Photocatalytic elimination of indoor air biological and chemical pollution in realistic conditions

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Abstract

The photocatalytic elimination of microorganisms from indoor air in realistic conditions and the feasibility of simultaneous elimination of chemical contaminants have been studied at laboratory scale. Transparent polymeric monoliths have been coated with sol-gel TiO$_2$ films and used as photocatalyst to treat real indoor air in a laboratory-scale single-step annular photocatalytic reactor. The analytical techniques used to characterize the air quality and analyze the results of the photocatalytic tests were: colony counting, microscopy and PCR with subsequent sequencing for microbial quantification and identification; automated thermal desorption coupled to gas chromatography with mass spectrometry detection for chemical analysis. The first experiments performed proved that photocatalysis based on UVA-irradiated TiO$_2$ for the reduction of the concentration of bacteria in the air could compete with the conventional photolytic treatment with UVC radiation, more expensive and hazardous. Simultaneously to the disinfection, the concentration of volatile organic compounds was greatly reduced, which adds value to this technology for real applications. The fungal colony number was not apparently modified.

Key Words

Photocatalysis, bioaerosols, disinfection, indoor air, VOC, supported TiO$_2$. 
1. Introduction

The comfort feeling of a building occupant depends on different interrelated environmental parameters. Air quality, temperature, relative humidity or air distribution are amongst the most relevant (Mendell, 2003; Wong et al., 2008). One of these parameters, air pollution, was traditionally related only to the presence of dangerous concentrations of chemicals in the atmosphere. Cleaning products, furniture, curtains, electronic devices, etc. are important indoor sources of volatile organic compounds (VOCs) emissions, which are amongst the most worrying pollutants. Nowadays, indoor concentration of bioaerosols is cause of health concern as well. Moreover, confined air may present an elevated microbial content composed of a wide range of bacteria, fungi and virus. This causes the so-called “Sick Building Syndrome” and the contamination of the air in public facilities such as hospitals or manufacturing plants, causing health and quality control problems. Taking into account that an average citizen spends most of his time indoors, there is a clear demand for efficient air purification and disinfection systems to control the quality of the indoor air and also for qualitative and quantitative analytical techniques able to characterize the indoor air quality and the performance of these aforementioned systems.

In the field of air cleaning technologies, heterogeneous photocatalysis is a well established technology widely investigated regarding the oxidation of many pollutants present in the indoor air (Blake, 2003). Nowadays more than 2000 companies commercialize different photocatalytic products (Fujishima and Zhang, 2006), mainly for self-cleaning applications. Although the bactericidal effect of photocatalysis is not still well understood (Maness et al., 1999; Benabbou et al., 2007), this technology is gaining interest as an alternative or a complement to other air disinfection technologies like the non-destructive filtration or ventilation, ozonation (with subsequent residual ozone release) and thermal or chemical treatments, that require the isolation of the contaminated zone. In 1985 Matsunaga and co-workers published that it was
possible to kill microbial cells by means of photocatalysis; since then, the photocatalytic inactivation of many bacteria, such as *Escherichia coli*, *Bacillus pumilus*, *Salmonella typhimurium*, *Staphylococcus aureus*, several *Streptococcus*, etc., has been explored (Blake et al., 1999), and the oxidative decomposition of cell mass to carbon dioxide and water vapour has been proved (Jacoby et al., 1998; Maness et al., 1999). Moreover, not only the elimination of bacteria, but also of some virus, fungi and algae has been tested (Cho et al., 2005).

Heterogeneous photocatalysis has been used for water disinfection with aqueous TiO$_2$ suspensions (Benabbou et al., 2007; Sichel et al., 2007a) or cell suspensions on TiO$_2$-coated substrates (Jacoby et al., 1998), but also for air disinfection (Keller et al., 2005; Guillard et al., 2008). Some studies have evaluated the effect of the type of photocatalyst and operating conditions, such as radiation (type, periodicity and intensity) (Chen et al., 2009), temperature or humidity (Goswami et al., 1997), but very few applied the technology in realistic conditions: Grinshpun et al. (2007) investigated an air purification technique which combines unipolar ion emission and photocatalytic oxidation in test chambers simulating a real room; Paschoalino et al. (2008) selected a 67 m$^3$ meeting room to evaluate with real air the performance of a high flow rate UVC photoreactor. However, in spite of the long time since both photocatalytic detoxification and disinfection processes have been studied, the simultaneous elimination of chemical and biological pollution with UVA photocatalysis has scarcely been reported.

