CHEMICAL ENGINEERING TRANSACTIONS

VOL. 82, 2020

A publication of AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Bruno Fabiano, Valerio Cozzani, Genserik Reniers

ISBN 978-88-95608-80-8; **ISSN** 2283-9216

DOI: 10.3303/CET2082077

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

Youcef Serhane*, Abdelkrim Bouzaz, Dominique Wolbert, Aymen Amin Assadi

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

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 TiO_2 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, TiO_2 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. 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 (Prasad et al., 2009) to meet different protection requirements and different pollutants according to INRS-ED 6106. 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 (Vuong, 2016). In general, it is activated carbon (INRS-ED 98). 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 (Chauveau, 2014. Vuong, 2016).

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 (Boyjoo et al., 2017, Van Gervan et al., 2007). Photocatalysis has many advantages in this area (i) The majority of organic and mineral pollutants can be degraded (hydrocarbons,

Paper Received: 5 March 2020; Revised: 10 June 2020; Accepted: 30 July 2020
Please cite this article as: Serhane Y., Bouzaza A., Wolbert D., Assadi A.A., 2020, Elimination of Cyclohexane by Using a Filter Cartridge a Photocatalytic Filtering Reactor, Chemical Engineering Transactions, 82, 457-462 DOI:10.3303/CET2082077

nitrogen, halogenated, oxygenated or sulfur compounds (Boyjoo et al., 2017) and the end products are little or not dangerous CO_2, H_2O, 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 (Boyjoo et al., 2017. Mo et al., 2009). The photocatalytic process is based on the use of low-energy UV-A photons to excite a semiconductor catalyst (most often TiO_2) leading to the formation of electron-hole pairs. Electrons and holes lead to the formation of highly reactive hydroxyl radicals in the gas phase (Moctezuma et al., 2007. Zhong et al., 2010). The latter have the capacity to destroy many toxic organic pollutants (Zhong et al., 2010). 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 (INRS-ED 6106. INRS-ED 98. Chauveau, 2014. Vuong, 2016).

2. Materials and methods

2.1 The pollutants studied

The cyclohexane used is supplied by Sigma-Aldrich in liquid form (purity> 98%). Its physico-chemical properties are summarized in Table 1

Table 1: Physico-chemical properties of cyclohexane

Formula	C_6H_{12}	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/m^3	Density	0.779-0.784

2.2 Photocatalytic supports

2.2.1 TiO2 deposed fiber optic media

It is a media composed of TiO_2 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 LumiGram SARL society and the TiO_2 was deposited by using sol-gel method in the laboratory of the National School of Chemistry of Rennes.

2.2.2 The cellulosic TiO_2 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 of 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 1.

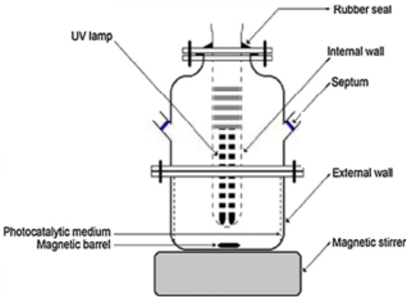
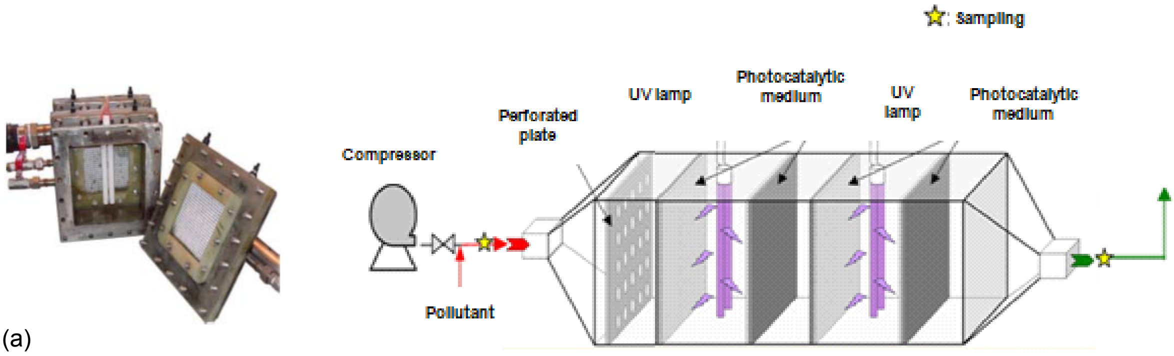


Figure 1: Diagram of a discontinuous photocatalytic reactor

2.4.2 Photocatalytic Filtering reactor (PFR)

The PFR reactor Figure 2.a was alimented by compressed air from the laboratory's internal network, the humidity of which is constant at 5% (so-called "dry" air), a Gallus G4 gas meter 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 m^2 and a total volume of approximately 4 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 2.b illustrates the principle of the photocatalytic Filtering reactor (PFR) driver.



