, confirming  
610 the similar surface characteristics of these carbonaceous materials derived from the coconut  
611 shells produced in the same batch. Insights about the nitrogen and iodine speciation  
612 regarding the TEDA and KI impregnation, were also presented. The investigated AC are found  
613 to be essentially microporous (> 94 %), in agreement with AC produced from coconut shells.  
614 In addition, both the  $S_{\text{BET}}$  and  $V_{\text{micro}}$  decrease with the total impregnation due to the partial  
615 blocking of the AC porosity (especially the micropores) induced by the presence of TEDA and  
616 KI species within the internal porosity. A such micropore blockage becomes more significant  
617 for total molar impregnation ratio exceeding 0.4% (3 wt. % TEDA and 5 wt.% KI).

618 The investigation of  $\text{CH}_3^{131}\text{I}$  adsorption behavior at RH = 40% and 90% revealed different  
619 features. At RH = 40%, all the tested AC exhibit good performance of  $\text{CH}_3^{131}\text{I}$  trapping, with a  
620 DF up to  $2.2 \times 10^5$ . More particularly, it is observed that the DF decreases paradoxically with KI  
621 impregnation where the isotopic exchange was found to be absent. This decrease is due to  
622 the increased amount of the adsorbed  $\text{H}_2\text{O}$  results from the nucleation effect of KI  
623 impregnation, leading to the diminution of the available microporosity for physisorption. On  
624 the contrary, the DF evolution for TEDA at RH = 40% is found to be a compromise between  
625 the diminution of the available microporosity and the increase of the chemisorption *via* TEDA,  
626 with an optimal TEDA impregnation at 5 wt.%. At RH = 90%, a drastic decrease of DF is  
627 observed for all the AC, with DF about 1000 times lower than that at RH = 40%. The optimal  
628 impregnation at RH = 90% is obtained with 1% KI and 5% TEDA, in agreement with the  
629 composition of the nuclear grade activated carbons. The increase of the DF with TEDA and KI  
630 at RH = 90% was found to be directly related to the chemisorption and the isotopic exchange  
631 respectively. The extent of the DF increase when using TEDA was found to be more important  
632 as a comparison with KI, thanks to its higher reactivity  $\text{CH}_3\text{I}$  under different conditions.

633 Furthermore, the effect of the isotopic exchange led by KI was slightly and only observed  
634 through adsorption experiments at RH = 90%, by assuming its occurrence under breakthrough  
635 phase in agreement with literature studies.

636 In these works, different parameters of the AC towards their ability for radiotoxic CH<sub>3</sub>I  
637 retention under semi pilot scale have been evaluated. Additional investigation of the AC  
638 performances will be further conducted under lab scale. The main objective is to elucidate  
639 the importance of the isotopic exchange by measuring the breakthrough curves of both  
640 CH<sub>3</sub><sup>131</sup>I and CH<sub>3</sub><sup>127</sup>I for KI impregnated AC. The roles of AC parameters towards the isotopic  
641 exchange will also be evaluated.

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