The objective of this work was to study the photocatalytic and photolytic destruction of microorganisms in real indoor air at laboratory scale and to prove the feasibility of simultaneous photocatalytic elimination of chemical and biological pollution. With this purpose, analytical techniques were utilized to characterize biological compounds in air (PCR) and simultaneous measurements of VOCs (automated thermal desorption coupled to gas chromatography with mass spectrometry detection, ATD-GC-MS) were performed to evaluate the efficiency of the photocatalytic treatment with different radiation sources. TiO$_2$ supported on transparent
polymeric monoliths was used as photocatalyst. These structures may be employed as an architectural component in a future real application.

2. Material and methods

2.1. Photocatalytic system

The photocatalytic tests were performed in a single pass annular reactor made of borosilicate glass. During the tests, the reactor was connected to either a pump (Gillian LFS-113-DC, 200 mL min$^{-1}$) for VOC sampling or to a high-flow portable air impactor (SAS DUO 360, International PBI, Italy, 180 L min$^{-1}$) for biological sampling; in the latter case, the photoreactor was attached to one of the two sampling heads, as shown in Fig. 1 (left), while the other was used as a control test.

Irradiation was provided by a low-pressure mercury lamp placed in axial position (Fig. 1, right). Fluorescent TL 8 W/05 or CLEO Compact 15 W FAM were used for UVA ($\lambda_{\text{max}} = 360$ nm) and TUV 8 W FAM or TUV 16 W FAM for UVC ($\lambda_{\text{max}} = 253.7$ nm, no ozone generation) (Philips). TiO$_2$ was obtained by sol-gel at low temperature as reported elsewhere (Sánchez et al., 2006), by adding titanium isopropoxide (TIP, Aldrich) to an aqueous solution of nitric acid in the proportion 900:6.5:74 ($\text{H}_2\text{O}:\text{HNO}_3$:TIP). Subsequently, the suspension was stirred for 24 h and dialyzed to a final pH of 3.4. Polyethylene terephthalate (PET) honeycomb structures of 9 mm × 9 mm pitch cross-section, 0.15 mm wall thickness and 45 kg m$^{-3}$ density (WaveCore PET150-9/S, Wacotech GmbH. KG) were selected as a support.

Ten of these PET structures were coated with three TiO$_2$ layers, deposited by dip-coating technique at a rate of 1.5 mm s$^{-1}$ and dried at 50 °C between layer depositions. The monoliths were placed in the interannular space of the reactor and irradiated overnight to eliminate possible initial inactivation effects. Lamps were powered for stabilization at least 30 min before the tests (Portela et al., 2007). The reactor has an
internal diameter of 5.1 cm and the lamp diameter is 1.6 cm. The reactor has a 368 cm³ catalytic bed with 1820 cm² of catalytic surface.

A series of experiments under continuous flow conditions were run in order to compare the photocatalytic (with TiO₂) with the photolytic (without TiO₂) activity for real indoor air disinfection using both UVA and UVC radiation of two different intensities. The feasibility of simultaneous photocatalytic disinfection and detoxification during the test with the 8 W UVA lamp was explored. Blank experiments without irradiation were performed as well, in order to study the effect of the presence of reactor, lamp, monoliths and TiO₂, and to evaluate the adsorption of bacteria on the reactor packing and walls. The experiments were run in a laboratory room of 46 m² used by 5 people. During the experiments, windows and door were closed in order to avoid the interference of airflows transferring bacteria, fungi and VOCs. Temperature and relative humidity were monitored and oscillated between 22-26 ºC and 20-40%, respectively. The flow characteristics during the samplings are collected in Table 1.

