



## Research Article

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# Application of Luminous Textile Coated by TiO<sub>2</sub> For Photocatalytic Removal of Acetic Acid, Formaldehyde and Toluene from Indoor Air

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## Abstract

Luminous textile coated by silica and TiO<sub>2</sub> is studied for indoor air treatment. The textile aging induced by UV exposure in the presence of TiO<sub>2</sub> coating was studied, showing a good durability of the textile after protection by Silica layer unlike silica-free textile. Interesting photocatalytic activity was achieved for the photocatalytic luminous textile to remove three different VOCs in air which are acetic acid (AA), formaldehyde and toluene. The effect of number of photons and residence time was carefully highlighted for both TiO<sub>2</sub> P25 in powder or supported in the luminous textile. Then, a comparative study, between the classic system composed of TiO<sub>2</sub> powder and the innovative system integrating photocatalyst and light, was described. The advantage of the photocatalytic luminous textile is their performance associated to an important energy gain due to the use of one UV-LED to homogeneously irradiate an important surface of textile allowing the development of compact photocatalytic device.

**Keywords:** Luminous textile; Optical fibers; UV irradiation; Photocatalysis; VOCs degradation

**Abbreviations:** LED: Light-Emitting Diode; UV: Ultraviolet; VOCs: Volatile Organic Compounds; AOP Advanced Oxidation Processes; PMMA: Polymethyl Methacrylate; CCD: Charge Coupled Device; GC: Gaz Chromatography; ppmv: parts per million by volume

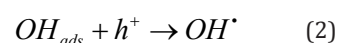
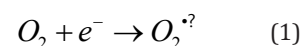
## Introduction

Air pollution from indoor environments is becoming increasingly a public health concern. The permanent presence of chemical pollutants causes various respiratory and chronic diseases [1]. From these various pollutants, there are volatile organic compounds (VOCs) and carboxylic acids which are present in air in different concentrations as a result of biogenic emissions, anthropogenic emissions, materials and lacquer coating [2-5]. Thus, their removal from air is a major challenge to prevent human health issues.

Photocatalysis is a very promising technology for air treatment. The main advantage of this process is not just the removal of VOCs but also their mineralization at room temperature and atmospheric pressure due to generation of reactive oxygen species, OH<sup>•</sup>, O<sub>2</sub><sup>•-</sup> and HO<sub>2</sub><sup>•</sup> from air and humidity. It occurs by activating a photocatalyst using a certain wavelength of UV light. A large range

of semi-conductors is available to induce photocatalysis, while TiO<sub>2</sub> is seen as one of the most promising photocatalysts for practical applications. This material is cheap, abundantly available and chemically stable.

The first step in a photocatalytic reaction is when photons with sufficient energy are absorbed by the photocatalyst, generating an electron and a hole (e<sup>-</sup> and h<sup>+</sup>). These electrons and holes can induce redox reactions, often via the formation of radicals as shown in equations 1 and 2. These radical species allow oxidation of organic compounds.



The photocatalytic process is an efficient method to remove organic pollutants present in gaseous phase [6]. However, there are

still some drawbacks with current methods, namely related to the reactor systems and UV light source. In fact, classical light sources are hazardous due to mercury toxicity with relatively high energy consumption (20-150W) and a relatively low durability which is about 2000 hours. They have generally a low photonic efficiency and they emit large spectral wavelength. The solutions proposed in the present work concern the use of a luminous textile with treated optical fibers. In fact, these fibers are connected to one ultra-violet light emitting diode (UV-LED) source. Consequently, it can carry and supply the UV light onto all over the textile area with little energy (3W) and a better durability which exceeds 17000 hours. Once coated using a suspension of  $\text{TiO}_2$ , the textile subsequently becomes a photocatalytic material leading UV light into the bulk of the photocatalytic bed and diffusing the light in a homogeneous manner over the entire surface. Some researches using optical fibers as a support and different reactors were developed for air and water treatment [3,4]. The first experimental study using optical fibers in photocatalysis was presented in 1994 for the water treatment of 4-chlorophenol by Hofstadler, et al. [7]. Then, various works using optical fibers as support of photocatalyst and different reactors were proposed for the air and water treatment [8-12]. This new luminous textile, called lightex® [13-14] has been developed by Brochier Technologies [15]. Then, its photocatalytic efficiency for VOC degradation was demonstrated through formaldehyde degradation by P-A. Bourgeois, et al. [16]. The coating method of the textile and its characterization was already studied [17]. For the present work, luminous textile coating was optimized by adding firstly silica to improve the textile durability in presence of  $\text{TiO}_2$  under UV in gas phase and the photoreactor was developed to be more adequate to the luminous textile and for industrial applications. Three different pollutants from three different chemical families are studied: a carboxylic acid, an aldehyde and an aromatic hydrocarbon acetic acid (99% purity), formaldehyde (99% purity) and toluene (99% purity) respectively.

