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1 **Continuous air purification by front flow photocatalytic reactor:**
2 **Modelling of the Influence of mass transfer step under simulated**
3 **real conditions**

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11 **ABSTRACT**

12 In this work, a solution for the treatment of toxic gases based on a photocatalytic
13 process using TiO₂ coated on a cellulosic support, has been investigated. Here,
14 cyclohexane was chosen as the reference for testing its removal efficiency via a
15 continuous front flow reactor as type A anti-gas filters. The photocatalytic support
16 was firstly characterized by EDX, to confirm its elemental composition. Then, the
17 experiments were carried out, starting with a batch reactor in order to evaluate the
18 degradation efficiency of the photocatalytic media, as well as the monitoring of the
19 photocatalytic process which allowed the establishing of a carbon mass balance
20 corresponding to the stoichiometric number of our target pollutant. The transition to a
21 continuous treatment with a front flow reactor aims to highlight the influence of the
22 input concentration (0.29 – 1.78 mM m⁻³) under different flow rates (12, 18 and 36 L
23 min⁻¹). The relative humidity effect was also investigated (from 5 to 90% of humidity)
24 where an optimum rate was obtained around 35 to 45%. In addition, the
25 mineralization rate was monitored. The major rates obtained were for a cyclohexane

26 input concentration of 0.29 mM m^{-3} in wet condition (38%) at an air flow rate of 18 L
27 min^{-1} , where the CO_2 selectivity reached 77% for an abatement of 62%. In order to
28 understand the limiting steps of the photocatalytic process, a model considering the
29 reactor geometry and the hydraulic flow was developed. The obtained results showed
30 that the mass transfer must be considered in the photocatalytic process for a
31 continuous treatment. The Langmuir-Hinshelwood bimolecular model was also
32 developed to represent the influence of the humidity.

33 **Keywords**

34 Air treatment, Photocatalytic front flow reactor, kinetic modelling, mass transfer.

35 **1. Introduction**

36 Air pollution is increasingly a major concern, the result of pollution caused by many
37 factors, often of human origin. Faced with the adverse effects of this pollution, both
38 on human health and the environment, scientists are still trying to find new
39 techniques and processes to remedy the problem. Advanced oxidation processes,
40 such as photocatalysis, are a promising process for this application because of its
41 ability to mineralize many volatile organic compounds (VOCs) into CO_2 , H_2O and
42 other by-products (Malayeri et al., 2019; Talaiekhosani et al., 2021). The design of
43 the photocatalytic reactor for environmental applications, including air treatment, is
44 both a major and difficult task because of the different factors involved in the process
45 namely, the pollutant, the catalyst as well as the photon flux. (Boyjoo et al., 2017;
46 Sundar and Kanmani, 2020; He et al., 2021).

47 Among the continuous photocatalytic reactors are with front flow configurations. This
48 configuration, even if it is less developed in the laboratory, remains interesting
49 because it allows to have a compact reactor able to work at high flow rates by

50 promoting mass transfer whatever the contact time is sacrificed (Vuong., 2011;
51 Debono et al., 2018; Malayeri et al., 2021; Oliveira De Brito Lira et al., 2021). It is well
52 known that tangential flow reactors are most common in the literature, where the
53 residence times is longer but the limitation by mass transfer is more important
54 (Dalida and Ramoso, 2017; Sundar and Kanmani, 2020). For continuous flow
55 reactors, it is generally assumed that they operate under ideal plug flow
56 configuration, and for which, degradation rates are determined ignoring
57 dispersion/diffusion phenomena (Zhong et al., 2017; Salvadores et al., 2020). It has
58 even been reported that when the flow rate is high enough (turbulent flow regime)
59 and the length to diameter ratio of the reactor is significant, the axial dispersion is
60 minimal; therefore, the flow in the reactor can be considered as plug flow (Davis,
61 M.E. and R.J., 2012). The performance of the photocatalytic reactor is often
62 interpreted by two successive phenomena: the transport of the mass of pollutants to
63 the catalyst surface and their elimination by photocatalytic reaction. Most studies
64 (Amrheinet al., 2012; Malayeri et al., 2019) have assumed that the process is limited
65 by kinetic reaction and mass transfer is often ignored in photocatalysis studies, the
66 reason is that they try to focus more on the catalyst activity and its efficiency, even
67 though knowledge of the mass transfer phenomenon plays an essential role in
68 interpreting the experimental results and scaling-up the photocatalytic reactor.

69 In this study, the photocatalytic performance in a front flow reactor was highlighted for
70 the abatement of cyclohexane, which is defined as a reference for testing the
71 effectiveness of type "A" gas filters (INRS., 2011, 2019; Vuong., 2017; Chauveau,
72 2018). The aim is to establish a kinetic analysis, which presents a powerful tool for
73 the evaluation of the catalytic properties of the experimental device and the reaction
74 rate in the photocatalytic oxidation process. This is done by determining the main
75 factors affecting the catalytic performance or the kinetic parameters of the

76 photoreaction, namely the adsorption capacity and the oxidation capacity of the
77 photocatalysts. Langmuir-Hinshelwood (L-H) model, which remains the most widely
78 used kinetic expression, was adopted to formulate the rate of reaction.

79 The novelty of this study is the development of a model, which considers both the
80 aerodynamic of the flow through the residence time distribution (RTD) determination and
81 the mass transfer limitations. Since the relative humidity influences the efficiency of
82 the photocatalytic process, it was therefore essential to consider water molecules in
83 the expression of the reaction rate. Consequently, the Langmuir-Hinshelwood (L-H)
84 biomolecular model was developed to consider the effect of competitions.

85 **2. Materials and methods**

86 In this part, the various commercial catalytic supports used as well as the polluted air
87 generation systems adopted, then the air treatment devices, the analytical
88 techniques, the methodology used are exposed

89 **2.1. Photocatalytic support**

90 The photocatalytic support used is supplied by the Ahlstrom company under the
91 reference Alhström 1049. It is a non-woven fabric made of synthetic and natural
92 cellulose fibers, where a winding press process has been used to coat them with a
93 mixture of TiO_2 and SiO_2 , whose masses per square meter are equal to 16 and 13.3
94 g m^{-2} respectively. The colloidal silica used has a specific surface area of about 700
95 $\text{m}^2 \text{g}^{-1}$, with elementary particles of 20-30 nm in diameter. It acts as an inorganic
96 binder, resistant to UV radiation and photocatalysis, transparent to UV and protecting
97 the TiO_2 fibers. The TiO_2 used for this deposit is a PC-500, marketed by Millennium.
98 The elemental crystals are between 5 and 10 nm in size, with an anatase crystal
99 structure (> 99%) and an S_{BET} surface area of approximately $320 \text{ m}^2 \text{g}^{-1}$. The energy
100 dispersive X-ray (EDX) technique (Fig. S1) allows the determination of elemental

101 composition of the cellulose media by highlighting these different elements such as:
102 titanium and oxygen, aluminum was a residual compound from the mechanical
103 processing of the textiles, and silicon corresponded to the silica deposit.

