|  |  |
| --- | --- |
| cetlogo ***CHEMICAL ENGINEERING TRANSACTIONS***  ***VOL. 82, 2020*** | A publication of  aidiclogo_grande |
| The Italian Association  of Chemical Engineering  Online at www.cetjournal.it |
| Guest Editors: Bruno Fabiano, Valerio Cozzani, Genserik Reniers  Copyright © 2020, AIDIC Servizi S.r.l. **ISBN** 978-88-95608-80-8; **ISSN** 2283-9216 | |

Elimination of Cyclohexane By Using a Filter Cartridge a Photocatalytic Filtering Reactor

Youcef Serhanea\*, Abdelkrim Bouzazaa, Dominique Wolberta, Aymen Amin Assadia

Univ Rennes - ENSCR / UMR CNRS 6226 "Chemical Sciences of Rennes" ENSCR, Campus de Beaulieu, av. du Général Leclerc, 35700 Rennes, France

[youcef.serhane@ensc-rennes.fr](mailto:youcef.serhane@ensc-rennes.fr)

In this study, we present an effective solution for the treatment of toxic gases, based on a photocatalytic process as destructive process. The aim of this investigation is to study the efficiency of the photocatalytic Filtering reactor (PFR), for the treatment of cyclohexane which is chosen as target pollutant of anti-gas cartridges of type 'A'. Indeed, the influence the input concentration (a range of Cyclohexane concentrations defined in the values and exposure limits recommended by the different French, European or American standards), residence time in reactor, and type of catalyst were studied in detail. In addition, the conversion rate was controlled under a respiratory flow (standards: ISO / DIS 8996). Moreover, a new type of catalysis TiO2 deposed on optical fiber was evaluated in these conditions. The obtained results confirm that this configuration of the reactor can present an extremely promising route for individual protection device as an autonomous cartridge for a gas mask.

Keywords:Photocatalytic filtration reactor, air treatment, cyclohexane,TiO2 on optical fiber.

* 1. Introduction

Nowadays, the quality of outdoor and indoor air has become one of the most important concerns because it has harmful impacts on human health and the environment. This is why scientists have developed many methods to treat polluted air. This pollution is caused by many factors, we can cite industrial activities, heating, transport …The most recurrent pollutants are nitrogen oxides (NOx), carbon monoxide (CO), organic compounds volatile (VOCs), and aromatic hydrocarbons. These compounds are highly toxic and cause serious illness. Their concentration can fluctuate over time, depending on weather conditions, temperature and human activities [1]. Faced with the risk of inhalation, and in order to guarantee the safety of people working in the presence of pollutants, volatile gases, the respiratory protection device constitutes an effective means to capture the pollutants contained in the working environment, anti-masks -gas have been developed [2] to meet different protection requirements and different pollutants [3,4]. This personal protective equipment allows the wearer to breathe air purified of toxic substances. This equipment is based on the principle of adsorption on a porous material. In general, it is activated carbon [5]. They are capable of capturing and storing contaminants and of being effective in protecting personnel for a fixed period. In fact, the adsorbent is made up of storage sites, which act as a barrier against most contaminants. Only, once all the sites are saturated, the cartridge cannot retain more contaminant and becomes ineffective. The contaminant may even be released. It is then necessary to change the cartridge before sites are saturated, with all the risks of cross contamination that this entails. Indeed, the contaminant is simply trapped, retaining all of its toxicity potential. For this reason, these protection systems have a drawback, the activated carbon cartridges become clogged and it is necessary to change it regularly in order to keep optimum protection [6,7].

Unfortunately, and faced with all these drawbacks, it is essential to find effective protection techniques to deal with different pollutants, a process that allows the degradation and elimination of these toxic compounds. Among these techniques; advanced oxidation processes, namely photocatalysis which is a promising process for this application since it can mineralize many organic compounds at room temperature by simply using a light source and a catalyst [8,9]. Photocatalysis has many advantages in this area (i) The majority of organic and mineral pollutants can be degraded (hydrocarbons, nitrogen, halogenated, oxygenated or sulfur compounds [8] and the end products are little or not dangerous CO2, H2O, mineral acids) (ii) The photocatalytic reaction takes place at room temperature and atmospheric pressure. Chemical activation is carried out exclusively by photon irradiation (iii) the implementation of the process is simple and economical. In addition, it requires only a small footprint which makes it usable in tight spaces; (iv) Operating costs are lower than traditional treatments for low concentrations and / or low flow rates due to limited maintenance and the use of no consumables [8,10]. The photocatalytic process is based on the use of low-energy UV-A photons to excite a semiconductor catalyst (most often TiO2) leading to the formation of electron-hole pairs. Electrons and holes lead to the formation of highly reactive hydroxyl radicals in the gas phase [11,12]. The latter have the capacity to destroy many toxic organic pollutants [12]. In this study, we are interested in the efficiency of the photocatalytic filtering reactor. For the treatment of cyclohexane which is defined as a benchmark for testing the effectiveness of type “A” anti-gas cartridges [4,5,6,7]. Moreover, a new configuration on optical fibers is used for cyclohexane removal. This geometry makes it possible to limit the distance from the UV catalyst source and therefore to increase the quantity of photons received by the photocatalyst.