The objectives of the publication are first to evaluate the aging of the photocatalytic luminous textile, then compare the disappearance and mineralization of acetic acid, formaldehyde and toluene in presence of photocatalytic luminous textile as a function of the number of photons activating the photocatalyst and finally compare the photonic efficiency and the electrical energy consumed using photocatalytic luminous textile and  $\text{TiO}_2$  powder using a UV-lamp at the same wavelength.

## Materials and Methods

### Elaboration of optical fiber textile

Optical fiber textile connected to UV LED is produced by Brochier Technologies Company (UVtex®). It is composed of polyester fibers, which provide mechanical properties to the textile, and optical fibers which are in poly-methyl methacrylate (PMMA) resin for the core with 480  $\mu\text{m}$  of diameter and covered with 10 $\mu\text{m}$  of fluorinated polymer [16]. These two types of fibers are fixed to the textile shape by binding weave following the Jacquard process meaning the interlacing, in a same plane, of fibers disposed in

the direction of the chain (textile fiber) and some fibers disposed perpendicular to chain fibers, in the direction of the weft (optical fibers). Classically, optical fibers are able to transmit light from the beginning to the end of the fiber. However, Brochier technologies has developed a micro texturing process which is a necessary treatment allowing a uniform light output across the surface of the optical fibers, according to their patents [13,14]. All optical fibers are gathered to one extremity in a connector sealed with organic adhesive. Once this textile is connected to light source, it allows homogeneous irradiance. The lamp connected to the luminous textile is a LED lamp 3W with UV emission centered at 365nm.

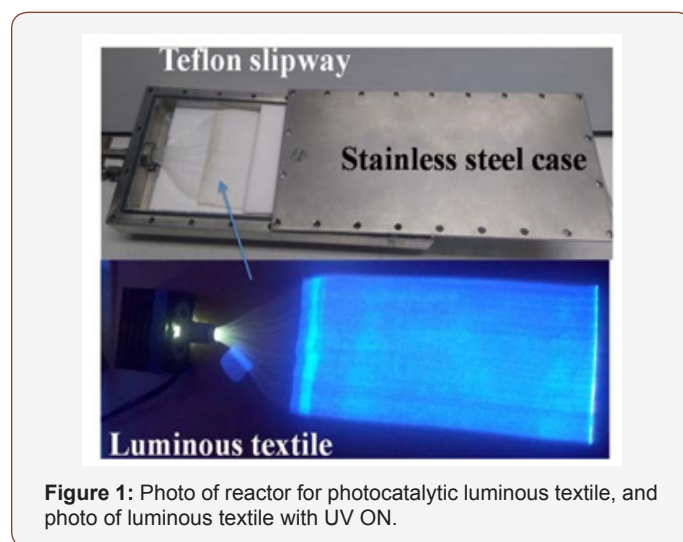
### $\text{TiO}_2$ deposition and aging study

The photocatalyst used is  $\text{TiO}_2$  Degussa P25. Before photocatalyst coating, luminous textile needs to be protected by silica suspension (Aerodisp W7622 purchased from Evonik Degussa) as demonstrated in a previous work of C. Indermuhle et al. [17].