(a)

(b)

Figure 2.: 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 Chromatography (GC) of the auto-system using a flame ionization detector (FID-GC) 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 oven, 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.

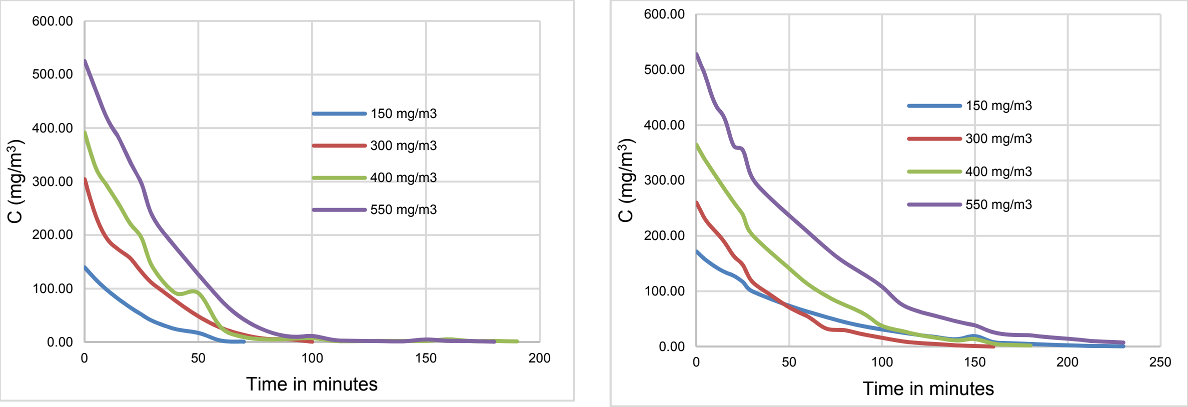
3. Results and discussions

3.1 Concentration effect and degradation kinetic modeling

At the start of each experiment, the batch reactor (*Figure 1*) 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 3 shows the kinetics of degradation of cyclohexane with a cellulosic TiO_2 medium having a surface of 80 cm² and TiO_2 coated on fiber media with amount of similar catalyst amount to that deposed on the cellulosic media, at different concentrations: 150, 300,400 et 550 mg/m^3.

Figure 3 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. Indeed, results of degradation curves of cyclohexane with the optical fiber media show that the pollutant is completely degraded after 1 hour.



(a)

(b)

Figure 3: Kinetics of cyclohexane degradation in a batch reactor with (a) TiO2 on cellulosic support and (b)TiO_2 on optical fibers

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 (Raillard et al., 2004. Kim et al., 2002):

$$r_0 = \frac{kKC_0}{1+KC_0} \quad \text{or} \quad \frac{1}{r_0} = \frac{1}{kK}\frac{1}{C_0} + \frac{1}{k} \qquad (1)$$

Where r_0 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 (m^3.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 oxidized. 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 (Table2).

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

C_0 (mg/m^3)	150	300	400	550
r_0 (mg m^{-3} min^{-1}) " cellulosic"	3.3	5.92	7.76	9.29
r_0 (mg m^{-3} min^{-1}) "optical fiber"	2.23	4.36	5.22	7.2

By drawing $r_0^{-1} = f(C_0^{-1})$ 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).

Table 3: Reaction rate and adsorption constants

media	cellulosic	optical fiber
k (mg.m^{-3}.min^{-1})	25,68	15,15
K (m^3.mg^{-1})	1.05.10^{-3}	7,69.10^{-4}
R^2	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

The comparison of two catalysts (TiO_2 on fiber optic and on cellulosic media) performance in term of specific initial degradation rate r_{0sp} ($mg.m^{-1}.min^{-1}.w^{-1}$') is illustrated in *Fig.4*. we note that with each catalyst, the rate of degradation increase with the increasing of the inlet concentration . This trend confirm that the limiting step is the transfer VOCs on the surface of TiO_2 (Brosillon et al., 2008).. On the other hand, with the TiO_2 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. Additionally with in-situ radiation, more active sites are created in the case of the optical fibers.