104 **2.2. Pollutant studied**

105 The cyclohexane used is supplied by Sigma-Aldrich in liquid form (purity > 98%). It is
106 then volatilized to obtain the desired gas concentrations. Its main characteristics are
107 given in Table S1.

108 **2.3. Reactor and experimental set-up**

109 **2.3.1. Batch reactor**

110 The batch reactor is shown in Fig. S2 and contains a central tube for the lamp and
111 ports for sampling/analysis. It is approximately 40 cm high and has a volume of 1.5 L.
112 The catalytic support, with a surface area of 81 cm², giving a mass of TiO₂ of 0.13 g,
113 is deposited on inner wall of the reactor. To generate pollution in the reactor, the
114 pollutant is injected as liquid drops which then evaporate. A magnetic stirrer and a
115 magnetic barrel make it possible to homogenize the gases. The fluorescent UV lamp
116 (Philips PL-L 24W/10/4P) used is purchased from Lum'On (France). This lamp has a
117 wavelength spectrum of 310-390 nm with a maximum of UV intensity at 365 nm. A
118 VLX-3W radiometer equipped with a CX-365 cell is used to measure UV intensity.

119 A control system based on oxygen analyzer, temperature, humidity and CO₂ sensors
120 was installed on the batch reactor. These sensors were connected to an Arduino
121 board allowing online acquisition of experimental data.

122 **2.3.2. Continuous process**

123 The front flow photocatalytic reactor (P50) illustrated in Fig. 1 is formed by four
124 mountable stainless-steel test chambers with a passage section of 0.01 m² and a

125 total volume of about 4 L. The first part is used for the main inlet of the flow of water
126 vapor, air, injection of pollutants, and sampling for analysis before handling. The
127 second part contained four photocatalytic media (4 m x 0.01 m of surface giving 0.64
128 g of TiO₂) and two Philips UV-A lamps (model PLS 9W / 10). The intensity of the light
129 incident at 365 nm on the surface of the catalyst is 20 W m⁻². The last element allows
130 the sampling for analysis after treatment and the exit of the air flow. The air leaving
131 the reactor is evacuated under a hood.

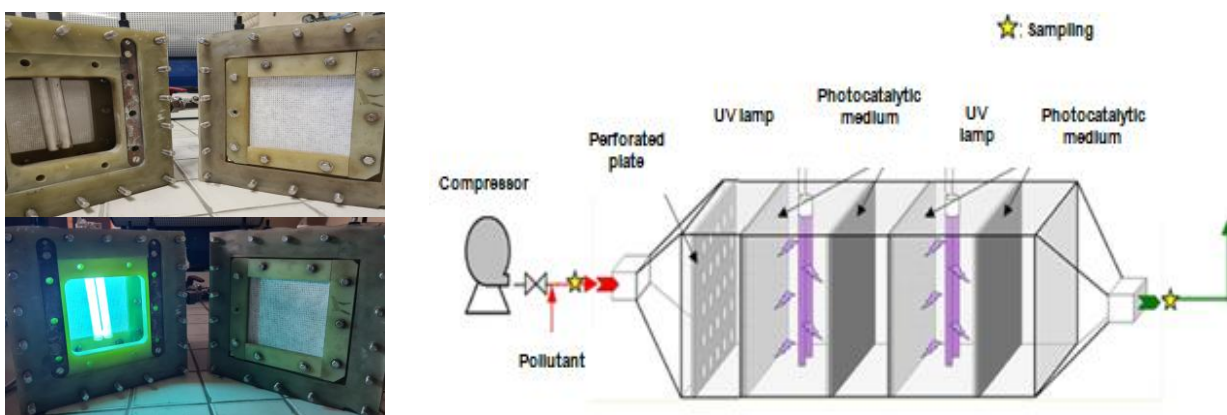


Figure 1: Photo and Schematic of P50, front flow continuous photocatalytic reactor

132

133 2.3.2.1. Experimental setup

134 The dry air coming from the network is the carrier gas, controlled by a valve and
135 estimated using a Gallus G4 gas meter of the Itrón brand. The flow rates tested is
136 equivalent to human respiratory flow rates 13, 18 and 36 L min⁻¹. These flow rates
137 correspond to contact times of 18, 13 and 7 ms respectively. To humidify the air, a
138 bubbler was installed in the circuit containing water to achieve humidity ranges of 30-
139 90%. The pollutant is injected continuously in liquid form by a syringe / syringe pump
140 combination. A heating tape, placed in the injection zone to facilitate the volatilization
141 of the pollutant and a static mixer makes it possible to homogenize the effluent
142 upstream of the photoreactor. Two septas downstream and upstream of the

143 photoreactor make it possible to sample the outlet and inlet gas with a syringe (Fig.
144 S3).

145 **2.3.2.2. Analytic tools**

146 The concentration of cyclohexane was measured by a Thermo electron corporation
147 gas chromatography (Focus GC) using a flame ionization detector (FID) and an
148 FFAP column (length = 25 m and internal diameter = 0,32 mm). Nitrogen was used
149 as a carrier gas. The temperature conditions of the oven, the injection chamber and
150 the detector were, respectively, 50, 190 and 190 °C. The analysis was performed by
151 direct manual sampling with a 500 µl syringe and injection into the GC. The
152 calibration was carried out by evaporating different quantities of cyclohexane on a
153 closed bottle. The correlation of the pollutant with a peak area of GC-FID as a
154 function of its concentration was carried out. Operation is done by Azur™ software.

155 The CO₂ was analyzed by a Fourier transform infrared spectrophotometer (FTIR)
156 from Environment SA (MIR 9000H).

157 The overall rate of photocatalytic degradation is an important factor in evaluating
158 VOC's removal performance. VOC's removal efficiency is defined:

$$159 \quad RE (\%) = \frac{[VOCs]_{in} - [VOCs]_{out}}{[VOCs]_{in}} 100 \% \quad (1)$$

160 The overall rate of photocatalytic degradation of cyclohexane is calculated as:

$$161 \quad r = \left(\frac{Q}{S}\right) \left(\frac{[VOCs]_{in}}{100}\right) RE (\%) \quad (2)$$

162 Where $[VOCs]_{in}$ and $[VOCs]_{out}$ are respectively the inlet and outlet pollutant
163 concentration (mM m⁻³), Q is the volumetric flow rate (L min⁻¹) and S the mean
164 surface of the support (m²).