Local emitted light intensities were measured by CCD spectrometer Avantes AvaSpec-ULS2048. Emitted light intensity was measured through 50 points on the surface of the textile before and after  $\text{TiO}_2$  coating. The study of the coated textile aging is based on the survey of the intensity as function of irradiation time.

### Analytical procedures and photocatalytic set-up

To generate a gas stream of pollutant in air at known concentration, a carrier gas (air quality zero) was sent into a COV generator from Bronkhost filled with paraformaldehyde solid (99% purity) or with acetic acid (99% purity) or toluene (99% purity) liquid.



**Figure 1:** Photo of reactor for photocatalytic luminous textile, and photo of luminous textile with UV ON.

The inlet concentration of formaldehyde, acetic acid and toluene are respectively 7, 3.5 and 1 ppmv. This textile was coated by  $\text{TiO}_2$  P25 and connected to a UV-LED lamp (Ultra-Violet Light Emitting Diode) by a sealed sleeve, was fixed in a plane and compact reactor (Figure 1). All experiments were performed under continuous flow with a flow rate of 1000  $\text{mL}\cdot\text{min}^{-1}$  and a relative humidity of 50%. The sample was treated overnight under UV

irradiation to degrade all organic impurities existing in the sample then three steps were followed: at first, pollutant concentration was stabilized and homogenized by passing the reactor (step1). Then, it was introduced into the reactor and maintained in the dark until reaching a steady state of pollutant concentration (step2). Finally, UV light was switched on and maintained until stabilization of the concentration (step3).

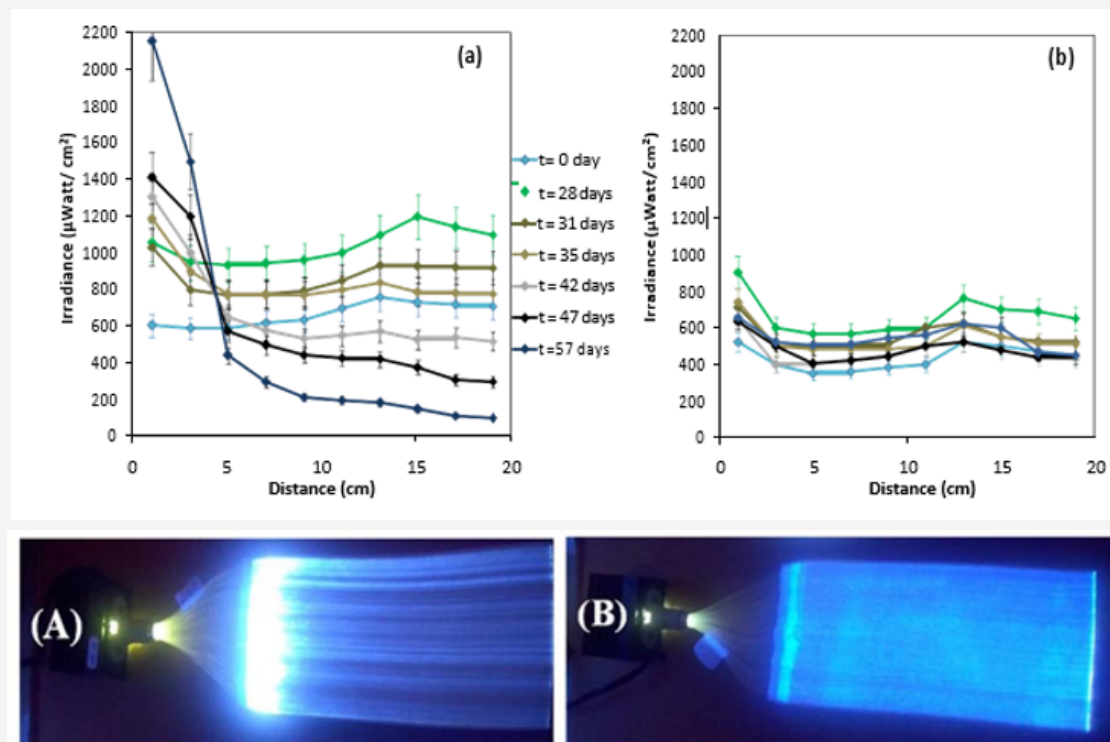
All products and intermediates were analyzed continuously using GC-PDID/FID (GC: Gas Chromatography; PDID: Pulse Discharge Ionization Detector; FID: Flame Ionization Detector) by filling the gas sample into two-loop injection valve. A 100 $\mu$ L loop sent the sample through a BP5-MS column to the FID detector, for toluene, acetic acid and oxygenated compounds separation, while a 500 $\mu$ L loop served a Shin carbon column connected to a PDID detector for CO<sub>2</sub> and hydrocarbons analysis. Helium was used as carrier and discharge gas.

