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Smart design for CBRN protection by coupling adsorption and photocatalysis: Regeneration adsorbent efficiency-CWAs' continuous purification

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26 compared to initial capacity. We note also that the working time decrease by 15% for
27 each regeneration step. The evaluation of the new coupling configuration aimed at
28 highlighting the influence of a sulfur compound was encouraging, with a regeneration
29 rate of the adsorbent of about 80%. Compared to MS, the regeneration seems to be
30 more difficult. This is due to by-products (SO_2 , MSH) formation which is highlighted
31 by the degradation pathway proposed. The removal efficiency of the coupling system
32 (UV-LED/AF) under continuous process, was equal to 36%. This leads an increase in
33 filter working time of 50 min over that of a conventional adsorption process. Special
34 attention was paid to validating the coupling system performance in real conditions.
35 The system was placed on a humanlike seated thermal manikin used to simulate an
36 occupant of a chamber of 30 m^3 with the realistic condition of applying chemical,
37 biological, radiological, and nuclear (CBRN) agent protection. The time protection
38 was 60 and 30 min for respective concentrations of about 150 and 300 mg.m^{-3} .
39 This global investigation addressed how to overcome the scientific barriers to
40 designing a compact, self-contained filtration cartridge for personal protection in
41 CBRN emergency response and management in accordance with the United Nations
42 Sustainable Development Goals (SDGs).

43 **Keywords**

44 chemical weapon agent's treatment, optimized coupling photocatalytic/adsorption
45 configuration; regeneration; CBRN emergency.

46 **1. Introduction**

47 To fight against chemical weapons, government authorities have conducted several
48 actions, either at the international level through a commitment to the Organization for
49 the Prohibition of Chemical Weapons (OPCW) and through the implementation of the

50 Convention on the Prohibition of the Development, Production, Stockpiling and Use
51 of Chemical Weapons and on Their Destruction [1]. or at the national level through
52 the elaboration of defense strategies (e.g., plans, laws, and treaties). These
53 application have prepared personnel to improve their capacity to act and their
54 research and development, in particular, for developing new processes for treating
55 chemical warfare agents, which has become the main subject of study for
56 researchers [2][3][4]. Chemical warfare agents, the current state-of-the-art technology
57 of air filtration materials for protection against highly toxic chemicals, is mainly based
58 on the proposal of new, innovative, efficient, environmentally friendly, and
59 economically viable textiles that provide additional protection for people in direct
60 contact with a chemical weapon. These are effectively intelligent textiles that possess
61 reagents or active sites capable of degrading toxic compounds (passive-to-active
62 protection) [5][6][7][8].

63 For gas masks, research is much more focused on improving the properties of the
64 adsorbent, which is most often activated carbon (AC) for protection against chemical
65 warfare agents [9][10][11]. A significant disadvantage of these protection systems is
66 that the filter cartridges have limited autonomy, thus reducing the action time of the
67 personnel involved [12]. Consequently, regularly changing them to maintain optimal
68 protection is necessary. Thus, developing effective self-cleaning filters is crucial for
69 guaranteeing the safety of personnel intervening in emergencies, particularly CBRN
70 situations.

71 This work is part of this protection context. Indeed, treating (or simulating) toxic gases
72 by coupling adsorption and photocatalysis is of interest. The association between the
73 two processes is based on the adsorbent allowing for temporary storage during peak
74 exposures and photocatalyst activation improving the adsorption of the pollutant and

75 restoring the active sites by degrading the stored contaminant into CO₂ and H₂O [13–
76 17]. This work aimed to remove scientific obstacles to designing a compact, self-
77 contained filtration cartridge for individual protection for intervening in and managing
78 CBRN emergencies.

79 Adsorptive removal and photocatalytic oxidation are two effective technologies for
80 efficiently removing toxic compounds. The literature has shown that most of the work
81 on coupling the two processes focuses on developing hybrid compounds based on
82 nano-photocatalysts and an adsorbent [18][19]. The interest in this combination is to
83 develop efficient process, usually based on TiO₂ with excellent recycling properties
84 for practical application in the degradation of high-concentration pollutants.
85 Adsorbents can be based on adsorbent fibers, carbon nanotubes, graphene, AC and
86 biochar [19][20][21][22][23].

87 Another way to link the two processes is to place the photocatalytic reactor in a
88 series with the adsorbent filter. Wan-Kuen and Chang-Hee (2009) [24] tested the
89 suitability of putting an adsorbing filter before a photocatalytic reactor. In this case, it
90 was instead of an outlet protection mechanism. Thus, from the breakthrough,
91 residues pass through the adsorbent filter, which would be harmful if no
92 photocatalytic reactor were downstream. This configuration allows the filter to be
93 operated longer without worrying about pollutants passing through. This solution was
94 also used in a multidisciplinary project CUBAIR (2019) [25]. However, putting the
95 photocatalytic reactor upstream of the adsorbing filter is more sensible. Many
96 researchers, including Jain et al. (2007) [26] and Lim et al. (2011) [27] have analyzed
97 this configuration. This configuration aims to delay the filter's inevitable breakthrough
98 and extend its life as much as possible. Furthermore, Mamaghani et al. (2021) [28]
99 adopted a promising strategy to improve the efficiency of air treatment systems in

100 which the combination of TiO₂ and ACF showed better efficiency than TiO₂ coated on
101 nickel foam filter (NFF) and uncoated activated carbon fiber. Due to ACF's high
102 affinity and adsorption capacity, MEK molecules were concentrated around TiO₂,
103 which improved the reaction rate and led to higher removal efficiency. Nonetheless,
104 the photocatalytic degradation of MEK could effectively increase the breakthrough
105 time of the ACF. TiO₂ continuously oxidized the MEK adsorbed on the ACF's surface,
106 leading to *in situ* regeneration.

107 Another advantage of coupling the two processes in a series is the possibility of
108 regenerating the adsorbent and reusing the filter several times. Yet, after a few
109 cycles, the amount of adsorbed pollutants decreased with each regeneration until the
110 filter became inefficient. Considering the example of water treatment, the presence of
111 H₂O₂ during regeneration made the adsorbent more efficient, with a higher lifetime
112 (the number of cycles) [29].

113 This study applies an optimized version of photocatalytic module (optical fibers) with
114 a regeneration process by Joule effect (in situ heating) developed for the
115 regeneration of an AF support saturated with chemical warfare agent simulants
116 (mustard), methyl salicylate and Diethylsulphide.

117 The device combining the photocatalytic process with an adsorbent was also tested
118 for continuous treatment under realistic conditions in a climatic chamber in the
119 presence of a dummy (FeTHeMa), with the aim of proposing a new advanced
120 technique for respiratory protection against highly toxic chemical compounds with an
121 active aspect.

122 This detailed study aims to overcome the scientific barriers to the design of a
123 compact, self-contained filter cartridge for personal protection in CBRN emergency
124 management and response, in line with the Sustainable Development Goals (SDGs).

125 The literature review did not reveal any work presenting a compact configuration
126 coupling the photocatalytic process on luminous tissue with an adsorption process
127 with an integrated regeneration pathway, especially considering that the coupling
128 configuration has been developed and tested for chemical warfare agent treatment
129 applications.

130 **2. Material and methods**

131 *2.1. Pollutants studied*

132 In this study, target molecules were chosen for specific reasons, converging on the
133 effectiveness of respiratory protection. Accordingly, the first compound is
134 cyclohexane, a reference for the effectiveness tests of type A anti-gas filtration
135 cartridges [12][30]. The second compound was a simulated mustard gas with sulfur
136 ($C_4H_8Cl_2S$), namely methyl salicylate ($C_8H_8O_3$), a compound in which studies of
137 adsorption and desorption showed that it effectively mimicked the behavior of
138 mustard gas [31][32][33][34].

139 Since mustard gas is a sulfur compound, validating its degradation and the system's
140 performance against a sulfur compound was necessary. Therefore, sulfur diethyl
141 (C_2H_6S) was chosen for these tests [35][36][37,38].

142 Sigma-Aldrich provided the studied compounds in a liquid form with purities of >98%,
143 >99%, and >98% for cyclohexane, methyl salicylate, and sulfur diethyl, respectively,
144 which volatilized obtaining the desired gas concentrations.

145 *2.2. Supports*

146 2.2.1. Photocatalytic support

147 The photocatalytic substrate tested during this study was a new double-sided optical
148 fiber (OF) photocatalytic media manufactured by Brochier Technologies (UVtex®)
149 (Fig. 1a), with TiO₂ (Degussa P25) deposited equal to 26 g.m⁻². Previous publications
150 have presented further information on these media [39][40][41]. Details on the
151 manufacturing process of the media and the results of a characterization of the
152 surface texture of the photocatalytic media by scanning electron microscopy (SEM-
153 JEOL JSM 7100F) (Fig. S1 and S2) are provided in supporting information
154 [42][43][44].

155 2.2.2. Adsorption supports

156 In this work, adsorption media provided by the DACARB was used (Fig. 1b). It was
157 made of activated carbon felt (AF) under the reference FEU-CS-V-4 and
158 manufactured based on viscose at high temperatures and in the presence of water
159 vapor. This support had a specific area of 1,100 m².g⁻¹ with a pore volume of 0.8
160 cm³.g⁻¹, 40% of which was mesoporous; a thickness of 4 mm; and a weight of 250
161 g.m⁻².

162 The supplier communicated the AF's surface functions. The main surface functions
163 were carboxylic (0.01 mmol.g⁻¹), phenolic (0.17 mmol.g⁻¹), and basic (0.20 mmol.g⁻¹).