2.2. Biological characterization

The air was sampled with an air impactor through two 219-hole sieved head plates and over 90 mm Petri dishes at a flow rate of 180 L min⁻¹. According to preliminary tests, the sampling volume was adjusted to 1800 L in the case of bacteria and 750 L in the case of fungi, in order to have adequate sensitivity avoiding plate saturation.

The Petri dishes attached to the sampler heads contained growth medium for bacteria or fungi. Bacterial samples were collected using Nutrient Agar (3 g meat extract, 10 g peptone, 5 g NaCl and 15 g agar in 1 L distilled water, pH = 7.2-7.4) and incubated at 37 ºC for 48 h. Fungal samples were collected using Malt Extract Agar (malt extract and agar, 20 g of each in 1 L distilled water, pH = 5.5 ± 0.2) and incubated at 28 ºC for 48 h. Every test was repeated three times with each one of the two sampling heads.
After incubation, the colonies were counted. The concentration of microorganisms in the air, expressed in CFU m\(^{-3}\), was calculated using Eq. 1

\[
[bioaerosol] = \frac{n_c}{Ft}
\]  

(1)

where \(F\) and \(t\) are the flow rate and the sampling time, respectively, and \(n_c\) the colony counts after positive hole correction. \(n_c\) for a multiple-hole impactor with 219 jets can be calculated from Eq. 2 (Hinds, 1999):

\[
n_c = n_f \left( \frac{1.075}{1.052 - f} \right)^{0.483} \quad \text{for } f < 0.95
\]  

(2)

where \(n_f\) is the number of CFUs or filled impaction sites and \(f = n_f/219\).

The colonies were then isolated for identification. Fungi identification, based on the morphology of the colonies and their microscopic features, was made using an Olympus SZH10 Research Stereo microscope and an Olympus Vanox AHMT3 microscope, both with a Color view III 5 MegaPixel digital color camera incorporated. Bacteria identification was performed by molecular biology techniques (PCR and sequenciation). Bacterial DNA was extracted as described by Bell et al. (1998). The 16SrRNA gene of every colony was amplified using the PCR with universal primers for bacteria (27F and 1492R) (Weisburg et al., 1991). The PCR products were purified (JetQuick, Genomed kit) and sequenced directly as described by Moore et al. (1999). Sequences were automatically analyzed on an ABI model 377 sequencer (Applied Biosystems) and compared with the National Center for Biotechnology Information databases using the Basic Local Alignment Search Tool to identify the closest related sequences.
2.3. Chemical characterization

The photocatalytic experiments were carried out feeding the reaction with the real air from the laboratory. VOC samples were collected using stainless steel tubes containing Tenax TA as adsorbent and connected to a pump (Gillian LFS-113-DC) that forced the air to pass through the reactor set up. The tubes were placed in the reactor outlet under the influence of irradiation or without irradiation. The temperature and relative humidity were the same than in the biological test. The experimental device was cleaned for 120 min before sample acquisition to ensure steady state conditions. Reference samples from the laboratory indoor air were taken in all the experiments. The VOCs were desorbed and analyzed by means of an ATD (ATD-Turbo Matrix 650, Perkin-Elmer) connected to a GC/MS (6850 network GC system/5973, network mass selective detector, Agilent) equipped with a HP-5MS column. Most representative compounds of different nature (aromatic, aliphatic, terpenes, aldehydes, among others) were selected for calibration. The compounds were identified using a reference mass spectra library (NIST-02) or reference compounds and quantified by external standard.