165 The overall selectivity of CO₂ can be a useful parameter in evaluating the
166 performance of the photocatalytic reactor with respect to the removal of VOCs. It
167 makes it possible to estimate the rate of mineralization, that is to say the final
168 reaction step of the process. The global selectivity of CO₂ is expressed as follows

$$169 \quad S_{CO_2} (\%) = \frac{[CO_2]_{out} - [CO_2]_{in}}{N_c RE (\%) [VOCs]_{in}} 10^4 \quad (3)$$

170 Where [CO₂]_{in} and [CO₂]_{out} refer respectively to the concentration of carbon dioxide at
171 the air inlet and outlet (mM m⁻³). The number N_c represents the stoichiometric
172 coefficient of the overall degradation reaction (in our case, it is equal to 6).

173 **2.3.2.3. Experimental procedure**

174 With batch reactor, different amounts of pollutants are injected in liquid form with a
175 syringe. The stirrer is turned on and the reactor is covered with an opaque bag.
176 When adsorption equilibrium is reached (approximately 30 min), the UV lamp is
177 turned on and samples are taken regularly (every 5 min), to monitor changes in
178 concentrations. The samples are taken with a 500 µl syringe and are directly
179 analyzed by gas chromatography with flame ionization detection.

180 Concerning the P50, once the adsorption process reaches equilibrium (depending on
181 the concentration), as indicated by an identical input / output Volatile Organic
182 Compound concentration, the UV lighting is turned on, a transient period precedes a
183 steady state phase which is established when the concentration of pollutant at the
184 outlet becomes constant.

185 After completing the experiments, the reactor is rinsed under UV lighting for 1 h in
186 ambient air. No deactivation observed during the entire operating time.

187 **3. Results and discussions**

188 **3.1.1. Photocatalytic kinetic degradation with using the batch reactor**

189 The performance of the TiO₂ on cellulosic media was investigated in terms of
190 degradation efficiency, degradation and elimination rates at different pollutant
191 concentrations and UV intensity.

192 Fig. 2a and 2b show the evolution of the concentrations of cyclohexane during
193 photocatalytic reactions under different UV irradiations as a function of time at
194 different input concentrations. From Fig. 2a and by comparing the degradation rate
195 for the different input concentrations at about 20 min. It is observed that the
196 degradation rate decreases proportionally as the initial concentration increases (from
197 70% for 1.78 mM m⁻³ to 52.5% for 6.53 mM m⁻³). The same trend is always observed
198 when UV intensity is higher (Fig. 2b). This can be interpreted by the unavailability of
199 active sites (Elfalleh et al., 2017).

200 The results show that at low input concentration, degradation follows pseudo-first
201 order kinetics where degradation is proportional to the input concentration. This can
202 be explained by the fact that all the active sites are not occupied and an increase in
203 the concentration generates a higher surface coverage which implies a better rate of
204 degradation. It also means that the chemical reaction is the limiting step in the
205 process. The results show that light intensity is also an important parameter, which
206 influences the performance of photocatalytic processes. Indeed, the increase in UV
207 intensity seems to be significant on the generation of the active site (Herrmann, 2010;
208 Palau et al., 2012). This can be explained by the fact that as the UV intensity
209 increases, the number of photons hitting the surface of the photocatalyst can
210 increase and lead to more electrons and holes (Brosillon et al., 2008; Assadi et al.,
211 2014).

212 Thus, the results show a similar behaviour to what is reported in the literature with
 213 other pollutants such as toluene, decane and trichloroethylene (TCE) (Debono et al.,
 214 2017), Ethylene (Stroe and Rosendahl, 2019), also 2,3-butane-dione (Abidi et al.,
 215 2020).

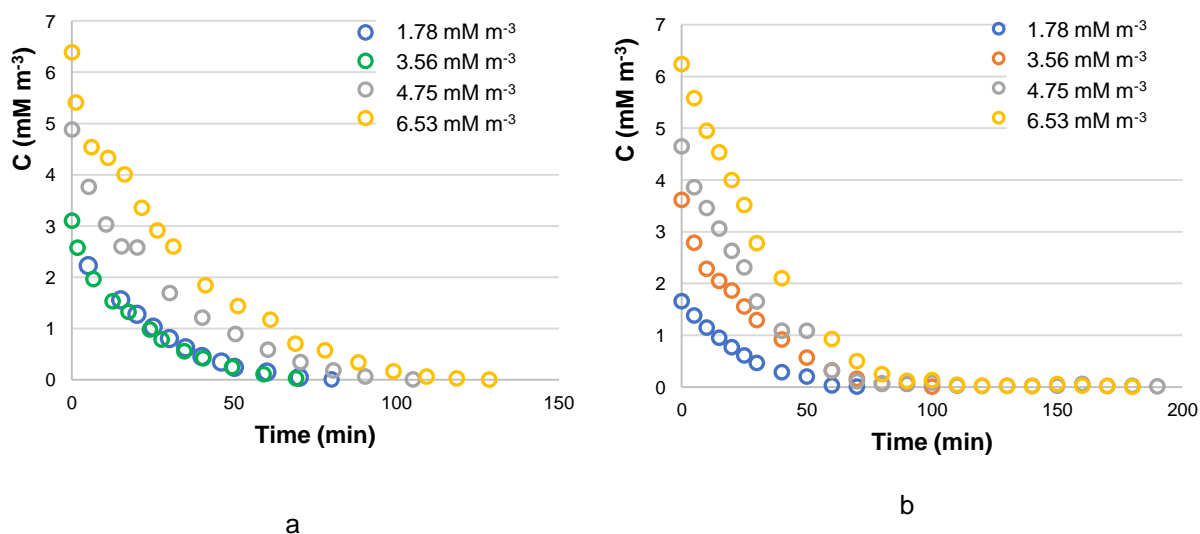


Figure 2: Kinetics of cyclohexane degradation in a batch reactor at: (a) UV intensity = 1.5 W m^{-2} and
 (b) UV intensity = 12 W m^{-2}

216
 217 The degradation kinetics are generally represented by Langmuir – Hinshelwood (L-H)
 218 model. The latter is defined by the following equation at initial degradation rate (Abidi
 219 et al., 2020) .

$$r_0 = \frac{kK C_0}{1 + K C_0} \quad (4)$$

$$\text{Or } \frac{1}{r_0} = \frac{1}{kK C_0} + \frac{1}{k} \quad (5)$$

222 where r_0 is the initial reaction rate ($\text{mM m}^{-3} \text{ s}^{-1}$), k the reaction rate constant
 223 ($\text{mM m}^{-3} \text{ s}^{-1}$) et K is the adsorption constant ($\text{m}^3 \text{ mM}^{-1}$).

