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# Retention of radioactive methyl iodide in the context of nuclear industry: on the quantification of isotopic exchange contribution inside activated carbons

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**Abstract:**
In this paper, the behavior of TEDA and KI impregnated activated carbons (AC) towards the capture of methyl iodide ($CH_3I$) is investigated using complementary methodologies. On the one hand, radioactive $CH_3I$ decontamination factors (DF) were determined at different water vapor contents for various commercial activated carbons. A combination between the retention performances and the physico-chemical properties is performed to gain insights about the AC influencing parameters on γ-labelled $CH_3I$ capture. On the other hand, new experimental methodologies are developed in order to measure both stable and γ-labelled $CH_3I$ breakthrough curves (BTC) for KI or TEDA impregnated AC {T = 20 – 30 °C, dry conditions}. These works improve the knowledge about the role played by KI and TEDA. Indeed, TEDA is found to enhance $CH_3I$ retention especially under humid conditions and, for the first time, the KI contribution is isolated and quantified: the KI action towards $^{131}I$ is highlighted after the breakthrough phase through an isotopic redistribution mechanism.

## 1 INTRODUCTION

The efficient capture of volatile radioactive iodine species (namely $I_2$ and $CH_3I$) potentially released from nuclear facilities remains a very major issue to improve nuclear safety. The specific interest on iodine species stands from their high mobility and their specific affinity for thyroid gland [1,2]. Activated carbons (AC) are employed within the ventilation circuits of nuclear facilities to prevent from volatile iodine dissemination into the environment [3]. These adsorbents display a well-developed microporosity ($d_{pore}$ < 2 nm) promoting $CH_3I$ physisorption (kinetic diameter of 0.5-0.6 nm [4]). In the nuclear field, these adsorbents are co-impregnated with triethylenediamine (TEDA, content ≤ 5 wt.%) and potassium iodide (KI, content about 1 wt.%) in order to ensure a specific and stable storage towards traces of $CH_3I$ as comparison with contaminants present in large excess (namely water vapor) [3]. In addition to the physisorption, different mechanisms are therefore involved for methyl iodide retention by AC. On the one hand, TEDA reacts with $CH_3I$ through chemisorption whose mechanism is reported to be dependent on the relative humidity [5,6]. On the other hand, KI impregnation is associated to an isotopic exchange reaction [7]. Despite the massive and historic use of these adsorbents in the nuclear field, a poor knowledge exists about the most influencing AC parameters towards $CH_3I$ retention efficiency. In addition, uncertainties are persisting about the isotopic exchange mechanism but also on its contribution for total $CH_3I$ uptake under different experimental conditions. Indeed, the postulated retention mechanism due to KI is rarely studied in the litterature as a comparison with chemisorption phenomena due to TEDA [5,6]. In the present research work, we aim to bridge these gaps by combining several complex test benchs towards $CH_3I$ retention with physico-chemical characterizations of the tested adsorbents. A first part will be dedicated to establish structure-activity relationships between AC intrinsic properties and their retention performances in terms of decontamination factors (DF). Then, a specific attention will be devoted to KI-impregnated AC through breakthrough curves measurements towards both stable and radioactive $CH_3I$.

## 2 MATERIALS AND METHODS

### 2.1 Presentation of the tested adsorbents

Different commercial AC impregnated separately with KI or TEDA are selected for the present study. The theoretical contents in impregnants are reported in Table 2 (see section 3.1.).

### 2.2 Physico-chemical characterizations

$N_2$ porosimetry at 77 K completed by $H_2O$ sorption isotherms at 25°C are performed in order to assess the AC available microporosity. Moreover, chemical analyses at different scales are conducted in order to gain insights on {KI, TEDA} quantities and their dispersions within the porous network.

### 2.3 Experimental setups

Robust and complementary methologies are developped in order to assess the retention performances towards $CH_3I$. Decontamination Factors (DF) of radioactive $CH_3I$ are determined through standardized protocols [8,9] in order to assess the role played by KI and TEDA as a function of relative humidity. Moreover, BreakThrough Curves (BTC) are measured towards both stable and radioactive $CH_3I$ through two separate setups to study the temporal evolution of isotopic exchange reaction. Table 1 summarizes the main characteristics and principles of each tested experimental configuration.