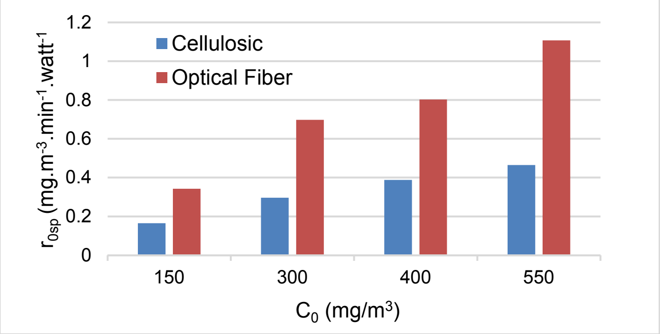


Figure 4: Comparison of the specific initial degradation rate of ellulosic and optical fiber TiO_2 medias at different initial concentrations (UV lamp Intensity = 20 Wm^{-2}, UV-LED Intensity= 7 Wm^{-2})

3.3 Photocatalytic degradation in a continuous reactor:

By applying different flowrates, equivalent to the respiratory flow rates 13, 18 and 36 L/min corresponding respectively to physical activities, according to international standard ISO / DIS 8996. These flowrates correspond to residence times of 20, 13 and 7 s.

The VOC removal efficiency is defined as (Assadi et al., 2012. Assadi et al., 2014. Abou Saoud et al., 2017):

$$\text{IRE}\ (\%) = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \qquad (2)$$

Where C_{in} and C_{out} are respectively the input and output pollutant concentrations (mg/m^3).

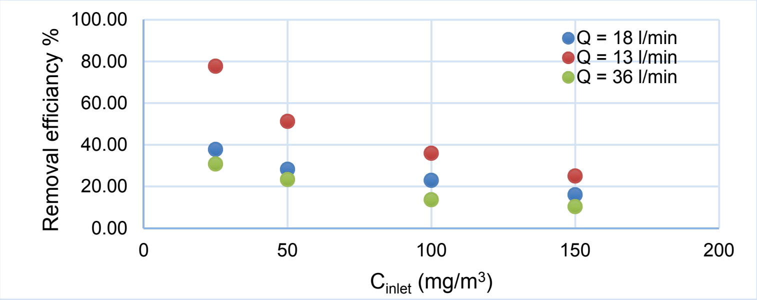


Figure 5: Removal efficiency (RE) of cyclohexane at different inlet concentrations with different flow rates (HR = 5 %, T=20 °C, UV intensity = 20 Wm^{-2})

The concentration is varied in order to understand its influence on the performance of the photocatalytic reactor. The removal efficiency (RE) of cyclohexane at different inlet concentrations with different flow rates is illustrated in *Fig. 5*.. As expected, the behavior is similar to what has been reported in the literature for certain VOCs (Assadi et al., 2012. Assadi et al., 2014). For a given flow, we note that at a higher concentration of pollutants, the removal efficency will tend towards a limit (less than 15%), this can be explained by the unavailability of active sites. Also, it can also be noted that the RE 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 (Assadi et al., 2012)

4. Conclusion

In this work, the photocatalytic degradation of cyclohexane was investigated in Batch and continuous reactors with using two types of catalyst. The results show that the use of TiO_2 coated optical fiber media can be adopted as a solution in order to optimize the photocatalytic treatment, in particular, the compacity of photocatalytic reactor. Additionally, these results allow us to envisage a new configuration for the treatment of contaminated environments at pilot scale.

References

Assadi A.A., Bouzaza A., Wolbert D., 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.

Assadi A.A., Bouzaza A., Wolbert D., Petit P., 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.

Abou Saouda W., Assadi A.A., Guiza M., Bouzaza A., Aboussaoud W., Ouederni A., Soutrel I., Wolbert D., Rtimi S., 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.

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

Brosillon S., Lhomme L., Vallet C., Bouzaza A., Wolbert D., 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.

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

INRS - ED 6106 : Respiratory protection devices, choice and use.

INRS - ED 98 : Respiratory protection devices.

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

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

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

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

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

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

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

Raillard C., Héquet V., Le Cloirec P., Legrand J., 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.

Vuong F., 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.

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

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