224 Initial reaction rate can be obtained from the initial slope of the curve $C=f(\text{time})$ where
225 the influence of by-products is supposed to be negligible. The results are shown in
226 Fig. S4.

227 By plotting $r_0^{-1} = f(C_0^{-1})$ (Fig. S5) and from the values of the slope and the intercept,
228 the value of the Langmuir-Hinshelwood constants for the two intensity were
229 determined and summarized in table S2.

230 The results showed that the increase in light intensity leads to a faster elimination of
231 the VOC, reflected by an increase in the kinetic constant from 0.0027 to 0.0051
232 $\text{mM m}^{-3} \text{ s}^{-1}$ for $I = 1.5$ and 12 W m^{-2} respectively. It is well known that the degradation
233 rate is linked to the activation of the catalyst. A power relation law is usually used
234 ($k_{\text{app}} = k_0 \cdot I^\alpha$) where α is around 0.5 for intermediate intensities. In our case α seems
235 to be equal to 0.25. This is mainly due to the recombination of the e^- / h^+ pairs versus
236 charge transfer. (Brosillon et al., 2008; Queffeulou et al., 2010; Assadi et al., 2014).

237 **3.1.2. Photocatalytic degradation mechanism of cyclohexane**

238 There is still a need to identify intermediate products of photocatalytic degradation
239 that could be a potential tool to explore the intrinsic kinetics of photocatalytic
240 oxidation. The literature has shown that the gaseous by-products of cyclohexane
241 degradation cannot be identified by GC analysis (Geng et al., 2013). To identify them,
242 other methods have been used where it has been shown that the main degradation
243 intermediates are cyclohexanol and cyclohexanone and the final degradation
244 products are water and CO_2 (Selishchev et al., 2012; Geng et al., 2013; Sannino et al.,
245 2013).

246 From the above works, a follow-up experiment to monitor the removal of
247 cyclohexane. (millimole per cubic meter), accumulation of CO_2 (millimole per cubic

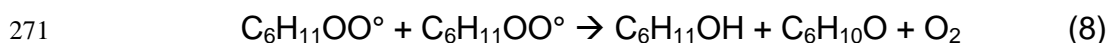
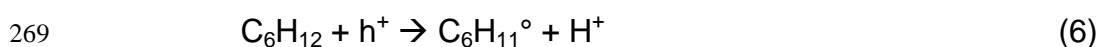
248 meter) and H₂O (absolute humidity 'grams per cubic meter of air') in the batch reactor
249 was performed. The results are shown in Fig. S6.

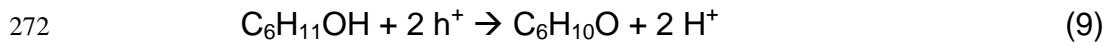
250 The results show that when the UV lamp is tuned ON and the photocatalytic process
251 start, a clear change in the amount of CO₂ and H₂O formed in proportion to the
252 degradation of cyclohexane is observed.

253 The result of the balance between the quantity of CO₂ formed at the end of the
254 degradation process ([CO₂]_{Formed} = 130.1 mM m⁻³) relative to the concentration of
255 Cyclohexane introduced initially ([Cyclohexane]_{initial} = 23.3 mM m⁻³), shows that 1
256 mole of Cyclohexane gives an equivalent of 6 moles of CO₂. This carbon balance
257 corresponds to the stoichiometric number of Cyclohexane.

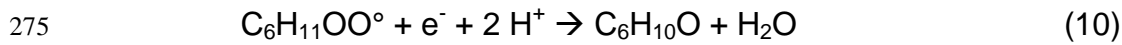
258 The carbon balance was naturally accompanied by an evolution of the quantity of
259 H₂O from 7.8 g m⁻³_{air} up to 13.45 g m⁻³_{air} which makes an equivalent production of
260 5.65 g m⁻³_{air} of Water. It should be noted that the quantity of O₂ was
261 sufficient throughout the degradation process.

262 The results are also consistent with the literature (Zhong et al., 2015; Xu et al., 2022,
263 2021) regarding the degradation mechanism of cyclohexane. Where initially
264 cyclohexane is oxidized by h⁺ to produce cyclohexyl radicals (C₆H₁₁[°]) (Eq. 6). the
265 latter react with O₂ to produce a peroxy radical (C₆H₁₁OO[°]) (Eq. 7). The reaction of
266 the peroxy radicals (C₆H₁₁OO[°]) (Eq. 8) produces cyclohexanone (C₆H₁₀O) and
267 cyclohexanol (C₆H₁₁OH) which will be oxidized by h⁺ in turn to produce
268 cyclohexanone (Eq. 9).

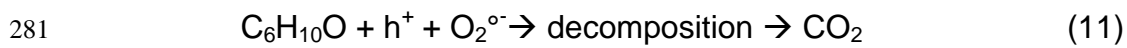




273 Cyclohexanone is also produced via the reduction of the radical $\text{C}_6\text{H}_{11}\text{OO}^\circ$ by e^- . This
274 reaction is accompanied mainly by the production of water (Eq. 10).



276 After all the steps of cyclohexanone production, it is then decomposed to CO_2 . Even
277 though the detailed decomposition mechanism is not yet clear, our results fit perfectly
278 with the one suggested by the literature (Shiraishi et al., 2017) where h^+ and the
279 reaction with $\text{O}_2^{\circ-}$ are involved in the oxidation mechanism of cyclohexanone (Eq.
280 11).



282 **3.2. Photocatalytic degradation in continuous reactor**

283 **3.2.1. Effect of flow rate and inlet concentration**

284 The inlet concentration of cyclohexane is varied between 0.29 and 1.78 mM m^{-3} , in
285 order to understand its influence on the performance of the photocatalytic reactor.

286 The removal efficiency of cyclohexane at different input concentrations with different
287 flow rates is shown in Fig. 3.