164 2.3. Reactors and experimental devices:

165 2.3.1. Reactor configuration

166 The reactor represented the construction of a new front-flow reactor configuration
167 (Fig. 1c), based on the same principle of chaining photocatalytic and adsorbent
168 media. The cross-section was 10 × 10 cm. The reactor was made of Bakelite, which
169 gave it high mechanical resistance (hard, rigid), electrical insulation, and good

170 temperature resistance (120 C°). The objective of this configuration was to optimize
171 photocatalytic treatment by reducing the residence time while ensuring good
172 degradation efficiency. This latter configuration was called PFR-LED optimized.

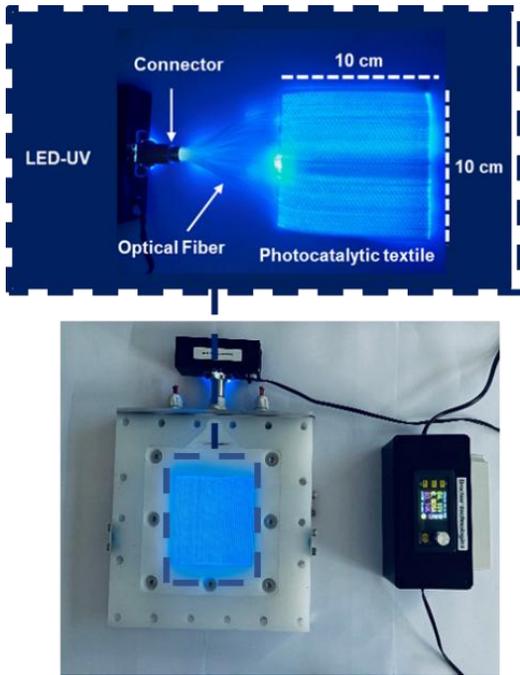
173 The PFR-LED reactor compartments were also adapted for installing adsorbent
174 support, in which two copper rods were integrated. Thus, the regeneration step was
175 conducted using the Joule effect. Therefore, installing copper electrodes in the
176 reactor compartments ensured the necessity of electrical connections.

177 The main characteristics of the photocatalytic module configuration are presented in

178 Table

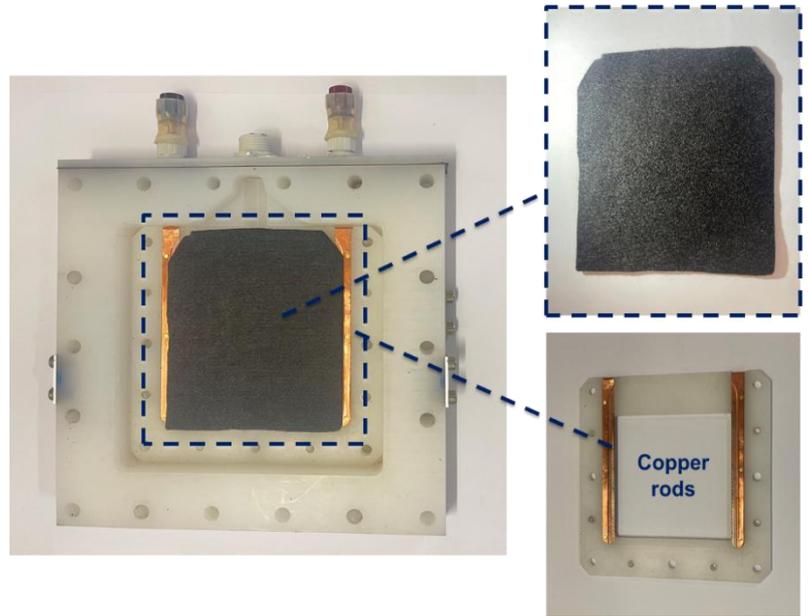
S1.

a)



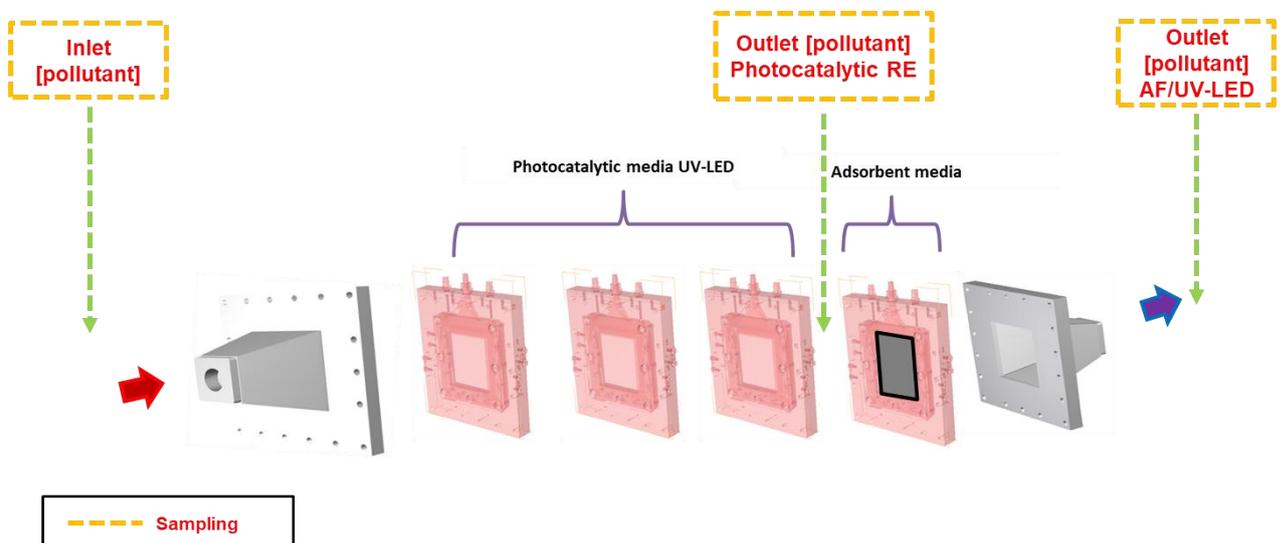
Photocatalytic support with TiO₂ coated on optical fiber

b)



Activated carbon felt (FEU-CS-V-4) "AF" support

c)



Photocatalytic front flow module based on Luminous tissue and AF filter

Figure 1: Front-flow module based on a) optical fibers photocatalytic media (PFR-LED) coupled to b) AF supports

180

181 2.3.2. *Experimental setup*

182 The system consisted of two configurations. One was for a continuous treatment in
183 which dry air returning from the network was the carrier gas. A mass flow meter
184 controlled its flow (Bronkhorst In-Flow). A bubbler containing water was installed in
185 the circuit to humidify the air. The pollutant was continuously injected in liquid form by
186 a syringe and pump assembly. A heating ribbon was placed in the injection zone to
187 facilitate the pollutant's volatilization. A static mixer allowed for the upstream
188 homogenization of the reactor's effluent. Two septa downstream and upstream of the
189 photoreactor allowed for sampling outlet and inlet gas with a syringe. The second
190 configuration was a closed-loop treatment in which a recirculation flow (about $1 \text{ m}^3 \cdot \text{h}^{-1}$)
191 was dedicated to studying adsorbent regeneration.

192 The desorption device used a Joule effect heating system (*in situ* heating). A 600 W
193 DC generator XG-60-14 (Amatek®) with voltage and working current ranges of 0–60
194 V and 0–10 A, respectively, was used. This system provided an electrical circuit with
195 a current of 5 A and a voltage of 35 V for thermal conduction heating of the
196 adsorbent media. To maintain the desorption temperature at a temperature level of
197 $70 \pm 2\text{C}^\circ$ throughout the experiment, a thermostat was set up and equipped with a
198 chromium-nickel alloy probe, with a linear response over the range of 0–1,000 K
199 installed on the support's surface. A temperature sensor was also installed at the
200 reactor entrance connected to an Arduino system, allowing one to follow the
201 temperature evolution by direct data acquisition on a PC. This system permitted the
202 maintenance of the necessary temperature for desorption throughout the experiment.