## Results and Discussions

### Optical fiber textile durability

In spite of the advantages of PMMA such as its high ductibility, its big core diameter and low cost, one of major problem to use it in photocatalysis is the photochemical degradation of PMMA optical fibers in presence of UV and TiO<sub>2</sub> [18,29]. Consequently, it is important to study their durability during UVA exposure in presence

of TiO<sub>2</sub>. In a previous work [17], durability of this textile under aqueous solution was studied. For the present work durability was studied under air, ambient temperature and atmospheric pressure. For this, two types of textile, with a surface of 200 cm<sup>2</sup>, were prepared. The first was coated by silica Aerodisp W7622, then coated by the photocatalyst, and the second was directly coated by the photocatalyst. Both were exposed to UVA at 365nm emitted by LED. The irradiance on the surface of the textile is about 1mW/cm<sup>2</sup> homogeneously distributed on all the textile surface throughout optical fiber textile. Along exposure time to UVA light, Irradiance is measured at 25 points on these textiles surface to have representative measurement using radiometric measurements (CCD). Then the irradiance is plotted as function of the average of each line. Figure 2 shows a significant difference between the two textiles coated by silica or not. In the case of luminous textile coated by silica and TiO<sub>2</sub> (Figure 2b), the irradiance could be considered as stable during the study of durability. However, in the case of textile coated directly with TiO<sub>2</sub> without silica (Figure 2a), an important inhomogeneity of the emitted light distribution over the overall surface of the textile was observed, as expected. The majority is emitted in the first centimeters of the fabrics. Therefore, it was demonstrated that the modification of emitted light intensity distribution is due to direct contact with TiO<sub>2</sub> and that the protection by silica avoids the attack of TiO<sub>2</sub> to the textile and allows having a good durability.



**Figure 2:** Irradiance measurements on optical fiber textile coated by only TiO<sub>2</sub> (a) and coated by silica and TiO<sub>2</sub> (b) with corresponding photos (A) and (B) showing the light emission distribution on the overall surface.

### Comparative study for the degradation of 3 different molecules using photocatalytic LED/textile

This present section is the comparison of photocatalytic activity of luminous textile to degrade the three different pollutants.

All samples were pretreated 24h under UVA irradiation using 1L min<sup>-1</sup> of air flow under 50% of relative humidity. The inlet concentrations are chosen to have an equivalent carbon number with 7, 3.5 and 1 ppmv for formaldehyde, AA and toluene respectively.

The conversion of pollutants was calculated from the difference between the inlet and outlet concentrations, using the following equation:

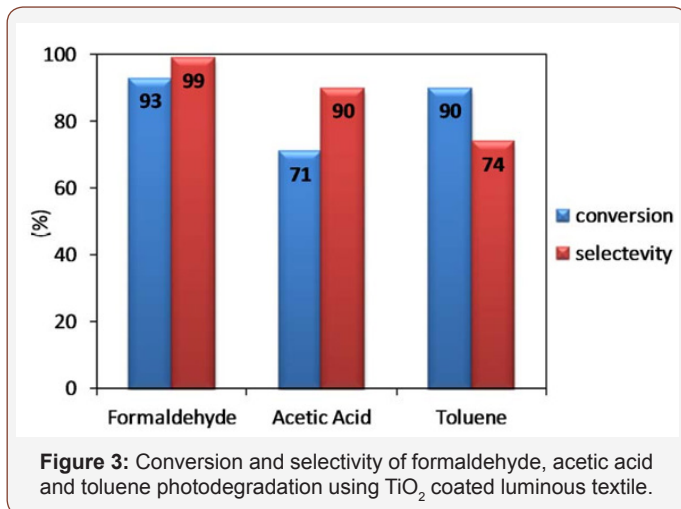
$$\text{Conversion}\% = \frac{C_{in} - C_{out}}{C_{in}} \times 100$$

In which:  $C_{in}$  is the inlet concentration and the  $C_{out}$  is the outlet concentration.