* 1. Materials and methods

2.1 The pollutants studied

The cyclohexane used is supplied by Sigma-Aldrich in liquid form (purity> 98%).the physico-chemical properties of cyclohexan are summarized in Table1

Table 1: Physico-chemical properties of cyclohexan

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Brute formula | C6H12 |  | | | Boiling point (1 atm**)** | | 80.75 °C | |
| Odor threshold | bas : 0,52 ppm haut : 784 ppm |  | | | Solubility in water | | at 25 °C Very low | |
| Vapor pressure | 10,3 kPa à 20 °C  24,6 kPa à 40 °C | |  | Conversion factor | | in the air | |
| Flash point | 44 à 53°C |  | | | Auto ignition | | 245-260 ° C | |
| Exposure limits (France) | 200 ppm / 700 mg/m3 |  | | | Density | | 0.779-0.784 | |

2.2 Photocatalytic supports

2.2.1 TiO2 deposed fiber optic media

It is a media composed of TiO2 of an amount of 13 g/m² deposited on a surface of 0.01 m² of luminous textile obtained by weaving textile fibers with plastic optical fibers (FOP) having flexibility and robustness improved. Optical fibers manufactured by Brochier Technologies Company (UVtex®).

|  |  |
| --- | --- |
|  | (c) |
| (d) |

Figure 1: SEM images of the textile (1a) in plan view, (1b) in section and (1 c & d) of an illuminated textile sample [13]

2.2.2 The cellulosic TiO2 media

The catalyst used is PC-500 titanium dioxide, sold by Millennium. The elementary crystals, the size of which is between 5 and 10 nm, of anatase crystal structure (> 99%) with an SBET specific surface of approximately 320 m².g-1. The packaging is a porous non-woven support based on cellulosic and synthetic fibers which takes the form of a filter; it makes it possible both to avoid a separation step and good irradiation of the catalyst.

2.3 Generation of polluted flows

A syringe pump system from the brand Kf scientory is used ofr the injection of a fixed flow rate of cyclohexane during the experiments. A heating tape is wrapped around the pipe at the injection level to vaporize the cyclohexane.

2.4 Photocatalytic treatment devices

2.4.1 Batch reactor

The batch reactor used 2.05 l in volume, is hermetically sealed and contains the polluted effluent to be treated. The UV lamp used for the experiments with cellulosic catalyst is a Philips PL-L 24W/10/4P. Whereas, for fiber optic experiments, power is supplied by a Glacial Power box. The samples are then taken by syringe via a septum in order to carry out the analysis. A diagram of a discontinuous photocatalytic reactor is presented in *Figure**2*.

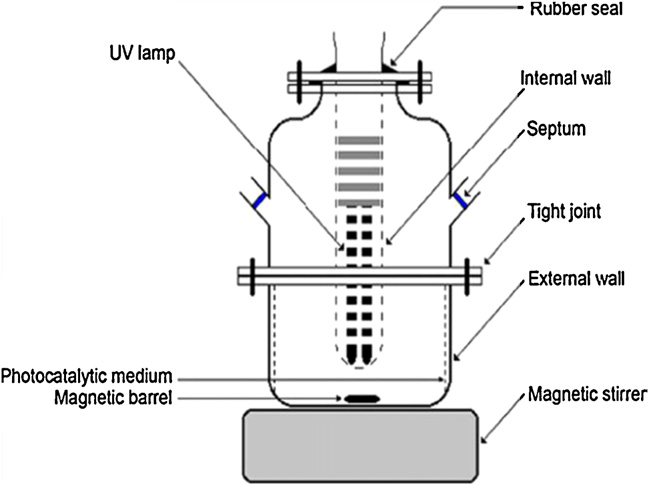


Figure 2: Diagram of a discontinuous photocatalytic reactor

2.4.2 Photocatalytic Filtering reactor (PFR)

The PFR reactor *Figure 3.a*I was alimented by a KNF Laboratory pump with ambient air. Upstream of this pump, a Gallus G4 gas meter from the Itrón brand is used to estimate the flow rate. The continuous reactor consists of four mountable stainless steel test chambers with a passage section of 0.01 m2 and a total volume of approximately 3 L. The first part is used for the main inlet of the flow of air, injection of pollutants, and sampling for analysis before handling. The second part contained four photocatalytic media and two Philips UV-A lamps (model PLS 9W/10). The emission spectrum of this lamp has a maximum at the wavelength of 365 nm. The last element allows the sample for analysis after treatment and the exit of the air flow. The air leaving the reactor is evacuated under a hood*. Figure 3.b* illustrates the principle of the photocatalytic Filtering reactor (PFR) driver.