203 Figure 2 shows the experimental procedure.

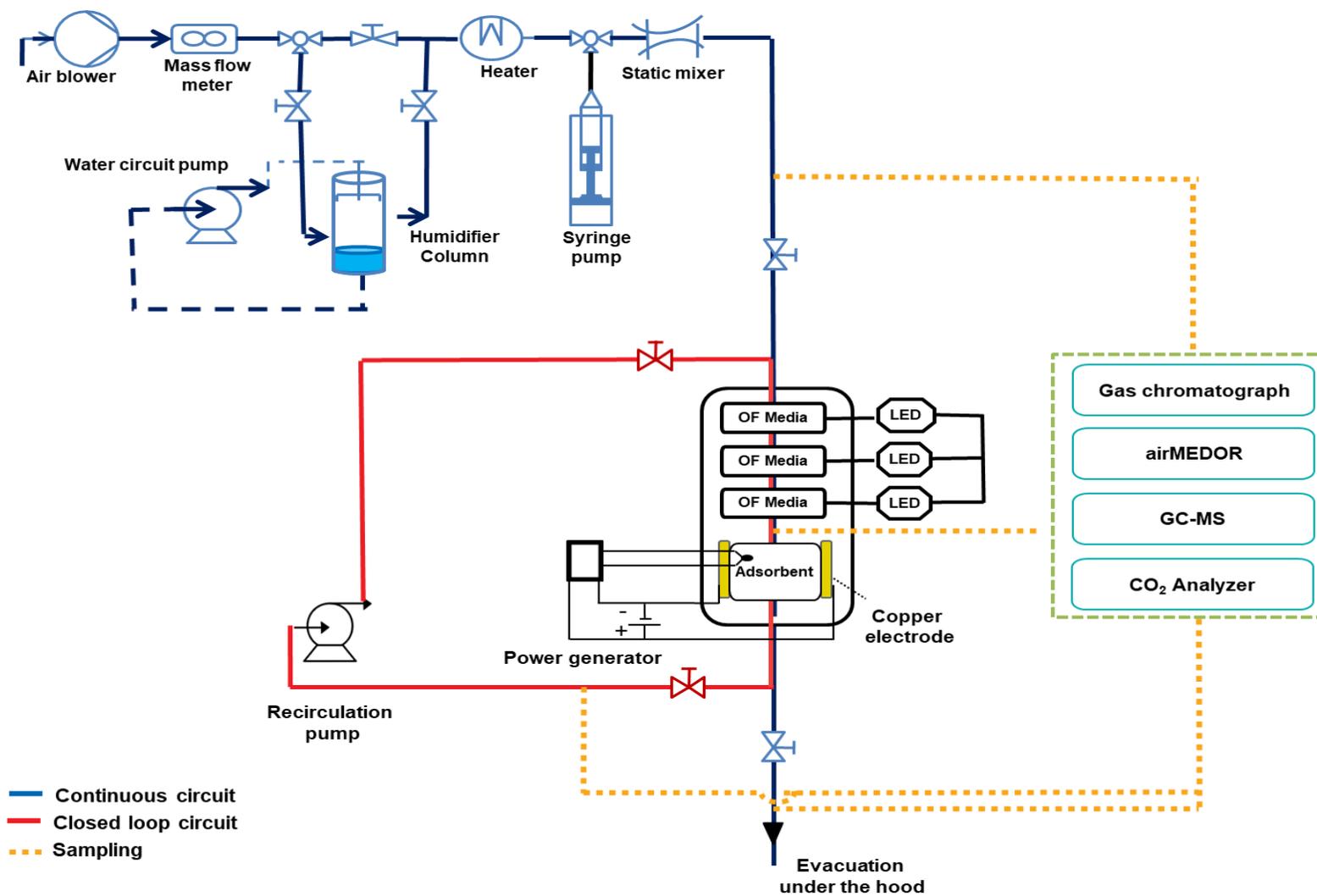


Figure 2: Diagram of the installation of the coupling configuration of the adsorbent with photocatalytic process with different desorption methods.

204 *2.4. Climatic chamber for full-scale tests*

205 The experiments were conducted in the climatic chamber QUALIDIF of the LGCGM
206 Laboratory (Fig. 3a) with the following dimensions: $L \times W \times H = 3.50\text{m} \times 3.50\text{ m} \times$
207 2.50 m . It was coupled to an air diffusion circuit, including an air handling unit (AHU).

208 The six inside faces were thermally controlled using a hydraulic circuit composed of
209 PER pipes inserted into the walls and connected to a heat pump for simultaneous
210 heating and cooling. The ambient temperature in the chamber was controlled with a
211 hydraulic circuit. The AHU generated by a ceiling air jet was equipped with a fan, a
212 heater, a chiller, and a CELLKRAFT stream generator E-6000 with an external
213 humidity sensor for accuracy $\pm(1.5 + 0.015 \times \text{reading})$, followed by a plenum box. The
214 air diffusion terminal unit was installed at the extremity of the plenum box. The inlet
215 flow rate and air temperature were controlled with sensors placed between the
216 handling unit and the plenum box and again measured at the jet exit using an ACIN
217 balometer (Flowfinder mk2). The accuracy in the flow rate measurement was $\pm 3\%$ of
218 the reading. The air returned to the AHU via an outlet at the bottom of a wall. This
219 return air was not mixed with fresh air from the outdoors; the AHU recirculated the air
220 already present in the chamber via airtight pipes.

221 The chamber was equipped with air temperature sensors (PT1000_1/3 DIN –
222 accuracy of $\pm 0.1^\circ\text{C}$) and omnidirectional anemometers (TSI 8475, accuracy of $\pm 3\%$
223 of the reading) to determine the RH percentage. Cameras were present in the
224 chamber to view the interior from the outside of the chamber.

225 The climatic chamber was also equipped with a humanlike thermal manikin (named
226 FeTHeMa, based on “female thermal manikin”; see Fig. 3b), mimicking the human
227 body due to 79 thermoregulated zones. This manikin was developed according to the

228 standard ISO 14505–2:2006, noted in P. Danca’s [45] thesis on local thermal comfort
229 measurement. A supplementary breathing system was integrated into the manikin to
230 study pollutant concentrations in the inhaled air when an ambient exposition risk
231 exists. In the present study, the twin tubes connecting the manikin’s nostrils to the
232 outside were attached to a pump. In the first step, the air samples in this (respiratory)
233 circuit were analyzed in the presence of cyclohexane C_6H_{12} [12] (a reference for
234 testing the effectiveness of anti-gas filter cartridges) in the chamber, which
235 represented the reference case of exposure. In the second step, the (respiratory)
236 circuit was connected to the filtration module (PFR-LED Optimized coupled to AF
237 support). The analysis of the filtered air at the outlet of the cartridge enabled the
238 testing of the effectiveness of the cartridge to protect anyone exposed to the
239 chemical agent. An air sampling system was installed in the chamber (Fig. 4) to
240 determine the various sampling points inside the room. It also monitored the
241 concentration of the pollutant at the inlet and outlet of the purification reactor from
242 outside the climate chamber.

(a)



(b)

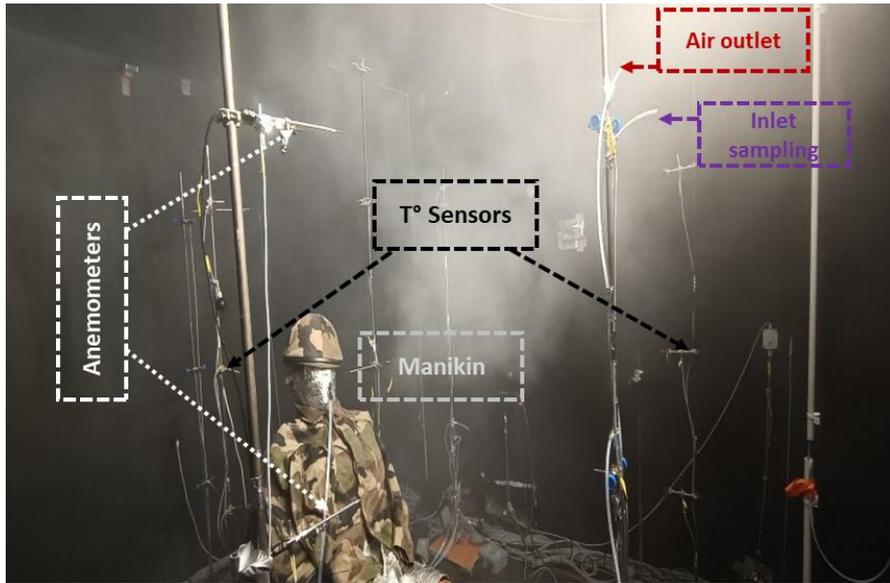


Figure 3: a) Climatic chamber QUALIDIF and FeTheMa thermal Manikin b) in a contaminated area.