The selectivity (%) was determined by comparing the concentration of carbon dioxide produced to the theoretical one (if mineralization is complete: 1 mole of toluene should lead to formation of 7 moles of  $CO_2$ , one mole of AA should lead to formation of 2 moles of  $CO_2$  and one mole of formaldehyde leads to 1 mole of  $CO_2$  as follows:

$$\text{Selectivity} = \frac{[CO_2]_{MEASURED}}{[CO_2]_{THEORETICAL}} \times 100$$

As shown in figure 3 conversions of the three different pollutants are interesting with 93%, 71% and 90% for respectively formaldehyde, acetic acid and toluene. The selectivity of  $CO_2$  is relatively high with 99%, 90% and 74% putting in evidence the photocatalytic ability of this promising photocatalytic textile to remove these kinds of molecules. In this case, it is important to evaluate this system in terms of number of photons.



In fact, the number of photons is one of important parameters in photocatalysis. Therefore, the disappearance of different pollutants has been followed as function of the intensity of UV light as presented in figure 4. The number of photons was determined by the equation below:

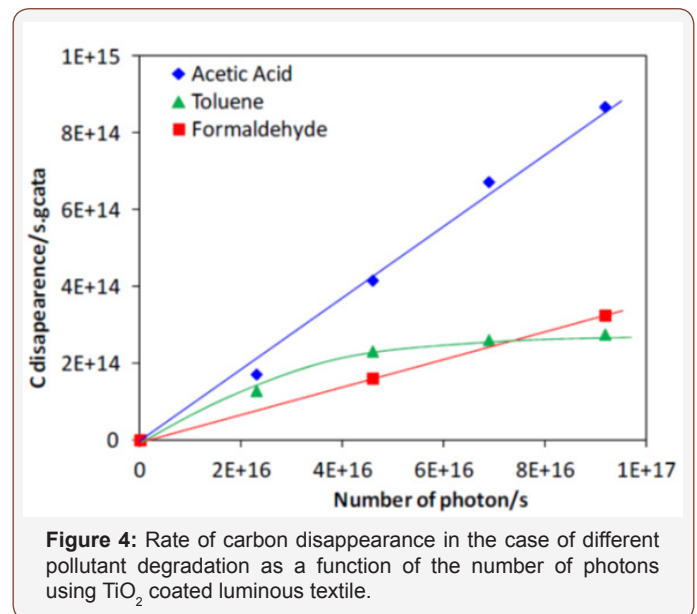
$$N_{\text{photon}} = \frac{I \times S}{E_{\text{photon}}}$$

In which I: the irradiance ( $Watt \cdot cm^{-2}$ ); S: the reactor surface ( $cm^2$ );  $E_{\text{photon}}$  is the energy of one photon ( $Watt$ ) The rate of the pollutant degradation is determined by this equation:

$$rC_{\text{disappearance}} = \frac{C_0 \times Conv \times F \times N}{(n \times N)}$$

In which  $rC_{\text{disappearance}}$  ( $mol \cdot min^{-1} \cdot mg^{-1}$ ): the rate of Carbon degradation;  $C_0$ : inlet concentration ( $mol \cdot L^{-1}$ ); Conv: conversion (%); F : flow rate ( $L \cdot min^{-1}$ ); N : Avogadro number; n : number of carbon in the molecule; m : weight of  $TiO_2$  in the textile (mg).