3. Results and Discussion

3.1. Bactericidal activity during the first set of experiments

Results of blank, photolytic and photocatalytic tests are shown in Table 2. Bacterial concentration in control samples varied from 50 to 200 CFU m\(^{-3}\). Bacteria elimination values are the mean values of six repetitions. As expected, the incorporation of the photoreactor with the lamp to the air sampler in the dark did not modify the bacterial concentration measured. Nevertheless, when PET monoliths, with or without TiO\(_2\), were incorporated to the experimental device, there was a slight reduction in the bacteria concentration in the reactor head, below 10%, attributed to adsorption on the monolith walls.
Both UVA and UVC irradiation significantly reduced the concentration of bacteria. As shown in Fig. 2a, the photolytic bactericidal effect of UVA irradiation was not competitive with that obtained with UVC, which reduced the presence of bacteria in the air with an efficiency of 70 and 80% when the lamp power was 8 and 16 W, respectively. Logically, in the range studied higher irradiance enhances the photolytic activity for both types of radiation.

The bactericidal effect promoted by the presence of the photocatalyst significantly increased the disinfection attained with UVA irradiation to values similar to the UVC, which indicates that photocatalysis with UVA radiation may be competitive with UVC photolysis for bacteria reduction in air. Taking into account the high total flow selected and therefore the low residence time during the performance of the tests ($t_r = 0.12$ s), the results obtained are very promising. No beneficial effect of the photocatalyst was observed in the case of UVC radiation. In this case the presence of TiO$_2$ seems to be detrimental for the disinfection capacity. The absorption of radiation by the photocatalyst could be responsible for the lower photolytic rate.

SEM images and EDX analysis of the photocatalyst after the tests (Supplementary Material) revealed the presence of adsorbed bacteria and rests of organic matter on the surface. Although the mechanism of bacterial photocatalytic degradation is still not clear, some experimental work has been performed by other authors to clarify this issue. Matsunaga et al. (1988) proposed that direct photochemical oxidation of intracellular coenzyme A caused respiration difficulties that led to cell death. Later, Saito et al. (1992) proposed that the TiO$_2$ photochemical reaction caused disruption of the cell membrane and the cell wall. Sunada et al. (1998) found that endotoxins were destroyed under photocatalytic conditions. Maness et al. (1999) concluded that TiO$_2$ photocatalyst damaged the lipid membrane. Subsequently, essential functions that rely on intact cell membrane architecture, such as respiratory activity, were lost, and cell death was inevitable.
3.2. Bactericidal activity during the second set of experiments

Regular repetitions of the disinfection experiments reported above were performed under the very same experimental conditions. After several coincident results, a sudden decrease of the reactor efficiency was observed with both UVA and UVC radiation and this low efficiency was maintained in further repetitions. The experimental procedure was checked in an attempt to explain this efficiency decrease: brand new lamps were used; temperature, humidity and irradiation of these lamps were measured and found to be similar to the values obtained during the first set of experiments; new Nutrient Agar was prepared; the air samplers were checked and then substituted by the model SPIN AIR V2 (IUL S.A., Barcelona, Spain), which works with lower air flow (100 L min\(^{-1}\)) and, according to tests performed in the laboratory, is more precise (Sánchez-Muñoz et al., 2011). The efficiency values were always low, as shown in Fig. 2b, even with UVC lamps, with around 30% of bacterial destruction against the 60-80% found in the previous tests.

Fresh photocatalysts were prepared with new TiO\(_2\) sol synthesised with new reagents and the same low efficiency values were obtained. The photocatalytic activity of the new monoliths was tested under UVA radiation for trichloroethylene (TCE) photocatalytic elimination in the experimental set-up described elsewhere (Suárez et al., 2008). The results showed normal values of around 80% degradation. Additional experiments were performed between January and June changing the location of the photoreactor in the building and the results did not improve significantly. The only difference observed between the first and second set of experiments was the low amount of CFUs collected during the experiments of the second set, 20-80 against 50-200 CFU m\(^{-3}\) collected during the first set of experiments. Therefore, it must be concluded that the photoreactor disinfection efficiency was affected by the type or concentration of microorganisms in order to explain the contradictory results. Unfavourable outdoor environmental conditions, like a cold winter with high rainfall and snow, could be responsible for the low concentration of bacteria observed in the second
set of experiments and possibly for a different distribution of bacteria species, prevailing species more resistant to the photochemical treatment than before.