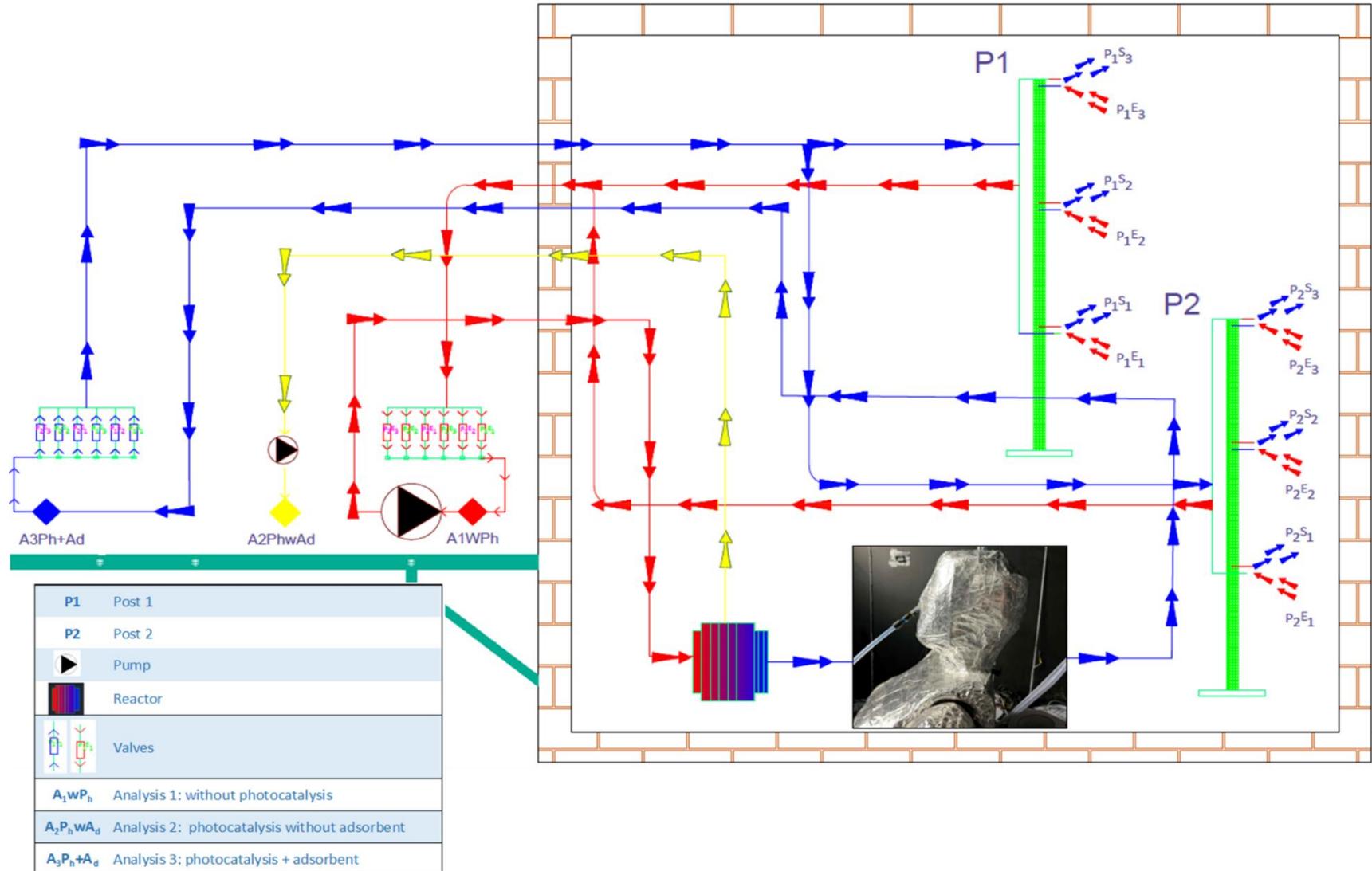


Figure 4: Experimental principle diagrams of purification tests in realistic situations.

243 2.5. Analytic tools

244 Different main factors were considered for evaluating the performance of the different
245 photocatalytic configurations and coupling modules, such as the adsorption capacity
246 of the adsorbent media in the dynamic tests. The adsorption capacity was calculated
247 using Eq.1:

$$q_e = \frac{M_e}{M} \quad \text{where, } M_e = Q \int_0^\infty (C_e - C) dt \quad (1)$$

248

249 q_e is the adsorption capacity ($g_{\text{pollutant}} / g_{\text{adsorbent}}$); C_o and C are the initial and
250 instantaneous concentrations at a given time, respectively; and Q and t are the
251 adsorbate flow rate ($L \cdot \text{min}^{-1}$) and time (min), respectively.

252 The breakthrough adsorption behavior was predicted using Clark's dynamic
253 adsorption model [46]. This model was based on the concepts of mass transfer,
254 which consider the dynamic phenomenon and isothermal Freundlich equation
255 representing equilibrium. They were also based on the assumption that fluid flow is of
256 a piston type. The model's equation is expressed as follows:

$$\frac{C_s}{C_0} = \left[\frac{1}{1 - A e^{-rt}} \right]^{1/(n-1)} \quad (2)$$

257 The breakthrough time is expressed using Eq. 3:

$$tp = \frac{\ln A - \ln \left(\frac{C_0}{C_p} \frac{n-1}{n-1} - 1 \right)}{r} \quad (3)$$

258

259 The material balance and the energy balance of electrical power consumed during
260 the regeneration process were the basis for a better evaluation of regeneration
261 performance, the average specific elimination rate, and the desorption rate:

$$\text{Average elimination rate} = \text{Mass eliminated} / \text{Degradation time} / \text{Mass of TiO}_2 \quad (4)$$

$$\text{Desorption rate} = \text{desorbed mass of pollutant} / \text{Desorption time} \quad (5)$$

$$E_{\text{consumed}} = E_{\text{regeneration}} = E_{\text{desorption}} + E_{\text{Photocatalyse}} \quad (6)$$

262

263 2.6. Analytical Instruments

264 The different analytical methods used in this work are detailed in the information
265 material. The studied gases were analyzed using two gas-phase chromatographs
266 coupled to an FID detector. One had an FFAP column for analyzing cyclohexane,
267 and the other had an HP5 column for analyzing methyl salicylate. Sulfur diethyl was
268 analyzed using airMEDOR. Detailed information about the analysis setup was
269 presented in previous work [47].

270 3. Results and discussions

271 3.1. Study of adsorbent regeneration by a photocatalytic module

272 The adsorption performance of the used support was developed in a batch study to
273 highlight its effectiveness in retaining the selected pollutants [48][49]. Table S2
274 summarized the results of the adsorption parameters. The order of magnitude of the
275 obtained adsorption capacities was consistent with those in the literature [12],
276 Freundlich and Langmuir models provided a good correlation of the experimental
277 results.

278 3.1.1 Adsorption and desorption cycle studies of AF media with the PFR-LED 279 Optimized module during in situ regeneration

280 This study aimed to evaluate the evolution of the adsorption capacities of AF media
281 during adsorption–desorption cycles in the same sample. For this purpose, different

282 regeneration cycles were conducted on the adsorbent medium (AF) by *in situ*
283 desorption with an optimized PFR-LED photocatalytic module (Fig. 5). The
284 concentration of MS injected to obtain adsorption equilibrium, the operating
285 conditions, and the electrical power applied for desorption were kept identical for
286 each cycle. Monitoring of the absolute humidity during the regeneration process was
287 also implemented to better evaluate the photocatalytic degradation of the pollutant
288 during the regeneration process. Notably, the adopted saturation rate corresponded
289 with the respiratory rate for light physical activities, and the saturation rate
290 corresponded with the respiratory flow rate for light work in accordance with the ISO
291 standard ISO/DIS 8996 [50].

292 The material balance (Fig. 6a) was based on an analysis of the amount adsorbed
293 during different adsorption cycles. The results of the balance showed a decrease in
294 the adsorption capacity of the AF media after each regeneration cycle (8.01 mmol in
295 cycle 1 and 7.81 mmol in cycle 2) compared to the amount adsorbed at the beginning
296 (8.44 mmol). The regeneration rate (Fig. 6b) confirmed this finding, in which a loss
297 was observed after each regeneration cycle. A decrease in the working time of the
298 filter was also recorded after each regeneration cycle (a decrease of 15.49% and
299 31.59% after the first and second regeneration cycles, respectively) (Fig. 6c). This
300 decrease in the performance of the AF media may have been due to the incomplete
301 regeneration of the media. This incomplete regeneration could be because of the
302 limitation of the photocatalytic reaction on the sites as a result of competition with
303 water molecules, as many researchers have noted [51][52][53][54][55]. Figure 6
304 shows an increase in absolute humidity during the regeneration of the AF generated
305 by the photocatalytic process until reaching saturation level.

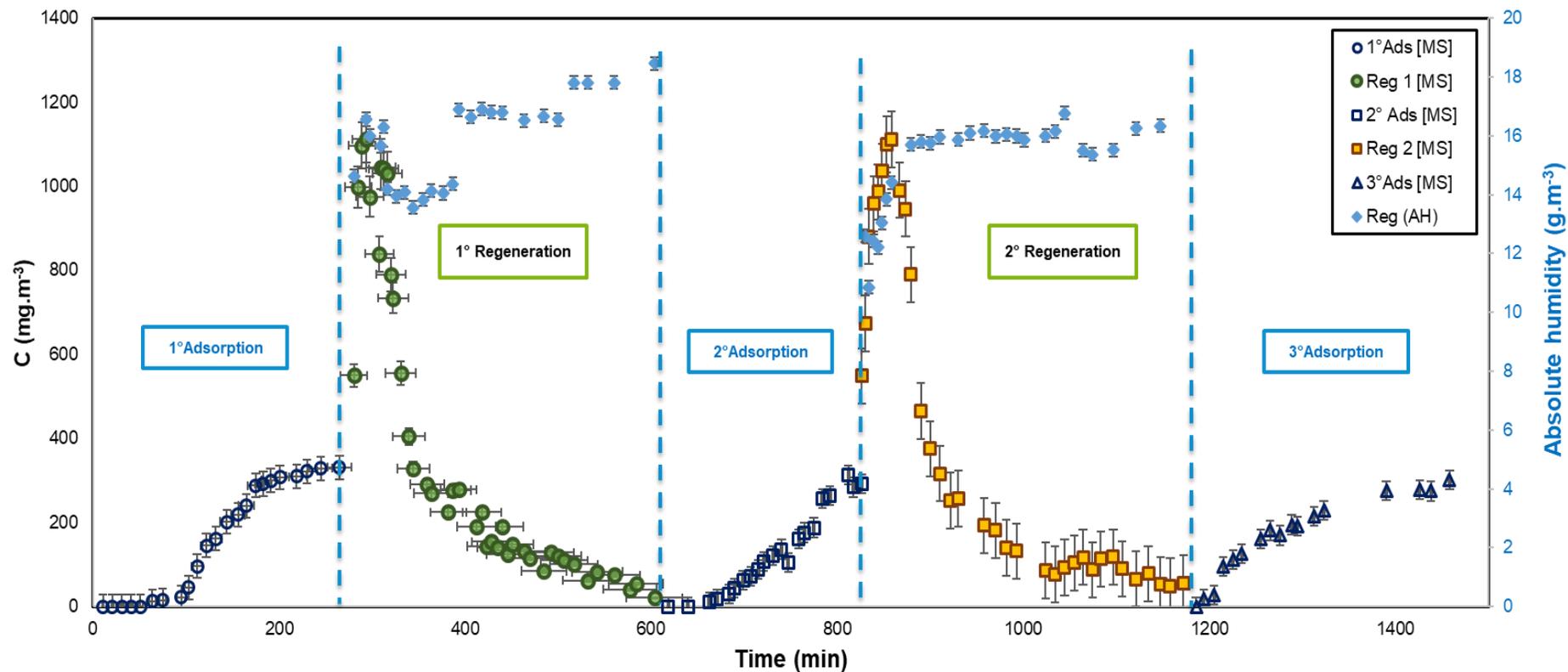


Figure 5: Adsorption and regeneration cycles of AF with optimized PFR-LED photocatalytic configuration, with absolute humidity monitoring: PFR-LED (Optimized) ($m_{\text{TiO}_2} = 0,78 \text{ g}$, $I = 7,8 \text{ W.m}^{-2}$, $m_{\text{AF}} = 2,5 \text{ g}$). Methyl Salicylate : $C = 300 \text{ mg.m}^{-3}$ / $Q = 18 \text{ L.min}^{-1}$ / $\text{HR} = 40 \pm 2 \%$, $T = 20 \pm 2 \text{ C}^\circ$, $T_{\text{in situ}} = 70 \text{ C}^\circ$ (35 V- 5 A), $Q_{\text{recirculation}} = 1 \text{ m}^3.\text{h}^{-1}$.