*Table 1: Main characteristics of the investigated experimental configurations.*

| | **Dynamic adsorption experiments towards $CH_3{}^{127}I$** | **Dynamic adsorption experiments towards $CH_3{}^{127+131}I$ (γ-labelled $CH_3I$)** | |
|---|---|---|---|
| **Objective** | BTC curves | DF determination | BTC curves |
| **AC conditioning** | Grain size selection between 1 and 1.4 mm<br>*Ex-situ* pretreatment at 100°C overnight<br>Mass of about 10 g | Grain size between 2 and 3 mm<br>Pre-equilibration under flowing water vapor for at least 16 hours (T = 20°C, RH = 40% or 90%)<br>Mass of 35-40 g | Grain size selection between 1 and 1.4 mm<br>*Ex-situ* pretreatment at 100°C overnight<br>Mass of about 10 g |
| **Principle** | Continuous injection of $CH_3I$ from a certified bottle up to the AC saturation | Pulse injection of radioactive $CH_3I$ (30 min) followed by an elution under air (1h) | Continuous injection of radioactive $CH_3I$ (certified bottle + permeation tube) up to the AC saturation |
| **Flow conditions** | C = 10 ppmv,<br>T = 30°C, RH = 0%<br>v = 25 cm/s, residence time = 0.2 s | C = 0.6 ppmv, $^{131}I$ activity : 62 kBq (RH=90%) or 617 kBq (RH=40%)<br>T = 20°C, RH = 40% or 90%<br>v = 25 cm/s, residence time = 0.2 s | C = 10 ppmv,$^{131}I$ flowrate = 150 Bq/min<br>T = 20°C, RH = 0%<br>v = 25 cm/s, residence time = 0.2 s |
| **Detection method** | Online measurement by Gas Chromatography coupled with a Pulsed Discharge Electron Capture Detector (PD-ECD) | *Ex-situ* measurement by γ-spectrometry at the end of test | Continuous sampling and *ex-situ* measurement by γ-spectrometry up to the AC saturation |

## 3 RESULTS AND DISCUSSIONS

### 3.1 Main properties of the investigated adsorbents

According to XRD and SEM/EDX analyses, TEDA and KI molecules were found during our previous study [10] to be well dispersed within the internal porosity without clusters formation on the external surface. The presence of these species may alter the accessible microporosity to $CH_3I$ physisorption. Hence, a peculiar attention is devoted to the textural properties of the tested materials as deduced mainly from $N_2$ porosimetry at 77 K (Table 2). Generally, high specific surface areas (around 1000 $m^2/g$) are obtained, with an important contribution due to the micropores (> 94%), in line with developed AC for the nuclear field [11]. A closer look to the data reported in Table 2 indicates a different behavior depending on the impregnation

nature. KI/AC display a rather similar microporosity due to their low KI content (< 0.4 % in molar, Table 2). However, a decreasing evolution can be noticed for $S_{BET}$ and $V_{micro}$ for TEDA/AC, especially after 3 wt.% in TEDA (Table 2). This partial micropore blocking may be assigned to the presence of TEDA entities within or in the micropores openings, consistently with XRD and SEM/EDX analyses [10]. $N_2$ porosimetry analyses are completed by $H_2O$ adsorption isotherms at 25°C in order to better assess the influence of water vapor on the starting adsorbents before exposure to $CH_3I$ (DF measurements, section 3.2). At low RH, the water uptake is found to increase with KI content, due to the nucleation effect [10,12]. In contrast, TEDA impregnated AC are less sensitive to water molecules as a comparison with KI/AC [10]. At high RH, the water uptake is rather dependent on the AC microporosity in agreement with former works [12].

*Table 2: Textural properties of the tested adsorbents as deduced by $N_2$ porosimetry at 77 K.*

| AC designation | Molar ratio (%) | $S_{BET}$ ($m^2/g$) | $V_{micro}$ ($cm^3/g$) | AC designation | Molar ratio (%) | $S_{BET}$ ($m^2/g$) | $V_{micro}$ ($cm^3/g$) |
|---|---|---|---|---|---|---|---|
| Non-impregnated (NI) | 0 | 1142 ± 67 | 0.453 ± 0.031 | Non-impregnated (NI) | 0 | 1142 ± 67 | 0.453 ± 0.031 |
| **0.1%***KI/AC | 0.007 | 1174 ± 67 | 0.469 ± 0.026 | **1%**TEDA/AC | 0.107 | 1217 ± 90 | 0.489 ± 0.043 |
| **0.5%**KI/AC | 0.036 | 1171 ± 154 | 0.470 ± 0.066 | **3%**TEDA/AC | 0.321 | 1097 ± 59 | 0.441 ± 0.028 |
| **1%**KI/AC | 0.072 | 1213 ± 134 | 0.486 ± 0.058 | **5%**TEDA/AC | 0.535 | 1022 ± 31 | 0.410 ± 0.012 |
| **2%**KI/AC | 0.145 | 1174 ± 0 | 0.469 ± 0.002 | **7%**TEDA/AC | 0.749 | 938 ± 90 | 0.380 ± 0.035 |
| **5%**KI/AC | 0.361 | 1132 ± 69 | 0.456 ± 0.032 | **10%**TEDA/AC | 1.070 | 824 ± 146 | 0.332 ± 0.059 |

* The reported percentage is related to the theoretical massic content for KI or TEDA.