Bacterial identification was done in order to know which species were resistant to the photocatalytic treatment in our experimental conditions. There is a great variability of species found in the air and sometimes very few species coincide from one year to another, which made it very difficult to identify the resistant and non-resistant species and compare one experiment to another. Apparently, the results showed that species (accession number, maximum identity - degree of correspondence between two subsequences -) like *Staphylococcus pasteuri* (FR839669.1, 100%), *Staphylococcus saprophyticus* (JN409469.1, 100%), *Micrococcus luteus* (HQ220044.1, 100%), *Acinetobacter radioresistens* (FJ608261.1, 100%), *Kocuria rosea* (JN084149.1, 100%), *Naxibacter haematophilus* (EU554441.1, 100%), *Bacillus endophyticus* (JN585716.1, 100%) were resistant to our UVA photocatalytic treatment. *M. luteus* (FJ229461.1, 99%) was also resistant to UVC photocatalysis together with *Stenotrophomonas maltophilia* (JF427723.1, 100%), *Arthrobacter luteolus* (GU18881.1, 100%), *Curtobacterium flaccumfaciens* (JN378724.1, 100%), *Staphylococcus hominis* (JN644561.1, 100%), *Acinetobacter sp* (HQ449642.1, 97%) and *Macrococcus equipercicus* (NR_044926.1, 100%).

Some of these species have special properties that could explain their resistance to the treatment. For instance, *Bacillus sp.* are spore-forming bacteria, which make them able to resist harsh conditions like heat, desiccation, radiation or disinfectants. The dormant spores are able to survive thousands if not millions of years (Atrih and Foster, 2002). *M. luteus* can be found in human skin, water, dust and soil and their cells can live for long periods (Greenblatt el al., 2004). Evidences support the view that this specie (and related members of the genus) has numerous adaptations for survival in extreme nutrient-poor environments; this trait will assist in the bacteria persistence and its dispersal in the environment. *C. flaccumfaciens* is very
resistant to drying and can remain viable for up to 24 yr stored in the laboratory. It has been known to survive in soil for at least two winters (EPPO/CABI, 1997).

Our group is currently working on new photoreactor configurations in order to repeat and improve the efficiency results. But from our point of view, it is very important to point out that the differences found between the first and second set of experiments show that the scientific community should be very careful when talking about indoor air microbial characterization and disinfection in realistic conditions.

3.3. Fungicidal activity

The analysis of the indoor air showed the presence of several fungal species, mainly of the genera *Cladosporium, Alternaria, Aureobasidium, Penicillium, Mucor* and yeasts, which are commonly found in indoor air and food (Samson, 2004). The photocatalytic treatment was not able to significantly reduce the amount of any of the fungi detected in both set of experiments. One reason could be related to the fungal ability to form a high number of spores that are difficult to eliminate due to the complex composition of their cell walls. The presence of spores in the photocatalytic surface has been observed by SEM (Supplementary Material). Moreover, only few studies have dealt with fungal photocatalytic inactivation (Lonnen et al., 2005; Sichel et al., 2007b) and long irradiation times were required. For example, Vohra et al. (2006) using filters coated with TiO$_2$ saw that the photocatalytic destruction of fungal spores was 78% after 24 h, around 91% in 36 h and as much as 48 h were required to achieve complete inactivation of *A.niger* spores (Vohra et al., 2006). Experiments varying several factors like at higher residence time, light intensity or catalyst dosage are being performed in order to increase the efficiency of fungi elimination.
3.4. VOCs elimination

Samples for VOC analysis were taken at three different photocatalytic experiments using UVA radiation. Figure 3 shows an example of the chromatograms obtained for the inlet and outlet of the reactor. Data obtained with control samples were similar to those given from the air passing through the reactor with the light off, indicating that VOCs come from the indoor air and not from the experimental device. The chromatograms show the presence of many VOCs similar to those founded by Hippelein et al. (2004). Aromatic compounds such as toluene and xylene, siloxanes (octamethylcycloptrixiloxane, decamethylcyclopentasiloxane or dodecamethyl cyclopentasiloxane), aliphatic hydrocarbons such as tetratetecane, pentadecane, or hexadecane, and hexanol were some of the most representative compounds detected. Comparing both chromatograms, a noticeable decrease of peak intensity with UVA photocatalysis can be observed.