288

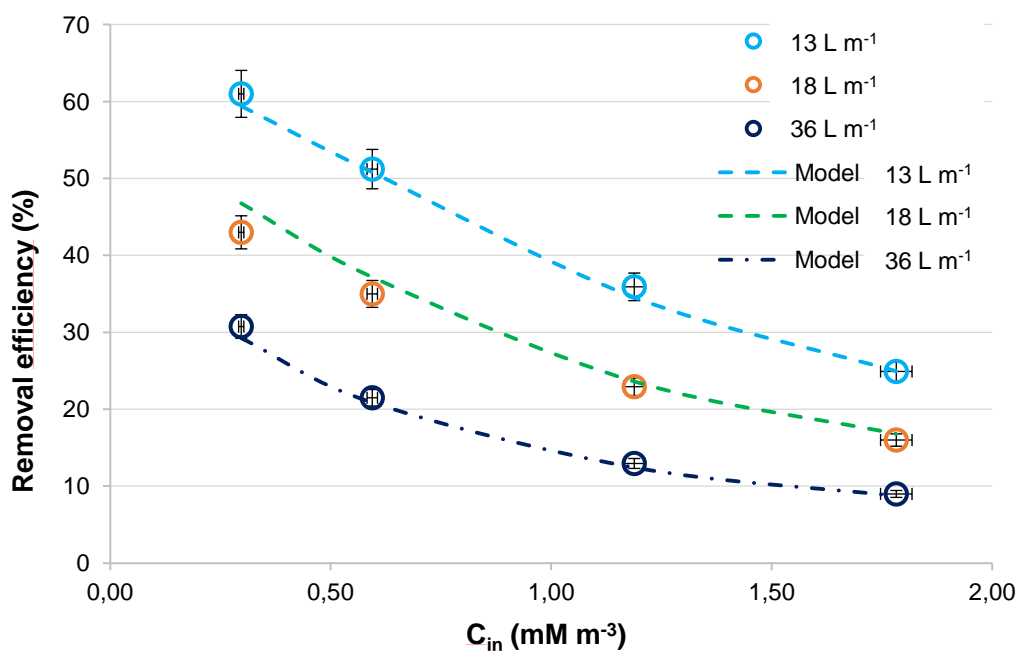


Figure 3: Influence of the inlet concentration and the flow rate on the elimination of cyclohexane ($HR = 5\%$, $UV\ Intensity = 20\ W\ m^{-2}$, $T = 20 \pm 2\ ^\circ C$). Model taking into account the mass transfer step

289

290 For a given flowrate, at a higher concentration of pollutants, the rate of degradation
 291 will tend towards a limit ($RE \sim 9\%$ for $1.78\ mM\ m^{-3}$), which may be linked to a
 292 limitation by the chemical reaction step due to the unavailability of active sites (Abou
 293 Saoud et al., 2017, 2018). It can also be noted that the removal efficiency of
 294 cyclohexane decreases with increasing flow rate, this is due to a reduction in the
 295 contact time between the compound and the catalytic active sites. in line with what
 296 was obtained when studying the impact of residence time on the removal efficiency of
 297 Methyl Ethyl Ketone (MEK) and toluene (Mamaghani et al., 2018), also, Propionic
 298 acid and Benzene (Zadi et al., 2020).

299 3.2.2. Effect of relative humidity

300 In order to study the effect of relative humidity on the efficiency of continuous
 301 photocatalysis with the P50 reactor, it was necessary to apply a relative humidity

302 range between 5 % and 87 % at 20 ± 2 °C under the same concentrations mentioned
 303 above. The variation in the elimination efficiency of cyclohexane at different inlet
 304 concentrations and under different relative humidity is illustrated in Fig. 4.

305

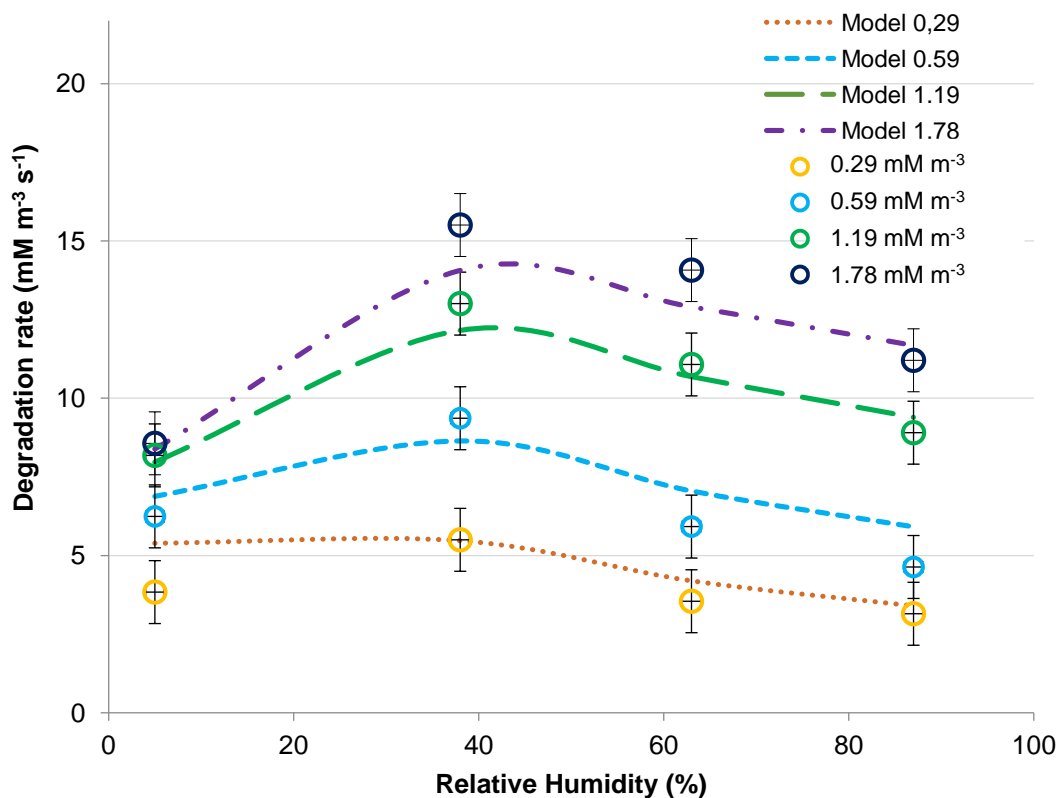


Figure 4: Influence of relative humidity on the elimination of cyclohexane and the Bimolecular model curves ($Q = 18 \text{ L min}^{-1}$, $UV \text{ intensity} = 20 \text{ W m}^{-2}$, $T = 20 \pm 2$ °C).

306

307 Firstly, the elimination efficiency of cyclohexane increases with increase of relative
 308 humidity, which could be explained by the generation of hydroxyl radicals. An
 309 optimum is observed, and thus a permanent decrease in the elimination efficiency
 310 occurs. In fact, the more the humidity increases, the more there is deactivation of the
 311 active sites of the catalyst due to competitive adsorption on the active sites of the

312 catalyst between the molecules of water vapor (H₂O) and Cyclohexane (Chen et al.,
313 2011; Vandenbroucke et al., 2011; Zadi et al., 2020; Zhang et al., 2020).