|  |  |
| --- | --- |
| (a) | (b) |
| Figure 3.: a) photocatalytic Filtering reactor (PFR ) and b) Schematic diagram | |

The use of the P50 reactor makes it easy to test the efficiency of the photocatalytic media. It also offers us the possibility of doubling the processing device.

2-5 Analysis system

The concentration of cyclohexane was measured by a Thermo electron corporation gas chromatograph (Focus GC) of the auto-system using a flame ionization detector (FID) and a FFAP column (length = 25 m and internal diameter = 0,32 mm). Nitrogen was used as the carrier gas. The temperature conditions of the furnace, the injection chamber and the detector were, respectively, 50, 190 and 190 C°. The analysis was carried out by direct manual sampling with a 500 µl syringe and injection into the GC. The calibration was carried out by evaporation of different quantities of closed cyclohexane bottles. The pollutant was correlated with a peak area of ​​GC-FID as a function of its concentration. The operation is done by Azur ™ software.

* 1. Results and discussions

3.1 Concentration effect and degradation kinetic modeling

At the start of each experiment, the batch reactor (*Figure 2*) is filled with unpolluted ambient air. Then a known quantity of pollutant is injected in liquid form. The geometry of the reactor makes agitation quite difficult; the equilibrium concentration of adsorption should be checked by three or four stable values ​​for half an hour. The concentration of the pollutant in the gas phase is followed by chromatography every (5-10) minutes throughout the degradation period and a quarter of an hour after the total disappearance of the pollutant from the air.

*Figure 4* shows the kinetics of degradation of cyclohexane with a cellulosic TiO2 medium having a surface of 80 cm² and TiO2 coated fiber media with amount of TiO2 similar to that of the cellulosic media, at different concentrations: 150, 300,400 et 550 mg/m3. Correspond to a range of Cyclohexane concentrations respecting the values ​​and exposure limits recommended by the different standards.

From *Figure 4*, shows a behavior similar to what is reported in the literature where, the evolution of the concentration curve as a function of time is in the form of a decreasing exponential. The observation of the degradation curves of cyclohexane with the optical fiber media also shows that our pollutant is completely degraded after 1 hour. A final observation that needs to be made is that the rate of degradation first increases in proportion to the concentration.

|  |  |
| --- | --- |
| (a) | (b) |

Figure 4: Kinetics of cyclohexane degradation in a batch reactor with (a) cellulosic and (b)TiO2 media

In order to have more clarification, in particular on the reaction rate taking place on the surface of the catalyst and the active sites involved, a modeling of the degradation kinetics was highlighted.

The kinetics of degradation is generally represented by the Langmuir - Hinshelwood model. The latter is defined by the following equation [14,15]:

|  |  |
| --- | --- |
|  | (1) |

Where r0 is the initial reaction rate (mg.m−3.min−1), k the reaction rate constant (mg.m-3.min-1), and K is the adsorption constant (m3.mg-1).

Due to the complex mechanism of the reactions, it is difficult to develop a model for the dependence of the rate of photocatalytic degradation on the experimental parameters throughout the duration of the treatment. the Langmuir-Hinshelwood model is then applied only at the start of the reaction, that is to say at the moment when the intermediate products are not yet generated. Thus, the kinetic modeling of the photocatalytic process is generally limited to the analysis of the initial rate of photocatalytic degradation. This can be obtained from the initial slope and the initial pollutant concentration.