Figure 4 shows the average efficiency of the three samplings for the different VOCs detected along to the initial concentration $C_0$ for calibrated compounds. For uncalibrated compounds, the conversion was obtained considering the integration of the area under the curve. Conversions above 80% are generally reached for most of the VOCs. Aromatic and aliphatic compound represent near 75% of the total VOCs detected.

The presence of aromatic compounds was related to the road traffic from outdoors. In some cases, benzene was detected in low concentration. Its presence is especially relevant due to the toxic character of this compound. Ethylbencene and xylene are used as additives in paints adhesives and varnish (Claeson et al., 2007). Some aliphatic compounds between C7-C18 were identified, among them, heptane was the one of the VOCs analyzed that presented the lower conversion. Considering the $C_0$ values included in Fig. 4, the heptane initial concentration was one order of magnitude higher than for the other aliphatic compounds. This
fact could be related to its lower reaction rate, but other factors such as its low molecular weight associated to diffusion limitations can not be rule out. Aliphatic compounds are classic solvents found in several product used for building construction and renovation. Moreover cyclic terpenes such as α-limonene and α-pinene were also identified. These terpenes are added in cleaning products, food industry and, in the latter case, wooden products. The presence of siloxanes has been described in the literature but their origin is unclear (Shields et al., 1996; Schweigkofler and Niessner, 1999). The siloxanes can be released form furniture coatings, deodorants, cosmetic and adhesives (Bosc et al., 2006). The results obtained in this study clearly indicate that under UVA irradiation the TiO$_2$ based material was able to efficiently destroy a large variety of VOCs that include aliphatic and aromatic compounds, terpenes, oxygenated compounds and siloxanes at ppb levels.

4. Acknowledgements

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5. References


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**Highlights**

- Adaptable TiO$_2$-coated transparent polymeric monoliths used as photocatalysts.
- UVA-photocatalysis competes with UVC-photolysis in indoor-air disinfection.
- Simultaneous elimination of bacteria and VOCs, added value for photocatalysis.
- Indoor air characterization and disinfection must be done in realistic conditions.
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Abstract

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Key Words

Photocatalysis, bioaerosols, disinfection, indoor air, VOC, supported TiO₂.
1. Introduction

The comfort feeling of a building occupant depends on different interrelated environmental parameters. Air quality, temperature, relative humidity or air distribution are amongst the most relevant (Mendell, 2003; Wong et al., 2008). One of these parameters, air pollution, was traditionally related only to the presence of dangerous concentrations of chemicals in the atmosphere. Cleaning products, furniture, curtains, electronic devices, etc. are important indoor sources of volatile organic compounds (VOCs) emissions, which are amongst the most worrying pollutants. Nowadays, indoor concentration of bioaerosols is cause of health concern as well. Moreover, confined air may present an elevated microbial content composed of a wide range of bacteria, fungi and virus. This causes the so-called “Sick Building Syndrome” and the contamination of the air in public facilities such as hospitals or manufacturing plants, causing health and quality control problems. Taking into account that an average citizen spends most of his time indoors, there is a clear demand for efficient air purification and disinfection systems to control the quality of the indoor air and also for qualitative and quantitative analytical techniques able to characterize the indoor air quality and the performance of these aforementioned systems.