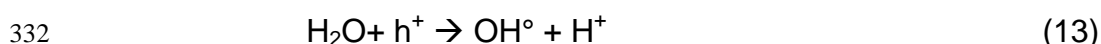
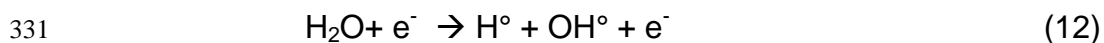
314 3.2.3. Selectivity of CO₂

315 Fig. 5a shows the dependence of the selectivity versus the inlet concentration of
316 Cyclohexane. As expected the input concentration exerts a significant influence on
317 the amount of CO₂ Selectivity, which decreases by increasing the concentration of
318 the pollutant. This is due to the fact that there is less availability of active sites on the
319 surface of the photocatalyst.(Assadi et al., 2014; Zadi et al., 2020). This behaviour
320 also confirms that the process is limited by the availability of active sites.

321 The increase of the inlet gas flow rate leads also to a decrease in mineralization rate
322 (Fig.5b). This can be explained by the fact that the contact time is insufficient which
323 will not allow by-products to be degraded. Moreover the competitive phenomena of
324 the by-products formed towards the active sites reduces the selectivity (Assadi et al.,
325 2012).

326 Under humid conditions (Fig. 5c), it's clearly voiced the influence of humidity on the
327 CO₂ selectivity for an inlet concentration of 1.78 mM m⁻³ where (i) the rate of
328 mineralization increases from 22.2% to 34.2% when RH increases from 5 to 38%.

329 This improvement is due to the increase in water molecules which helps generate
330 OH° hydroxyl radicals (according to Eq. (12) and (13)).



333 (ii) On the other hand, a decrease in the selectivity is observed (29.3% compared to
334 34.2%) when RH varies from 38 to 63%). This is due to competition between Water

335 vapor / Cyclohexane on the surface of the catalyst. These results are in agreement
 336 with those reported by literature concerning the oxidation of some VOCs (Assadi et
 337 al., 2013; Martinez et al., 2014; Zadi et al., 2018).

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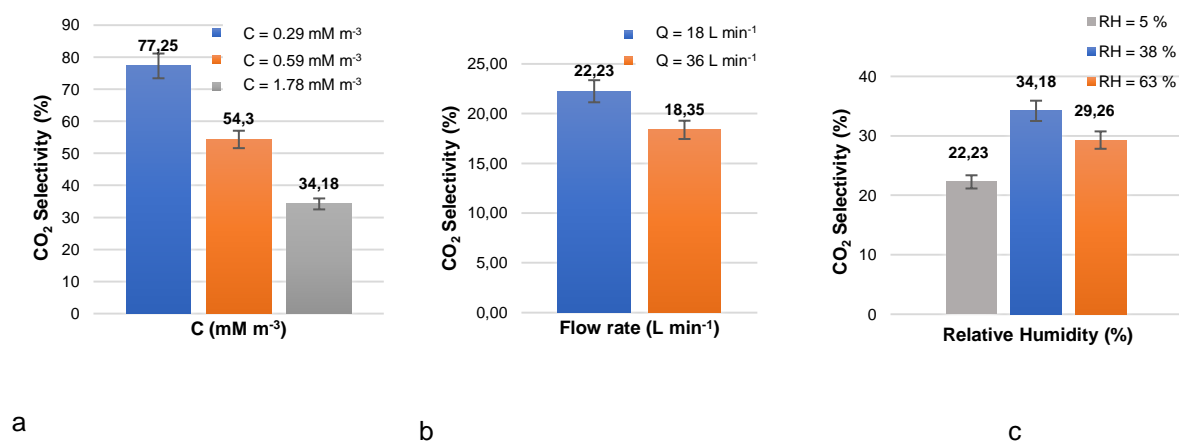


Figure 5: Variation of the CO₂'s selectivity (%) with a) the Inlet concentration of Cyclohexane (Q = 18 L min⁻¹, RH = 38 ± 2 %, UV intensity = 20 W m⁻², T = 20 ± 2 C°), b) the flow rate (C = 1.78 mM m⁻³, HR = 5 %, intensity = 20 W m⁻², T = 20 ± 2 C°) and c) at different Relative Humidity (C = 1,78 mM m⁻³, Q = 18 L min⁻¹, UV intensity = 20 W m⁻², T = 20 ± 2 C°)

339

3.2.4. Modeling of degradation kinetics and influence of mass transfer, comparison between the constants with batch reactor

342 The objective of the following part is to propose a model to describe the experimental
 343 observed kinetics. This kinetic model will consider the surface reaction and mass
 344 transfer step. The degradation kinetics of monocomponents in heterogeneous
 345 photocatalytic treatments is often represented by the Langmuir - Hinshelwood model
 346 (Queffeulou et al., 2010; Assadi et al., 2015; Muñoz-Batista and Luque, 2021)

347 Firstly, the aerodynamic conditions of the P50 reactor have to be determined.

348 A residence time distribution (RTD) experiment was performed. To characterize the
349 gas flow pattern in the photoreactor, and in order to simulate the pulse function (Dirac
350 delta function) a tracer (carbon dioxide) was injected for a very short time interval (
351 Gao et al., 2012; Bérard et al., 2021; Rodrigues, 2021). The output CO₂
352 concentration is measured using an infrared sensor connected to an Arduino board
353 allowing direct reading as a function of time on a PC. The stock model tanks were
354 used to describe the response of the system. RTD experiments revealed that our
355 flow-through reactor can be likened to a cascade of 18 elementary continuously
356 stirred tank reactors (Fig.S7). Thus our experimental reactor can be considered as a
357 plug flow reactor (Jafarikojour et al., 2014).

358 **3.2.4.1. Model without mass transfer**

359 In this part, only the surface reaction step is considered, that is to say that the mass
360 transfer is neglected, to describe the gas-solid phase reaction for heterogeneous
361 photocatalysis. Assuming that the mass transfer is not the limiting step and that the
362 effect of the intermediate product is negligible, then the reaction rate can be
363 expressed as:

$$364 \quad r = k \frac{KC}{1+KC} \quad (14)$$

365 Where r is the degradation rate ($\text{mM m}^{-3} \text{s}^{-1}$), K is the adsorption constant
366 ($\text{m}^3 \text{mM}^{-1}$), k is the reaction constant (with the same unit as the rate of degradation),
367 and C is the concentration of the contaminant (mM m^{-3}). In such a model, the
368 adsorption and desorption steps are kinetically negligible compared to the oxidative
369 reaction step. The pollutant adsorption rate is greater than any by-product adsorption
370 rate and the binding products do not interact with each other or modify the initial
371 activity of the reactive sites.