### 3.2 γ-labelled $CH_3I$ DF measurements

The obtained performances for TEDA and KI impregnated AC as a function of relative humidity (T = 20°C) according to the reported methodology in Table 1 are presented in Figure 1.

*3.2.1 T = 20°C, RH = 40%*

Different features can be highlighted as a function of the molecule nature. For TEDA/AC, an enhancement of DF is observed first from (106 286 ± 35 606) to (220 228 ± 46 423) for increasing TEDA contents from 1 to 5 wt.% (Figure 1 (A)), then a slight decrease in DF can be noticed when using higher TEDA contents (Figure 1 (A)). This behavior is explained by the occurrence of two opposite mechanisms for $CH_3I$ trapping : physisorption and chemisorption. The first one is dependent on the available microporosity which decreases after TEDA incorporation (Table 2). The second mechanism is driven by an alkylation mechanism in moderately humid conditions [6]. From DF evolution as a function of the available microporosity (Figure 1 (A)), the compromise between these two mechanisms seems to be a TEDA content of 5 wt.%.

However, lower retention performances are outlined for KI/AC. A paradoxical decrease of DF is even observed as a function of KI content from (10 917 ± 4 981) for non-impregnated AC to (236 ± 29) for 5 wt.% KI AC (Figure 1 (A)). It seems that the behavior of KI/AC at this set of condition is dominated by physisorption rather than isotopic exchange as evidenced from the increasing evolution of DF versus the available microporosity for these adsorbents (Figure 1 (A)). The absence of compromise between KI content and accessible microporosity, as observed with TEDA/AC, may indicate in other words the absence of isotopic exchange under the studied conditions {T=20°C, RH=40%}.

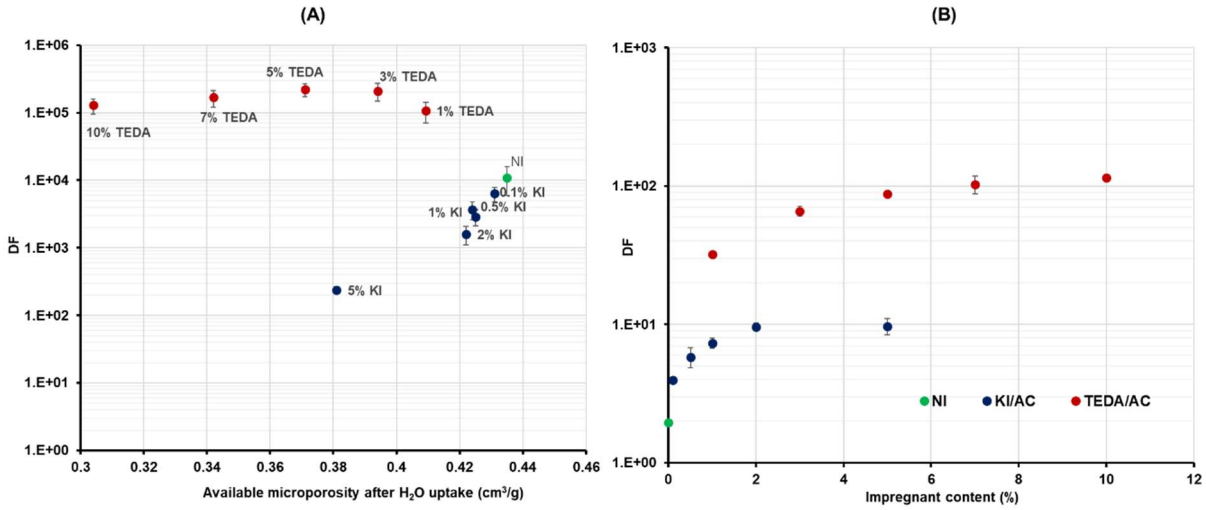


*Figure 1: (A) Evolution of $CH_3I$ retention performances for TEDA and KI impregnated AC as a function of the available microporosity calculated from $N_2$ porosimetry and $H_2O$ adsorption isotherms at {T = 20°C, RH = 40%}. (B) Evolution of $CH_3I$ retention performances as a function of the impregnant content at {T = 20°C, RH = 90%}.*