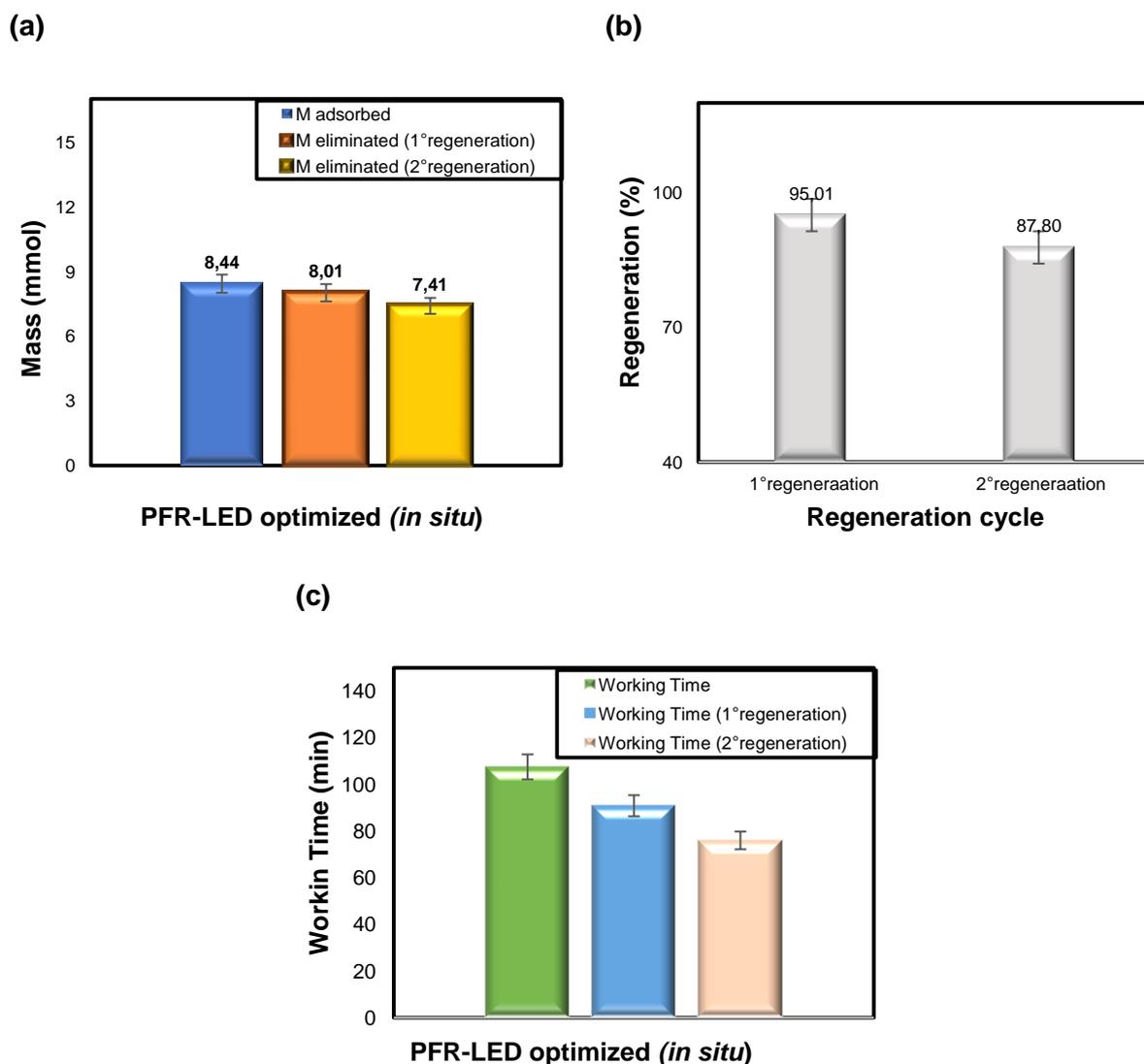


Figure 6: (a) Mass balance and (b) Regeneration rate and (c) Working Time: PFR-LED (Optimized) ($m_{TiO_2} = 0,78 \text{ g}$, $I = 7,8 \text{ W.m}^{-2}$, $m_{AF} = 2,5 \text{ g}$). Methyl Salicylate : $C = 300 \text{ mg.m}^{-3}$ / $Q = 18 \text{ L.min}^{-1}$ / $HR = 40 \pm 2 \%$, $T = 20 \pm 2 \text{ C}^\circ$, $T_{in \text{ situ}} = 70 \text{ C}^\circ$ (35 V- 5 A), $Q_{recyrculation} = 1 \text{ m}^3.h^{-1}$.

306

307 Furthermore, byproducts formed during the regeneration process by photocatalytic
 308 degradation, such as benzoic acid, were not desorbed [55]. There was also the
 309 phenomenon of the depletion of the adsorbent material, which the literature has
 310 noted [56][57]. Figure 7 shows the byproducts of the photocatalytic degradation of
 311 methyl salicylate analyzed by GC-MS, where the sample was collected by

312 concentration on Carbotrap™ (CA). From 0.1 to 1 L of gas was injected using a
313 thermal desorber (Dynatherm Analytical Instruments, model 890) with a desorption
314 temperature of 170 °C.

315 The average desorption rate, the average removal rate, and the energy consumed
316 through the process are presented in Figure S3.