As shown in figure 4, the rate of the pollutants degradation increases when the photon number increase as expected due to the more important formation of ( $e^-$ ,  $h^+$ ) pairs. In the case of toluene, a plateau is observed which is due probably to the formation of intermediate products on the surface of photocatalyst which exhibit competition reactions and which can saturate the photocatalyst active surface. This hypothesis is in agreement with the selectivity into  $CO_2$  which is only 74% opposite to the selectivity obtained in the case of acetic acid and formaldehyde which are 90%. While in the case of formaldehyde and acetic acid, the degradation rate is proportional to the number of photons with a linear curve confirming the facility of their degradation with fewer intermediates as they have less carbon than toluene and in agreement with their high  $CO_2$  selectivity.



The highest disappearance rate of acetic acid can be explained considering the mechanism of photocatalytic degradation. Indeed, in presence of carboxylic group ( $COOH$ ), this group can directly react with  $h^+$  according to photo-Kolbe reaction while in the case of the degradation of formaldehyde and toluene, the main reactions occur with hydroxyl radical.

### Comparative study between $TiO_2$ powder and $TiO_2$ coated on luminous textile

The photocatalyst used in the present study is commercial  $TiO_2$  P25 (anatase/rutile = 80/20) which has a particle size of 20-30nm. Its density is equal to 3.8 and its specific surface area is about  $50 m^2 g^{-1}$ .

A comparative study between the use of  $TiO_2$  P25 in powder form or supported in a luminous textile to degrade AA is the subject of the second part of this paper. For this, luminous textile was used as described previously. In the case of the tests performed in

presence of TiO<sub>2</sub> P25 powder, the photocatalyst is homogeneously distributed on the surface of a Durapore® filter (Millipore, porosity 0.45µm) located in a cylindrical reactor (diameter 5cm) made of stainless steel and equipped with an optical Pyrex glass window (diameter 4cm) allowing penetration of light from a mercury UV lamp (PLL 18W, Philips) deposited outside the reactor.

The operating conditions used for both experiments are summarized in Table 1.

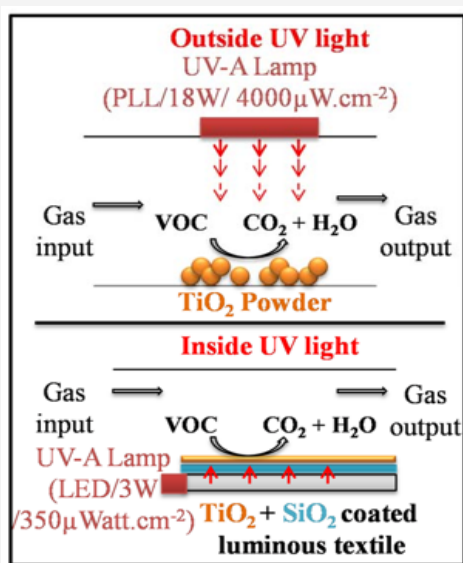
**Table 1:** Experimental conditions in the case of TiO<sub>2</sub>/P25 powder and TiO<sub>2</sub>/P25 supported on luminous Textile.

Experimental Parameters	Textile	Powder
Temperature (°C)	20	
Reactor volume (cm <sup>3</sup> )	84	16
Reactor surface (cm <sup>2</sup> )	200	11
TiO <sub>2</sub> amount (mg)	300	30
Emitted Irradiance (mW.cm <sup>-2</sup> )	0.4	4
Number of active photon/s	9.18 10 <sup>16</sup>	4.24 10 <sup>16</sup>
Inlet AA concentration (µmol. L <sup>-1</sup> )	3.9	19.5
Flow rate (ml.min <sup>-1</sup> )	1000	200
Molar Flow (mol. s <sup>-1</sup> )	6.5 10 <sup>-8</sup>	6.5 10 <sup>-8</sup>
Residence time (s)	4.8	4.8

**Table 2:** Photocatalytic performance for AA degradation in the case of TiO<sub>2</sub>/P25 powder and TiO<sub>2</sub>/P25 supported on luminous textile in the same residence time (4.8 s) and the same molar flow (6.5 10<sup>-8</sup> mol. s<sup>-1</sup>).