*3.2.2 T = 20°C, RH = 90%*

At the second set of conditions, a drastic decrease of DF is observed for AC. This detrimental effect can be overcome especially thanks to TEDA impregnation. Indeed, a DF increase from (32 ± 5.8) to (103 ± 4.6) can be noticed for TEDA loadings of 1 wt.% and 7 wt.% respectively, followed by a less pronounced enhancement at TEDA content of 10 wt.% (DF = (115 ± 5.9), Figure 1 (B)). Considering the same conditions, a beneficial role due to KI impregnation can also be highlighted with a slight increase of DF from (1.96 ± 0.08) to (9.71 ± 0.87) (Figure 1 (B)).

To sum-up, the physisorption contribution is significantly reduced at RH = 90%. The DF increase with both TEDA and KI impregnations is therefore assigned to chemisorption and isotopic exchange respectively. Nevertheless, the extent of DF increase due to KI impregnation is less important as a comparison with TEDA, owing to its high reactivity through a protonation mechanism as proposed in the litrerature [6].

*3.2.3 Discussions about isotopic exchange occurence*

Using the normalized procedures for DF determination, the isotopic exchange reaction *via* KI seems to be observed only under humid conditions. According to a previous work [13], the isotopic exchange effect was only evidenced during the breakthrough phase. At RH=40%, the KI/AC are still in the retention phase due to high obtained DF values. However, the low performances at RH=90% indicate the AC beakthrough, which explains the observation of this reaction only at humid conditions. Nevertheless, a slight contribution from this mechanism can be highlighted using the normalized protocol as a comparison with TEDA. The next section will be devoted to describe the results obtained with KI using BTC for both stable and radioactive $CH_3I$ in order to better assess this reactivity.

### 3.3 Breakthrough curves towards stable and γ-labelled $CH_3I$

The obtained $CH_3I$ sorption profiles for KI/AC are presented in Figure 2. A comparison with TEDA/AC for the capture of stable $CH_3I$ is also provided in Figure 2 (A).

*3.3.1 Stable $CH_3I$ breakthrough curves*

First, the investigation of KI/AC behavior towards stable $CH_3I$ (T=30°C, HR=0%) indicates as expected the occurence of only physisorption, which is dependent on the microporosity accessibility by the adsorbate [14]. Indeed, similar performances are observed for KI/AC (retention phase duration of about 5 hours, Figure 2 (A)) in agreement with their similar microporosity (Table 2). A significant improvement of stable $CH_3I$ retention performances can be outlined after TEDA incorporation (5 wt.%), with a retention phase duration of 12 hours (Figure 2 (A)). This enhancement is assigned to the occurence of chemisorption phenomena resulting in a strong storage of $CH_3I$ molecules in agreement with our previous batch reactor study [14].

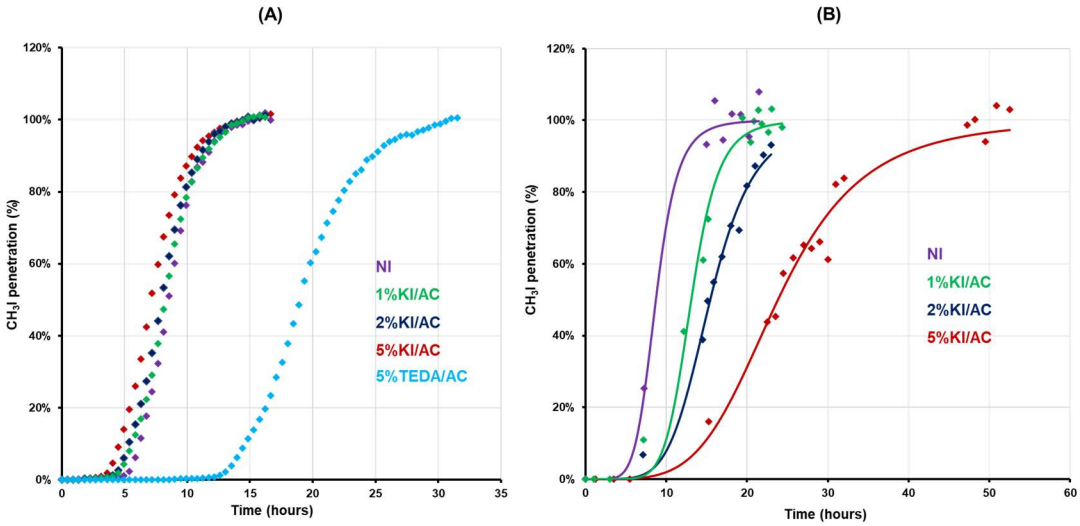


*Figure 2: (A) Influence of KI and TEDA impregnations on stable $CH_3I$ BTC at {T = 30°C, RH = 0%}. (B) Radioactive $CH_3I$ BTC over KI-impregnated AC at {T = 20°C, RH = 0%}. The fitted curves according to an improved Thomas model are presented in lines for γ-$CH_3I$.*