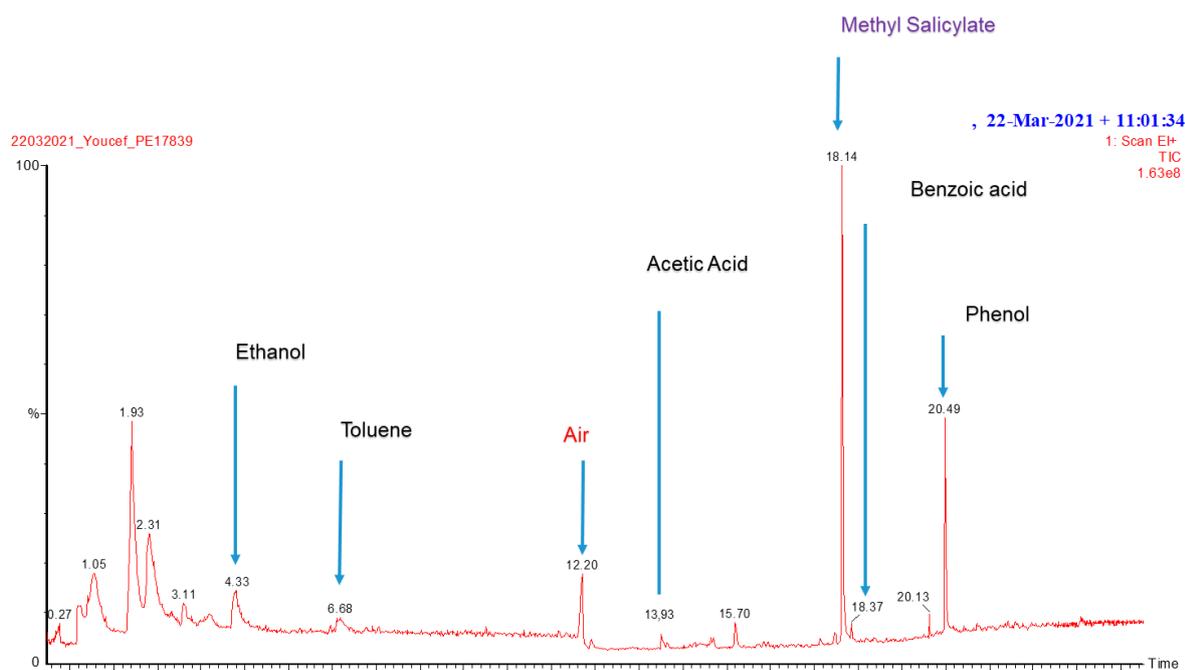


Figure 7: Photocatalytic degradation of the byproducts of methyl salicylate

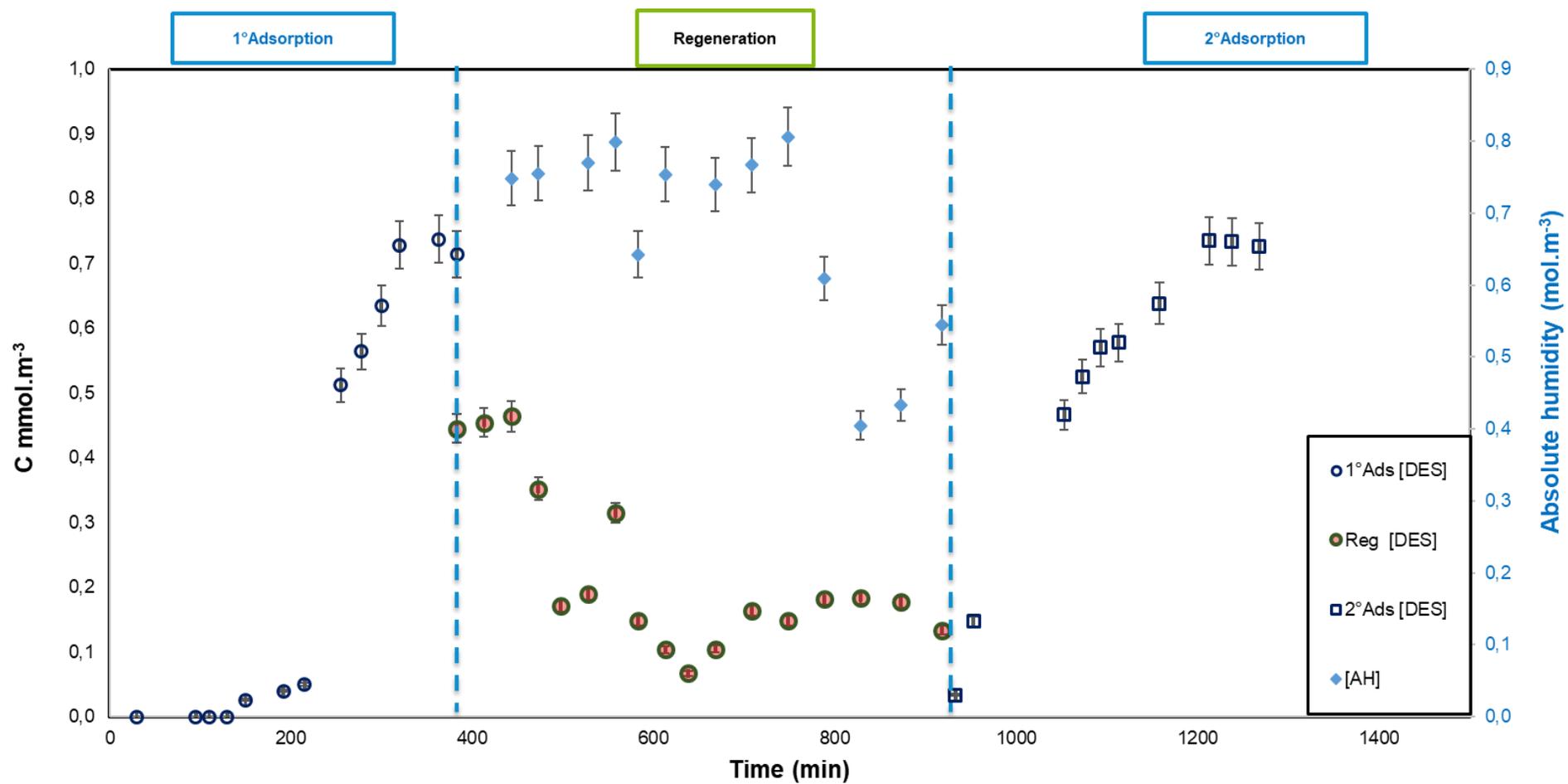
317

318 3.1.2 Performance study of the AF/PFR-LED Optimized process toward the sulfur 319 compound (Yprite “sulfur mustard”)

320 Since mustard is a sulfur compound, it was necessary to determine how the coupling
321 system behaved toward it. A closed-loop treatment to regenerate the DES-saturated
322 AF medium was studied. Of course, a final adsorption cycle must occur to reach
323 equilibrium.

324 During this experiment, the formation of the degradation byproducts and the absolute
325 humidity were monitored. The results are presented in Figure 8.

(a)



(b)

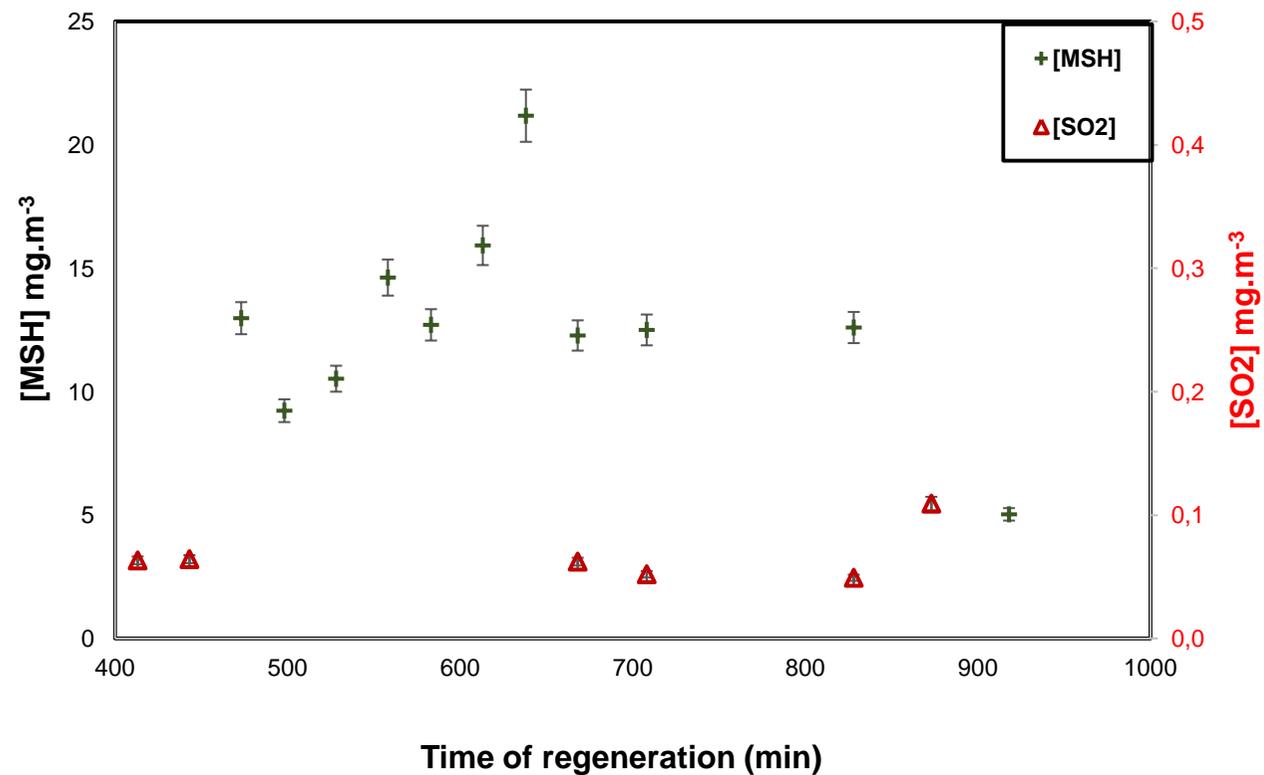


Figure 8: a) Adsorption under UV and the regeneration cycle of AF with optimized PFR-LED photocatalytic configuration with absolute humidity monitoring: PFR-LED (optimized) and b) the evolution of the byproducts during the regeneration cycle. ($m_{\text{TiO}_2} = 0.78 \text{ g}$, $I = 7, 8 \text{ W.m}^{-2}$, $m_{\text{AF}} = 2.5 \text{ g}$). Sulfur diethyl: $C = 0.9 \text{ mmol.m}^{-3}/Q = \text{L.min}^{-1}/\text{HR} = 40 \pm 2\%$, $T = 20 \pm 2^\circ\text{C}$, $T_{\text{in situ}} = 70^\circ\text{C}$ (35 V- 5 A), $Q_{\text{recirculation}} = 1 \text{ m}^3.\text{h}^{-1}$.

326 The analysis of the results also indicated a regeneration rate of AF support of
327 76.92%. This incomplete regeneration could be due to poor desorption of DES [56]
328 and the byproducts' degradation in which the phenomenon of competition occurred,
329 as reported in the literature [40][57], namely the SO₂, which is known for its tendency
330 to poison the catalyst (TiO₂) [58][59]. Moreover, an abundance of MSH was initially
331 seen in the formation of intermediates due to the desorption of the target compound.
332 The MSH formed was then degraded to ultimately form SO₂. This mechanism aligned
333 with the literature [5][60] for the degradation of DES, according to the mechanism
334 shown in Figure S4.