372 The reactor is plug flow in a stationary state, the continuous degradation of pollutants
373 along the axial direction should not be ignored. The continuity equation for a
374 contaminant is written:

$$375 \quad u \frac{dC}{dz} = -r \quad (15)$$

376 where z represents the axial position in the photoreactor. After rearrangement,
377 integration of Eq. (15) for the entire length of the reactor L leads to (Queffeuilou et al.,
378 2010; Assadi et al., 2015):

$$379 \quad \frac{\ln(C^{in}/C^{out})}{C^{in}-C^{out}} = \frac{k_{app}KL}{u} \frac{1}{C^{in}-C^{out}} - K \quad (16)$$

380 Where u is the superficial velocity of the gas (m s^{-1}). The L-H constants k and K are
381 determined by fitting the results for each flow and contaminant with the linear
382 equation. The cross-correlation coefficient is defined as the covariance of the pair k
383 and K divided by the standard deviation of each parameter k and K (Table S3 and
384 Fig. S8).

385 The model correlates quite well with the experimental data. However, and despite a
386 high R^2 , the values of k and K with this frontal flow reactor vary by varying the flow
387 rate. This variation is less significant compared to the results obtained with tangential
388 reactors, in particular those obtained during the study of (Assadi et al., 2012),
389 whether in the treatment of trimethylamine in an annular reactor or for the treatment
390 of isovaleraldehyde with annular and planar reactors (Assadi et al., 2016) where it
391 has been shown that the mass transfer was more important. This does not prevent
392 the conclusion of the dependence of these constants on the flow rate. Therefore, it
393 seems more appropriate to propose a new model where the mass transfer step is
394 considered.

395

396

397 **3.2.4.2. Model with mass transfer step**

398 The limitation of the internal mass transfer step is not considered due to superficial
399 reaction sites (Vincent et al., 2008; Assadi et al., 2012; Palau et al., 2012; Assadi et
400 al., 2013; Assadi et al., 2015; Costa et al., 2017). Therefore, only the external mass
401 transfer is considered. Thus, the mass transfer constant k_m which depends only to
402 the flow regime is considered.

403 The overall mass balances of the pollutant on the solid and gas phases in a
404 continuous piston reactor leads to the following equations (Yang et al., 2007;
405 Queffeuilou et al., 2010; Assadi et al., 2016):

406 In the gas phase:

$$407 \quad u \frac{dC}{dz} + k_m a_v (C - C^s) = 0 \quad (17)$$

408 In solid phase:

$$409 \quad k_m a_v (C - C^s) = \frac{k_{app} K C^s}{1 + K C^s} \quad (18)$$

410 where C and C^s are respectively the gas phase concentrations of the overall and
411 average surface area of VOC (mM m^{-3}), k_m is the mass transfer coefficient (m s^{-1})
412 and a_v is the average surface area per unit volume of the reactor ($\text{m}^2 \text{m}^{-3}$).

413 The mass transfer term k_m can be estimated by semi-empirical Williamson
414 expression. Correlation used exclusively for frontal flow (Petit., 2007; Vuong., 2011):

$$415 \quad k_m = 0.44 u Re^{-0.31} Sc^{-0.58}, \text{ if: } 125 \leq Re \leq 5000 \quad (19)$$

416 Where ($Sc = \frac{\mu}{\rho D_{mol}}$) and ($Re = \frac{d \rho u}{\mu}$) are Schmidt and Reynolds numbers,
 417 respectively. With the dynamic viscosity of the gas μ (Pa s), the gaseous density ρ
 418 (kg m^{-3}) and the equivalent diameter d (m).

419 The molecular diffusion coefficient D_{mol} is necessary for the calculation of the
 420 Schmidt number. In the case of gas phase applications, the Fuller, Schettler and
 421 Giddings relationship has been used. (Perry., 1997).

$$422 \quad D_{mol} = \frac{10^{-3} \sqrt{\frac{M+29}{M \cdot 29}}}{(20,1^{1/3} + V_m^{1/3})^2} \frac{T^{1,75}}{P_{atm}} \quad (20)$$

423 where P is the pressure of the gas flow (Pa), T the absolute temperature (K). V_m is
 424 the molecular volume of the gas ($\text{m}^3 \text{M}^{-1}$), and M is the molecular mass of the
 425 pollutant (g M^{-1}). The molecular diffusion coefficient D_{mol} is $0.0509 \text{ cm}^2 \text{ s}^{-1}$.

426 The key values are summarized in Table S4.

427 The Reynolds number varies from 1500 to 4600 for flow rates varying from 13 to 36
 428 L min^{-1} respectively. The flow regime thus confirms that the mass transfer step may
 429 be considered.

430 To solve Eq. (17) and (18), Maple software is used to develop a system under the
 431 series method. In addition, it was established that the second-order development is
 432 sufficiently precise (Assadi et al., 2013; Abidi et al., 2021). In the Eq. (21), the two
 433 unknown parameters are k and K . They are determined by numerical resolution with
 434 the Excel Solver.

$$435 \quad C^{in} - C^{out} = \frac{Lk_m a_v}{2u} \left[C^{in} + \frac{1}{K} + \frac{k}{k_m a_v} - \sqrt{\left(-C^{in} + \frac{1}{K} + \frac{k}{k_m a_v} \right)^2 + \frac{4C^{in}}{K}} \right] \quad (21)$$

436 The model allows a good description of the experimental results (Fig. 3 and 6). The
 437 obtained values of k and K are respectively $0,025 \text{ mM m}^{-3} \text{ s}^{-1}$ and $7,122 \text{ m}^3 \text{ mM}^{-1}$.
 438 Obviously, when transfer is neglected, the reaction rate constant (k) is slightly
 439 overestimated. Instead, the adsorption constant (K) is underestimated.
 440