*3.3.2 Radioactive $CH_3I$ breakthrough curves*

Using the methodology summarized in section 2.3. (Table 1), the obtained BTC for KI/AC towards γ-$CH_3I$ are presented in Figure 2 (B), with the corresponding fitted curves of the improved Thomas model [15]. Firstly, no significant change in the retention phase duration (around 5 h, Figure 2 (B)) is observed for γ-labelled $CH_3I$ adsorption as a comparison with stable $CH_3I$ (Figure 2 (A)). Considering the breakthrough phase, a progressive improvement of AC performances towards γ-$CH_3I$ can be noticed, with an enchancement of saturation time from 14 h (non impregnated AC) to about 46 h for 5%KI/AC (Figure 2 (B)). This behavior is due to the isotopic exchange reaction between $^{127}I$ (from KI) and $^{131}I$ (from γ-labelled $CH_3I$) [7,13], owing to the similar peformances towards stable and γ-$CH_3I$ for non-impregnated AC and TEDA/AC. This isotopic redistribution seems to be more significant during the breakthrough phase, in line with assumptions presented previously (section 3.2.3).

*3.3.3 Quantification of the relative contribution due to isotopic exchange*

For the first time, we are able to isolate the isotopic exchange phenomena. Two preliminary attempts to quantify this reaction are also performed. On the one hand, the relative contribution due to this mechanism can be expressed in terms of the time delay to reach the AC total saturation (penetration of 100%) towards γ-$CH_3I$ as a comparison with stable $CH_3I$. An increasing relative contribution is therefore calculated from 39% (1%KI/AC) to 70% (5%KI/AC). On the other hand, a more generalized expression of this contribution as a function of γ-$CH_3I$ penetration has been established for the first time in order to better evaluate the importance of this reaction in the AC working range within nuclear facilities (maximal penetrations of about 1-10%). More precisely, the extrapolation to a penetration of 1% through the use of an improved Thomas model for both stable and radioactive $CH_3I$ sorption profiles, has allowed to estimate a relative contribution of about 19% for 5%KI/AC. These first calculations highlight the importance of the isotopic exchange reaction from $CH_3I$ low penetrations.

## 4 SUMMARY

In this paper, we have presented recent research and development works about $CH_3I$ adsorption by TEDA or KI impregnated AC through complementary methodologies (DF measurements and BTC for both stable and radioactive $CH_3I$). For the first time, the contribution due to KI, still rarely studied in the literature, is isolated from the other dominant mechanisms (physisorption and chemisorption). A first quantification of the reactivity due to KI is also provided. This attempt highlights the important effect of isotopic exchange for the retention of radioactive $CH_3I$. Some technical improvements are nevertheless required about BTC acquisition towards radioactive $CH_3I$, to ensure a more accurate quantification of this reactivity at low penetrations and depending on the experimental conditions (T, R.H.). From a phenomenological point of view, we have also made significant progress to unravel the

relationships between KI, TEDA impregnants and the associated $CH_3I$ sorption profiles. On the one hand, the high affinity of TEDA for $CH_3I$ leads to the retention phase duration increase accompanied by DF enhancement and trapping stability improvement. A such reactivity is required to retain $CH_3I$ with good efficiency especially under stringent conditions (high temperature and humid conditions). On the other hand, KI action seems to be evidenced after the breakthrough phase allowing to slow down the desorption of physisorbed radioactive $CH_3I$. This reaction seems to be kinetically unfavored as a comparison with chemisorption or physisorption. This reactivity may play nevertheless a crucial role to prevent from an early AC filter replacement because of ageing phenomena.

Further studies will be performed during our research team with the aim to finely quantify the contribution due to isotopic exchange. The challenge is to identify new synthesis strategies promoting this reaction before its kinetic modelling under various experimental conditions. These aspects are crucial towards the development of a novel non-radioactive methodology for iodine traps periodic test to limit the radioactive discharges into the environment because of conventional radioactive methods.

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