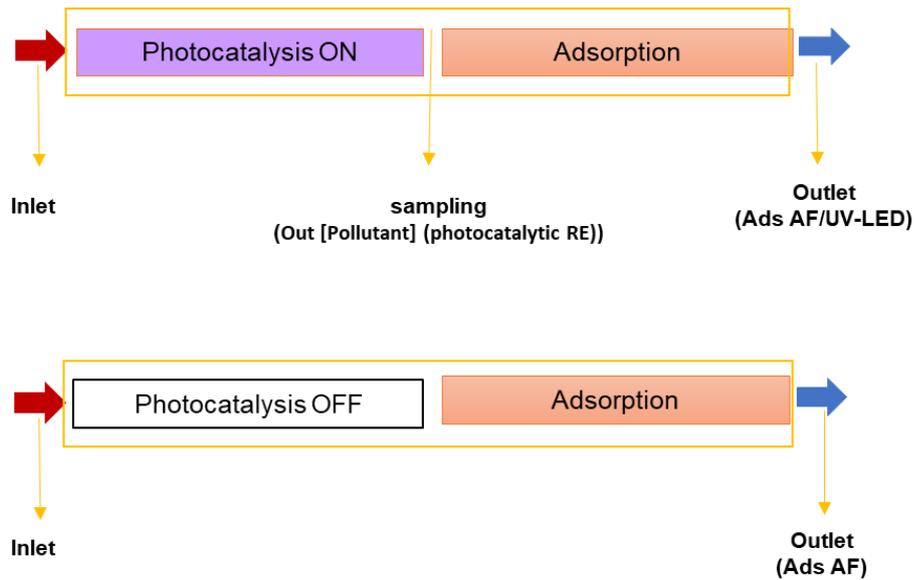
335 *3.2. Continuous coupling study*

336 *3.2.1 Continuous coupling for the Methyl salicylate treatment*

337 As previously mentioned, one configuration of adsorption and photocatalysis coupling
338 was the installation of the photocatalytic module upstream of the fixed adsorption
339 bed. The few authors who have studied continuous coupling to increase the running
340 time of the adsorption filter favor this solution [26][27] .

341 In this study, a photocatalytic module was placed upstream of an AF adsorption filter
342 to perform an air purification test with the mustard gas simulant MS. A comparative
343 study between classical adsorption with an AF filter alone and another one based on
344 the AF/UV-LED coupling was also presented. In this study, sampling was performed
345 at the inlet of the system, after the photocatalytic module in order to estimate its
346 performance and a last one at the outlet of the coupling system (after the module and
347 the adsorbent filter). The sampling system is shown in an explanatory diagram in
348 Figure 9a:

(a)



(b)

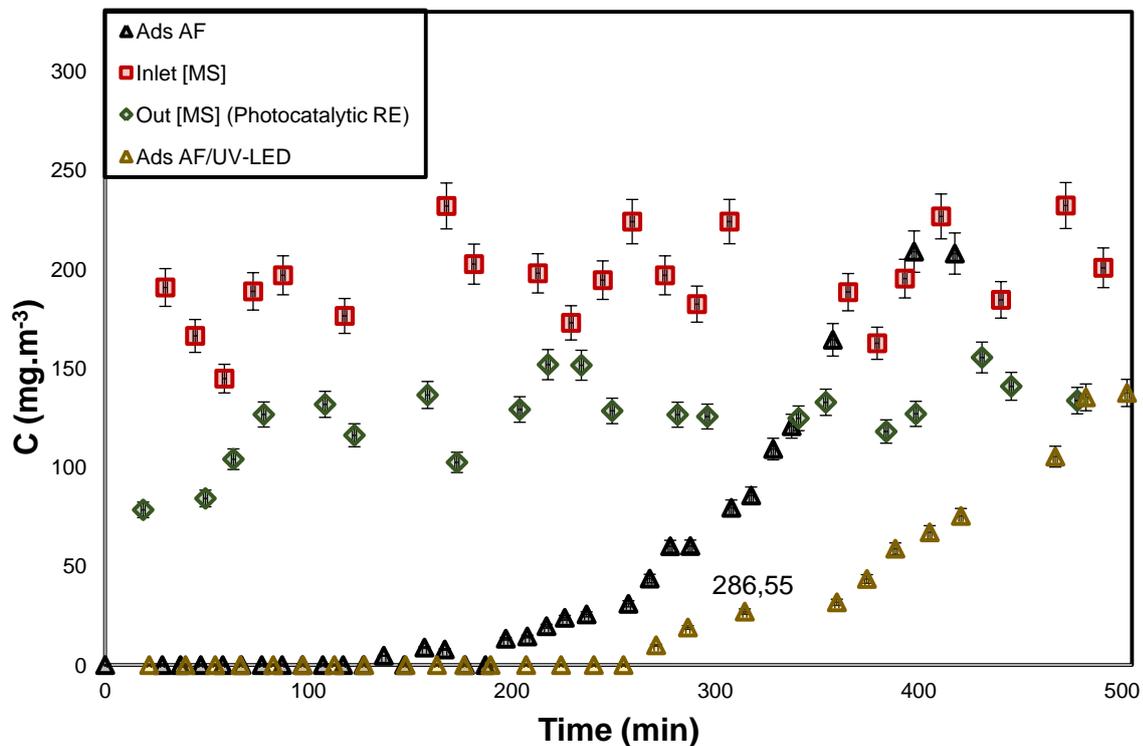


Figure 9: a) Sampling schematic and b) the result of continuous treatment of methyl salicylate with AF support alone and with front-flow photocatalytic optimized PFR-LED coupled with AF support: ($m_{TiO_2} = 0.78$ g, $I = 7.8$ W·m⁻², $m_{AF} = 2.5$ g). Methyl salicylate: $C = 200$ mg·m⁻³/ $Q = 18$ L·min⁻¹/HR = $40 \pm 2\%$, $T = 20 \pm 2^\circ$ C.

350 Figure 9b shows the concentration of methyl salicylate during adsorption with
351 activated carbon felt alone and with a combination of the optimized PFR-LED
352 photocatalytic module and the activated carbon felt. The MS concentration at the
353 outlet of the photocatalytic section was also measured to evaluate the photocatalytic
354 process's performance.

355 The results indicated that using a photocatalytic module upstream allowed for a
356 significant degradation of the pollutant, estimated at 36% of removal efficiency over
357 the entire treatment time (RE_{moyen}) with a CO_2 selectivity of 15%. This led to the
358 adsorbent support receiving decreased concentration [27][28]. This increased the
359 filter operating time by about 20%, resulting in a corresponding change in
360 breakthrough time (5 h versus 4 h for AF alone).

361 The equilibrium adsorption capacity was estimated at $0.61 \text{ g}_{MS} \cdot \text{g}_{AF}^{-1}$ for adsorption
362 alone and $0.48 \text{ g}_{MS} \cdot \text{g}_{AF}^{-1}$ for adsorption from the coupling. The equilibrium adsorption
363 capacity decreased proportionally to the input concentration, and the breakthrough
364 time increased when the latter decreased. This finding could be explained by the fact
365 that the higher the input concentration of the target gas, the greater the number of
366 molecules that can be adsorbed. Similarly, the breakthrough and saturation times
367 were shortened [61][62][63].

368 *3.2.2 Simulating exposure to chemical toxins in a real environment*

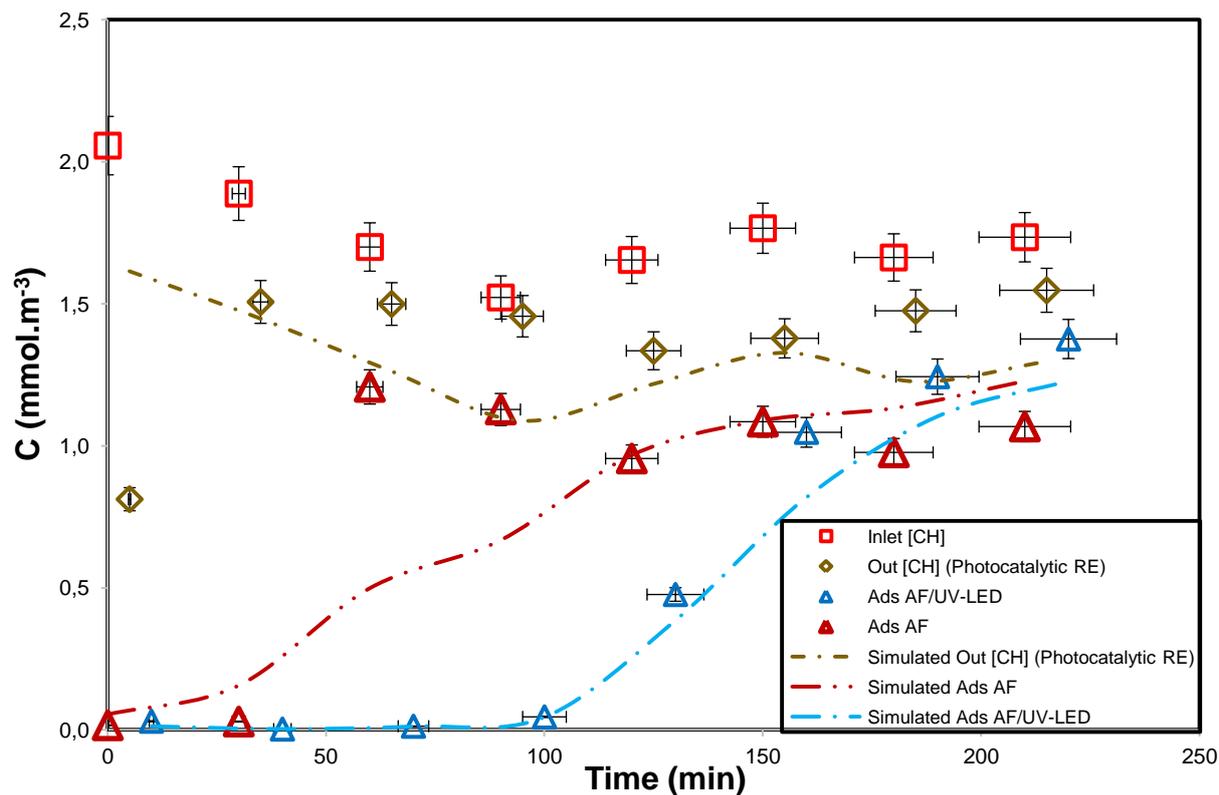
369 This study focused on human respiratory safety in toxic environments. Accordingly,
370 an optimized PFR-LED photocatalytic module and AF were tested to ensure the
371 respiratory protection of a FeTheMa thermal manikin. The challenge was to validate
372 a solution that would save time on filter life, namely continuous process coupling
373 while maintaining a comfortable thermal and ventilation environment. The FeTheMa

374 thermal manikin is used as an inhaled air quality assessment tool and as a thermal
375 comfort sensor.