*Table 2: Initial reaction rate with cellulosic and optical fiber media at different initials concentrations*

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| C0 (mg/m3) | 150 | 300 | 400 | 550 |
| r0 (mg m−3 min−1)  ‘’ cellulosic’’ | 3.3 | 5.92 | 7.76 | 9.29 |
| r0 (mg m−3 min−1)  ‘’optical fiber’’ | 2.23 | 4.36 | 5.22 | 7.2 |

By drawing r0−1 = f (C0−1) and from the values of the slope and the intercept, the value of the Langmuir - Hinshelwood (k) reaction rate constant and the Langmuir adsorption constant (K), for the two media were obtained:

*Table 3:* Reaction rate and adsorption constants

|  |  |  |
| --- | --- | --- |
| media | cellulosic | optical fiber |
| k (mg.m-3.min-1) | 25,68 | 15,15 |
| K (m3.mg-1) | 1.05.10-3 | 7,69.10-4 |
| R2 | 0,9958 | 0,9529 |

The degradation rate is modeled satisfactorily by a Langmuir-Hinshelwood type model, and a good fit of the model to the experimental data can be observed. It also means that the chemical reaction is the limiting step in the process.

3.2 Comparison of the photocatalytic performance of the two media studied

In order to decide on photocatalytic performance for the two media studied and as a reminder that the amount of catalyst is the same for both media. The comparison of the initial degradation rate with the intensity of the photon flux r0sp (mg.m-1.min-1.w--1') for TiO2 fiber optic and cellulosic media at different initial concentrations, illustrated in *Fig.5*, shows that with the cellulosic TiO2 medium, a very slight variation in the rate of degradation is observed at higher concentrations, taking into account the fact that the intensity being the same for the different concentrations, the limiting step is the transfer VOCs on the surface of TiO2 [16]. This variation can be interpreted in this case by the limitation of the material transfer due to the small surface of irradiated TiO2 (activated), which consequently reduced the capacity of the treatment. On the other hand, with the TiO2 fiber optic media, there is a significant increase in the rate of degradation with the increase in concentrations; this is due to the increase in energy efficiency by in situ lighting. In other words, for a given intensity, more active sites are created with the optical fibers.

*Figure 5: Comparison of the initial degradation rate with the intensity of the photon flux r0sp (mg.m-1.min-1.w-1) for the cellulosic and optical fiber TiO2 media at different initial concentrations (UV lamp Intensity = 20 Wm−2, UV-LED Intensity= 6.5 Wm−2)*

These results demonstrate that the use of an optical fiber-based reactor can really reduce the limitation of mass transfer and thus increase the reaction rate. Also, its power to illuminate the catalyst directly on its surface by overcoming the step of limitation, shading or loss of intensity by moving the catalyst away from the UV source.

**3.3 Photocatalytic degradation in a continuous reactor:**

By applying different volume flow rates, equivalent to the respiratory flow rates 13, 18 and 36 l/min corresponding respectively to physical activities at rest, light work and intense work, according to international standard ISO / DIS 8996 [17]. These flows give residence times in the reactor on the order of 14, 10 and 5 seconds.

The overall rate of photocatalytic degradation is an important factor in assessing the removal performance of VOCs. The VOC removal efficiency is defined as [18,19,20]:

|  |  |
| --- | --- |
|  | (2) |

Where Cin and Cout are respectively the input and output pollutants concentration (mg/m3).

*Figure 6: Elimination efficiency (IRE) of cyclohexan at different input concentrations at different flow rates (HR = 5 %, T=20 °C, UV intensity = 20 Wm−2)*

The concentration is varied in order to understand its influence on the performance of the photocatalytic reactor. The elimination efficiency (IRE) of cyclohexane at different inlet concentrations with different flow rates is illustrated in *Fig. 6*. The entry concentration of cyclohexane ranged from 25 to 150 mg/m3. As expected, the behavior is similar to what has been reported in the literature for certain VOCs [18,19]. For a given flow, we note that at a higher concentration of pollutants, the degradation rate will tend towards a limit, this can be explained by the unavailability of active sites due to the loss of intensity caused by the distance between the catalyst and the UV source, starting from the fact that the use of reactors with photocatalytic flow, that is to say of filtration, considerably reduces the problems of mass transfer [21]. Also, it can also be noted that the elimination efficiency of cyclohexane decreases with the increase in the flow rate, this is due to a decrease in the contact time between the compound and the active catalytic sites

* 1. Conclusion

In this work, the photocatalytic degradation of cyclohexane was investigated in Batch and continuous reactors with two types of catalyst. The results show that the use of TiO2 coated optical fiber media can be adopted as a solution in order to optimize the photocatalytic treatment, in particular, the volume of the reactor and therefore the residence time. Additionally, these results allow us to envisage a new configuration for a new photocatalytic filtering reactor (PFR) based on optical fiber, for the treatment of highly contaminated environments. An implementation which will allow us to limit the distance from the UV catalyst source and therefore to increase the active surface area or to preserve the quantity of photons received by the photocatalyst.

References

W.Yang, G.Yuan, 2019, Air quality assessment standards and sustainable development in developing countries. Journal of Sustainable, 2071-1050.