	AA (µmol/L) (µmol/L)	Conv (%)	AA molecules disap. /s	Photon efficiency (AA molecules) disap. /photon	Electrical energyconsumption (W)	Electrical energy consumption(molecule. s <sup>-1</sup> . W <sup>-1</sup> )
Textile	3.9	71	2.78E+16	0.31	3	9.3 1015
Powder	19.5	37	1.44E+16	0.34	18	0.81015

Table 2 summarizes the results obtained from experiments done by the two systems. Luminous textile demonstrates its efficacy by preserving an interesting photonic efficiency which is equivalent to the photonic efficiency of TiO<sub>2</sub> powder at a same residence time and a same acetic acid molecular flow.



**Figure 5:** Comparative schema between photocatalytic VOCs degradation in the case of TiO<sub>2</sub> powder and TiO<sub>2</sub> coated luminous textile.

Experiments were carried out at the same residence time and the same inlet AA molecular flow. Residence time was determined according to the following equation:

$$R_t = \frac{V_{reactor}}{F}$$

In which R<sub>t</sub>: Residence Time (s); V<sub>reactor</sub>: Volume of the reactor (L); F: Flow rate (L.s<sup>-1</sup>).

The kinetics and mechanism of the photocatalytic degradation of acetic acid using TiO<sub>2</sub> P25 powder was already well studied [20]. Otherwise, in the present work, the photocatalytic performance of the two systems is compared at the same acetic acid molecular flow and the same residence time.

As experiments with textile or TiO<sub>2</sub> powder were done using two different reactors, it is judicious to determine the quantum efficiency in both cases.

Photonic efficiency was determined according to the following equation:

$$Photonic\ Efficiency = \frac{r_{AA\ disappearance}}{N_{photon}}$$

However, the most important and interesting properties of these photocatalytic luminous textile is their good performance associated to a low electric energy consumption. The LED (3W) connected to luminous photocatalytic textile is compared to experiments using TiO<sub>2</sub> powder irradiated by PLL lamp (18W). In the case of LED/ photocatalytic textile system, the electrical energy consumption is 11.5 times lower than this one obtained with PLL lamp/ TiO<sub>2</sub> powder system. The photocatalytic luminous textile has the capacity to preserve the same photocatalytic performance with a lower electrical energy consumption, putting in evidence the photocatalytic ability of this luminous textile to remove volatile organic compounds with an interesting energy gain. Besides, the use of textile allows a better light distribution on the surface of the textile in a relatively large surface area using only one LED allowing the development of industrial compact photocatalytic device for air treatment (figure 5).

## Conclusion

In the present work, the photocatalytic degradation of formaldehyde, acetic acid and toluene under continuous flow in air was studied. Durability of luminous textile was firstly optimized by adding a silica layer between the textile and the TiO<sub>2</sub> coat. Then, this luminous textile coated with TiO<sub>2</sub> was used to remove three families of pollutants including carboxylic, aromatic and aldehyde functions, as function of irradiance intensity. Our results show the

efficiency of this type of luminous textile to remove and in particular mineralize VOC present in the indoor atmosphere containing VOC concentration below ppmv. Finally, two different systems which are classic system composed of TiO<sub>2</sub> P25 powder and TiO<sub>2</sub> coated luminous textile had been compared. At a same number of photons, a same residence time and a same inlet acetic acid molecular flow, degradation performance of AA in the presence of photocatalytic textile is equivalent to the degradation performance in presence of TiO<sub>2</sub> powder and in addition allows an important energy gain in terms of electrical energy consumption. Actually, at equivalent performance, an energy gain of more than 11 times was found by using this type of photocatalytic luminous textile comparing to the use of TiO<sub>2</sub> powder associated to classical lamp. This innovative photocatalyst combining TiO<sub>2</sub> and light has demonstrated its efficiency to remove different pollutants in gas phase and to solve some of problems associated to commercial sources such as low energy efficiency or short lifetime for conventional lamps. Furthermore, it shows a uniform surface of light and it is used to irradiate large area of photocatalyst, by using only one LED. In conclusion, this system is ideal for industrial applications using compact reactor.

### Acknowledgement

None.

### Conflict of Interest

No conflict of interest.

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