376 Before proceeding with the filtration coupling tests, it was essential to determine the
377 system's tightness and the contamination's homogeneity inside the chamber.
378 Therefore, different tests were conducted, namely a smoke test (Fig. S5) to
379 determine potential pollution and dead spots and a homogeneity test of the
380 concentration inside the environmental chamber (blank test). The conditions of the
381 environmental chamber and the thermal comfort of the manikin were also monitored
382 during these tests. The details and results of this section are summarized in the
383 supporting information. When the closed system allowed for a homogeneous
384 concentration over the entire chamber volume (Fig. S6), the system did not
385 significantly impact climatic conditions (Fig. S7). Moreover, the thermal comfort on
386 the different parts of the manikin's body was homogeneous (Fig. S8).

387 The tests were performed with an approximate respiratory flow rate for intense work,
388 according to the previously mentioned ISO/DIS 8996 standards.

(a)



(b)

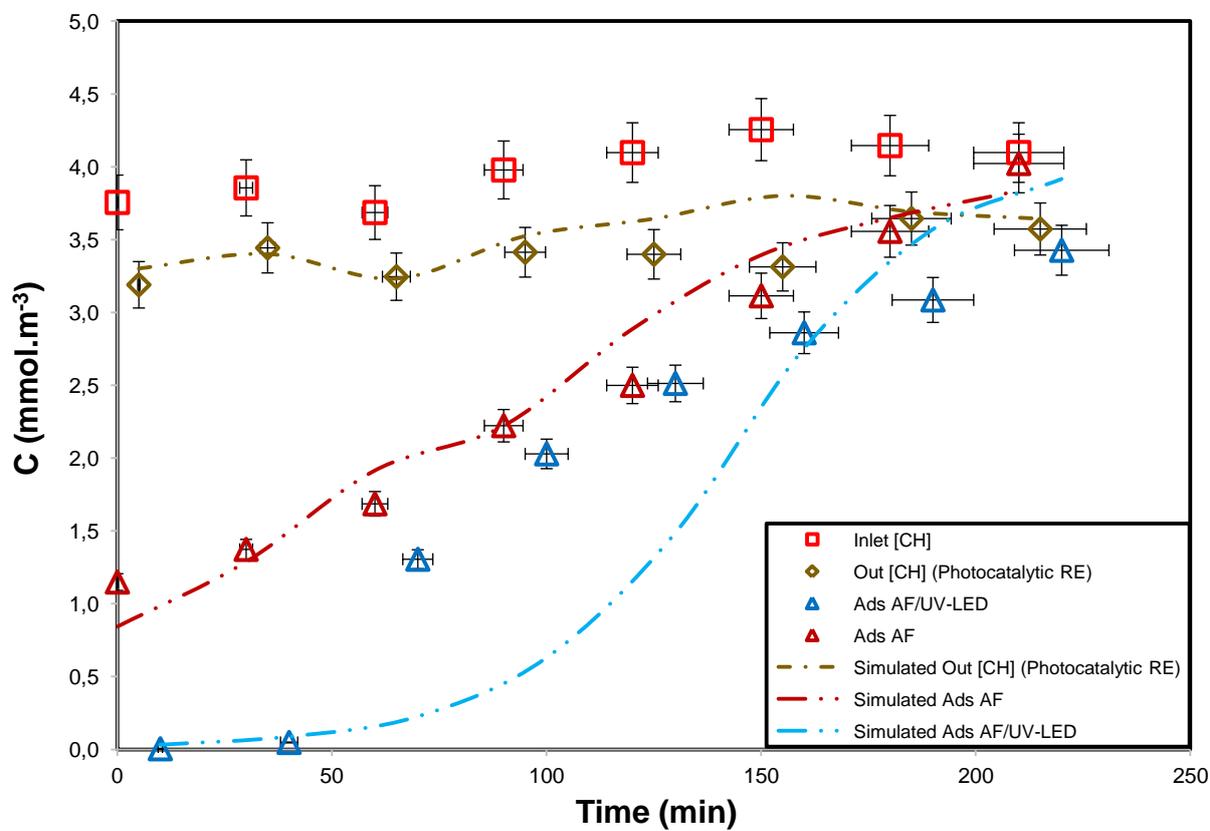


Figure 10: Continuous treatment of cyclohexane with AF support alone and with front-flow photocatalytic optimized PFR-LED coupled with AF support at different concentrations of the pollutant a) $[CH] = 150$ and b) $300 \text{ mg}\cdot\text{m}^{-3}$ ($m_{\text{TiO}_2} = 0.78 \text{ g}$, $I = 7.8 \text{ W}\cdot\text{m}^{-2}$, $m_{\text{AF}} = 2.5 \text{ g}$)/ $Q = 25 \text{ L}\cdot\text{min}^{-1}/\text{HR} = 44 \pm 2\%$, $T = 22 \pm 2^\circ\text{C}$.

389 Figures 10a and 10b show the air quality that FeTHeMa breathed. They compare the
390 quality of the air filtered with adsorbent AF alone and the air filtered with adsorption
391 coupled with the upstream optimized PFR-LED photocatalytic module. The room had
392 different contamination rates, but the same climatic conditions were maintained for
393 the different tests. The concentration of the pollutant in the air to be breathed was
394 measured at different points of the system, namely, the concentration at the inlet,
395 after the photocatalytic module, and the concentration at the outlet of the filtration
396 system, the latter representing the actual concentration that the manikin received.

397 The results showed that the upstream implementation of photocatalysis allowed for
398 relieving the AF adsorbent by lowering the concentration of the pollutant received by
399 the latter, extending its duration of use by allowing the dummy to breathe clean air for
400 60 and 30 min (Fig. 10a and 10b, respectively, referencing breakthrough time) more
401 than during air filtration with AF alone.

402 The results also showed similar behavior to what has been reported in the literature
403 on the effect of concentration. Such behavior was found in photocatalysis and its
404 limitation at high concentrations due to the unavailability of active sites [64–66], It
405 was also found in adsorption, in which the higher the input concentration of the target
406 gas was, the greater the number of molecules that could be adsorbed, consequently
407 decreasing the breakthrough time [67][68][69][63].

408 The results were simulated using a model proposed in the authors' previous work
409 [70] to describe the experimentally observed degradation. Details of the model are

410 provided in the reference paper. This model considered the reaction on the
411 photocatalytic surface and the mass transfer step Eq. S7 in the supporting
412 information. The kinetic constants (k and K) were obtained during laboratory tests at
413 different concentrations for different flow rates for the photocatalytic degradation of
414 cyclohexane with the optimized PFR-LED module, whose degradation efficiency
415 results were presented in the authors' previous work [41], The results of the modeling
416 are shown in Figure S9, in which a good fit of the experimental laboratory results with
417 the simulated results was noted.

418 This model also allowed for a good description of the experimental results under real
419 environmental conditions (Fig. 10a and 10b), in which the concentration resulting
420 from the simulated photocatalytic module (Simulated Out [CH] (photocatalytic RE))
421 was in agreement with the experimental concentration (Out [CH] (photocatalytic RE))
422 [66][71][72]. The Clark model also simulated the breakthrough curves to evaluate
423 adsorption with and without the photocatalytic module. The model correlates well with
424 the experimental results.

425 Notably, the pressure drop in this purification system based on the coupling of the
426 optimized PFR-LED photocatalytic module and the AF filter was estimated at 9 Pa.
427 This finding suggests the possibility of adding photocatalytic or adsorbent
428 compartments for better treatment efficiency, as indicated in previous work [41], while
429 remaining within the range of the pressure drop tolerated for anti-gas filtration means
430 (i.e., protective masks) [73].

431 The analysis of the thermic comfort of the different body parts of the manikin showed
432 a normal state and stability throughout the experiment (Fig. S8).

433 **4. Conclusions**

434 This study considered using photocatalysis and adsorption coupling to treat chemical
435 warfare agents, in which mustard gas simulants Methyl Salicylate and Diethyl
436 Sulphur were tested.

437 To regenerate an adsorbent filter, the photocatalytic module was improved by
438 implementing Joule desorption (*in situ*), thus increasing the regeneration of the
439 adsorbent. However, and as already expected, the results showed a decrease in the
440 adsorption performance of the support after each regeneration cycle. The optimized
441 coupling system was also tested to cope with the sulfur compound, and the results
442 were encouraging, counting the competition phenomenon with the by-products.

443 This new optimized coupling configuration with an upstream photocatalytic module
444 was proven effective for continuously treating chemicals in the laboratory and under
445 realistic conditions, relieving the pressure on the adsorbent filter and increasing its
446 working time, shifting the breakthrough time by 30 min in extreme conditions.

447 Finally, this exhaustive investigation overcame scientific obstacles to the design of a
448 compact, self-contained filter cartridge for personal protection in emergency response
449 and CBRN management. This new optimized version of the adsorption and
450 photocatalysis coupling could also have significant potential for onboard gas filtration
451 equipment's.

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