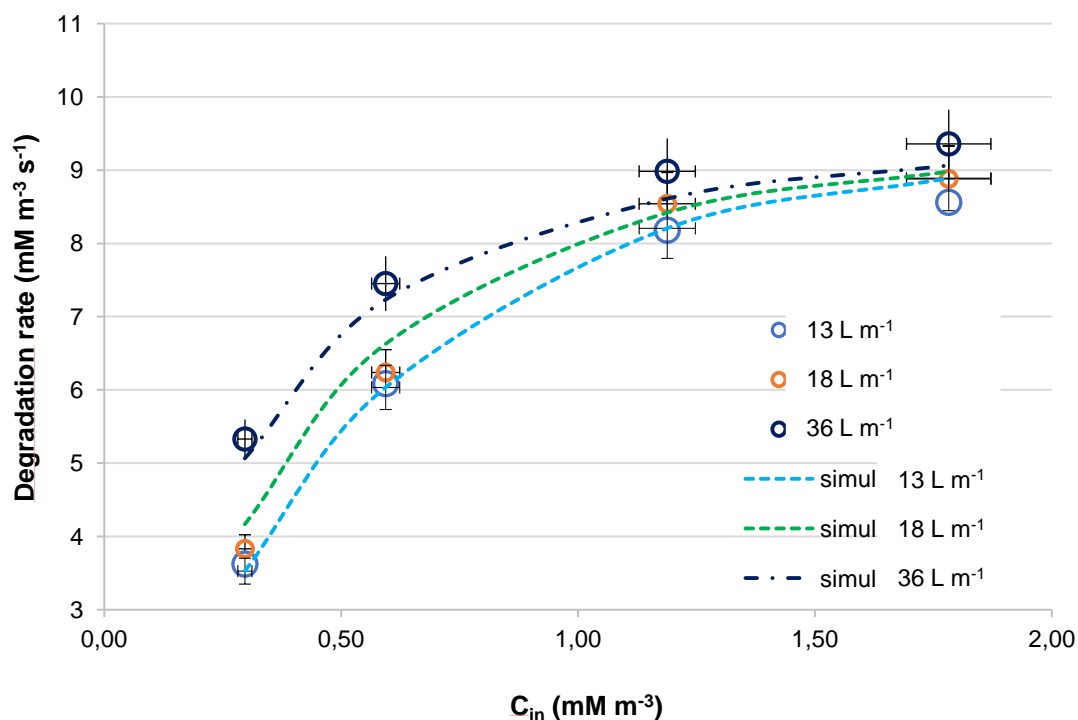


Figure 6: Influence of the inlet concentration and the flow rate on the degradation rate of cyclohexane ($Q = 18 \text{ L min}^{-1}$, $UV \text{ intensity} = 20 \text{ W m}^{-2}$, $T = 20 \pm 2 \text{ }^\circ\text{C}$). Model taking into account the mass transfer step

441
 442 In addition, it is interesting to note that these constants are not flow dependent. The
 443 influence of the flow regime is fully integrated by the k_m parameter. Indeed, the
 444 separation between the mass transfer and the chemical reaction steps is obtained. It
 445 is also noted that the constants determined in this study depend mainly on the
 446 geometry of the reactor, taking into consideration the hydraulics of the flow of the
 447 pollutant stream. (Qiao et al., 2012; Assadi et al., 2013; Abidi et al., 2021).

448 It can also be noted that unlike the effect of the flow rate on the pollutant removal
 449 efficiency, when the flow rate increases, the mass transfer rate increases between
 450 the gas and the surface of the photocatalyst, which leads to an increase in the
 451 reaction rate (Assadi et al., 2013).

452 Taking into consideration the amount of the catalyst (TiO₂) in the process of
 453 Cyclohexane treatment in the batch reactor and the continuous reactor P50 under
 454 the same UV intensity, the kinetic constants (k) can be compared, knowing that for
 455 the continuous reactor the mass transfer step has to be considered.

456 The Values of kinetic constants determined with L - H model in batch (0.13 g_{TiO2}) and
 457 continuous reactor P50 by considering Mass transfer (0.64 g_{TiO2}) are 0.0392 mM m⁻³
 458 s⁻¹ m_{TiO2}⁻¹ and 0.0391 mM m⁻³ s⁻¹ m_{TiO2}⁻¹, respectively. These constants are of the
 459 same order. This means that the mass transfer step is negligible for batch reactor
 460 due to good homogeneity of the gas phase (mixing). It's obviously shown that model
 461 taking account the mass transfer step, allows the access to the real reaction kinetics.

462 3.3. Effect of the relative humidity on the degradation rate

463 To correlate the experimental data, the Langmuir - Hinshelwood bimolecular model
 464 can be used (L. Zhang et al., 2020), considering the VOC-Water system as a binary
 465 mixture. The degradation kinetics can be expressed by:

$$466 \quad r_A = k_A F_A F_w \quad (22)$$

$$467 \quad \text{Where} \quad F_A = \frac{K_A C_A}{(1 + K_A C_A + K_W C_W)} \quad (23)$$

$$468 \quad \text{and} \quad F_w = \frac{K'_W C_W}{(1 + K'_A C_A + k K'_W C_W)} \quad (24)$$

$$469 \quad \text{therefore} \quad r_A = k_A \frac{K_A C_A}{(1 + K_A C_A + K_W C_W)} \times \frac{K'_W C_W}{(1 + K'_A C_A + k K'_W C_W)} \quad (25)$$

470 Where C_w is the concentration of water vapor, K_w is the Langmuir adsorption
 471 constant of water, K'_A et K'_w are respectively the competitive adsorption constant of
 472 the pollutant and water. Constants k_A and K_A are taken from the previous study,
 473 where the mass transfer was considered under dry air conditions.

K'_A ($m^3 \text{ mM}^{-1}$)	0,011
K'_w ($m^3 \text{ mM}^{-1}$)	0,0133
K_w ($m^3 \text{ mM}^{-1}$)	0,0129
R^2 (%)	99

474

475 *Table 1: Values of kinetic constants determined with the bimolecular model L – H*

476 All model constants are determined numerically using the Excel solver. The
 477 Langmuir-Hinshelwood bimolecular model Eq. (25) correlates well the experimental
 478 results and that the validity of this approach is confirmed (Table 1, Fig. 4).

479 The result shows an optimum humidity for photocatalytic degradation at about 35-
 480 45% at different input concentrations. This result is similar to that obtained with our
 481 previous works on isovaleraldehyde, trimethylamine, chloroform and glutaraldehyde (
 482 Assadi et al., 2012; Abidi et al., 2021), even on BTEX compounds (Martinez et al.,
 483 2014) as well as Methyl Ethyl Ketone (Malayeri et al., 2021).

484 **4. Conclusion**

485 The elimination of cyclohexane was studied in two reactors: batch and continuous
 486 reactor. The influence of the inlet concentration and the flow rate on the performance
 487 of the reactor was studied. The increase in these two parameters leads to a decrease
 488 in the efficiency of conversion and elimination of the pollutant. On the other hand, the
 489 complex effect of relative humidity on the elimination of Cyclohexane has been

490 studied. The presence of water vapor is beneficial at moderate concentrations due to
491 the formation of OH• radicals which contribute to increased degradation.
492 Moreover, the influence of mass transfer was estimated by testing two models based
493 on the Langmuir-Hinshelwood approach. With considering the limitation of mass
494 transfer, the constants are more realistic and not dependent on flow rates. A
495 bimolecular L-H kinetic model including the effect of relative humidity and the mass
496 transfer step has been highlighted. The model was satisfactory in correlating the
497 experimental data.

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