G.K. Prasad, Beer Singh, R. Vijayaraghavan, 2009, Review Respiratory Protection Against Chemical and Biological Warfare Agents, Defence Science Journal, 58,686-697.

Occupational health/prevention of occupational health risks/prevention/respiratory protection article/filter: <https://travail-emploi.gouv.fr.>

INRS - ED 6106 :  [Respiratory protection devices, choice and use.](http://www.inrs.fr/dms/inrs/CataloguePapier/ED/TI-ED-6106/ed6106.pdf)

INRS - ED 98 [: Respiratory protection devices.](http://www.inrs.fr/dms/inrs/CataloguePapier/ED/TI-ED-98/ed98.pdf)

R. Chauveau, 2014, Multiparameter modeling of the adsorption phenomenon: determination of the breakthrough time of gas mask cartridges, PHD Thesis, University of Lorraine, France.

F. Vuong, 2016, Modeling of the behavior of respiratory protection cartridges: exposure to complex atmospheres of organic vapors and effect of use cycles, PHD Thesis, University of Lorraine, France.

Y. Boyjoo, H. Sun, J. Liu, V.K. Pareek, S. Wang, 2017, A review on photocatalysis for air treatment: From catalyst development to reactor design, Chemical Engineering Journal, 310, 537–559.

T. Van Gerven, G. Mulc, J. Moulijn, A. Stankiewicz, 2007, A review of intensification of photocatalytic processes, Chemical Engineering and Processing, 46, 781-789.

J. Mo, Y. Zhang, Q. Xu, J.J. Lamson, R. Zhao, 2009, Photocatalytic purification of volatile organic compounds in indoor air: A literature review, Atmospheric Environment, 43, 2229-2246

E. Moctezuma, E.Leyva, G. Palestino, H.de Lasa, 2007, Photocatalytic degradation of methyl parathion: Reaction pathways and intermediate reaction products, Journal of Photochemistry and Photobiology A: Chemistry, 186, 71-84.

L. Zhong, F. Haghighat, P. Blondeau, J. Kozinski, 2010, Modeling and physical interpretation of photocatalytic oxidation efficiency in indoor air applications, Building and Environment, 45, 2689-2697.

P.A. Bourgeois,2011, luminous textile in optical fibers for a photocatalytic application in the gas phase, PHD Thesis, University of Lyon, France.

C. Raillard, V. Héquet, P. Le Cloirec, J. Legrand, 2004, Kinetic study of ketones photocatalytic oxidation in gas phase using TiO2-containing paper: effect of water vapour-Journal of Photochemistry and Photobiology A: Chemistry, 163, 425-431.

S.B. Kim, S.C. Hong, 2002, Kinetic study for photocatalytic degradation of volatile organic compounds in air using thin film TiO2 photocatalyst-Applied Catalysis B: Environmental, 35, 305-315.

S. Brosillon, L. Lhomme, C. Vallet, A. Bouzaza, D. Wolbert, 2008, Gas phase photocatalysis and liquid phase photocatalysis: Interdependence and influence of substrate concentration and photon flow on degradation reaction kinetics, Applied Catalysis B: Environmental, 78, 232-241.

International Standard ISO / DIS 8996 (2004) Ergonomics of the thermal environment, Determination of energy metabolism, www.iso.org.

A.A. Assadi, A. Bouzaza, D. Wolbert, P. Petit, 2014, Isovaleraldehyde elimination by UV/TiO2 photocatalysis: comparative study of the process at different reactors configurations and scales, Environ Sci Pollut Res, 21,11178-11188.

A.A. Assadi, A. Bouzaza, D. Wolbert, 2012, Photocatalytic oxidation of trimethylamine and isovaleraldehyde in an annular reactor: Influence of the mass transfer and the relative humidity, Journal of Photochemistry and Photobiology A: Chemistry, 236, 61-69.

W. Abou Saouda, A.A. Assadi, M. Guiza, A. Bouzaza, W. Aboussaoud, A. Ouederni, I. Soutrel, D. Wolbert, S. Rtimi, 2017, Study of synergetic effect, catalytic poisoning and regeneration using dielectric barrier discharge and photocatalysis in a continuousreactor: Abatement of pollutants in air mixture system, Applied Catalysis B: Environmental, 213, 53-61.

N. Petit, A. Bouzaza, D. Wolbert, P. Petit, J. Dussaud, 2007, Photocatalytic degradation of gaseous perchloroethylene in continuous flow reactors : Rate enhancement by chlorine radicals, Catalysis Today, 124, 266-272.