In the field of air cleaning technologies, heterogeneous photocatalysis is a well established technology widely investigated regarding the oxidation of many pollutants present in the indoor air (Blake, 2003). Nowadays more than 2000 companies commercialize different photocatalytic products (Fujishima and Zhang, 2006), mainly for self-cleaning applications. Although the bactericidal effect of photocatalysis is not well understood (Maness et al., 1999; Benabbou et al., 2007), this technology is gaining interest as an alternative or a complement to other air disinfection technologies like the non-destructive filtration or ventilation, ozonation (with subsequent residual ozone release) and thermal or chemical treatments, that require the isolation of the contaminated zone. In 1985 Matsunaga and co-workers published that it was
possible to kill microbial cells by means of photocatalysis; since then, the photocatalytic inactivation of many bacteria, such as *Escherichia coli*, *Bacillus pumilus*, *Salmonella typhimurium*, *Staphylococcus aureus*, several *Streptococcus*, etc., has been explored (Blake et al., 1999), and the oxidative decomposition of cell mass to carbon dioxide and water vapour has been proved (Jacoby et al., 1998; Maness et al., 1999). Moreover, not only the elimination of bacteria, but also of some virus, fungi and algae has been tested (Cho et al., 2005). Heterogeneous photocatalysis has been used for water disinfection with aqueous TiO$_2$ suspensions (Benabbou et al., 2007; Sichel et al., 2007a) or cell suspensions on TiO$_2$-coated substrates (Jacoby et al., 1998), but also for air disinfection (Keller et al., 2005; Guillard et al., 2008). Some studies have evaluated the effect of the type of photocatalyst and operating conditions, such as radiation (type, periodicity and intensity) (Chen et al., 2009), temperature or humidity (Goswami et al., 1997), but very few applied the technology in realistic conditions: Grinshpun et al. (2007) investigated an air purification technique which combines unipolar ion emission and photocatalytic oxidation in test chambers simulating a real room; Paschoalino et al. (2008) selected a 67 m$^3$ meeting room to evaluate with real air the performance of a high flow rate UVC photoreactor. However, in spite of the long time since both photocatalytic detoxification and disinfection processes have been studied, the simultaneous elimination of chemical and biological pollution with UVA photocatalysis has scarcely been reported.

The objective of this work was to study the photocatalytic and photolytic destruction of microorganisms in real indoor air at laboratory scale and to prove the feasibility of simultaneous photocatalytic elimination of chemical and biological pollution. With this purpose, analytical techniques were utilized to characterize biological compounds in air (PCR) and simultaneous measurements of VOCs (automated thermal desorption coupled to gas chromatography with mass spectrometry detection, ATD-GC-MS) were performed to evaluate the efficiency of the photocatalytic treatment with different radiation sources. TiO$_2$ supported on transparent
polymeric monoliths was used as photocatalyst. These structures may be employed as an architectural component in a future real application.

2. Material and methods

2.1. Photocatalytic system

The photocatalytic tests were performed in a single pass annular reactor made of borosilicate glass. During the tests, the reactor was connected to either a pump (Gillian LFS-113-DC, 200 mL min\(^{-1}\)) for VOC sampling or to a high-flow portable air impactor (SAS DUO 360, International PBI, Italy, 180 L min\(^{-1}\)) for biological sampling; in the latter case, the photoreactor was attached to one of the two sampling heads, as shown in Fig. 1 (left), while the other was used as a control test.

Irradiation was provided by a low-pressure mercury lamp placed in axial position (Fig. 1, right). Fluorescent TL 8 W/05 or CLEO Compact 15 W FAM were used for UVA (\(\lambda_{\text{max}} = 360 \text{ nm}\)) and TUV 8 W FAM or TUV 16 W FAM for UVC (\(\lambda_{\text{max}} = 253.7 \text{ nm, no ozone generation}\)) (Philips). TiO\(_2\) was obtained by sol-gel at low temperature as reported elsewhere (Sánchez et al., 2006), by adding titanium isopropoxide (TIP, Aldrich) to an aqueous solution of nitric acid in the proportion 900:6.5:74 (H\(_2\)O:HNO\(_3\):TIP). Subsequently, the suspension was stirred for 24 h and dialyzed to a final pH of 3.4. Polyethylene terephthalate (PET) honeycomb structures of 9 × 9 mm pitch cross-section, 0.15 mm wall thickness and 45 kg m\(^{-3}\) density (WaveCore PET150-9/S, Wacotech GmbH. KG) were selected as a support.

Ten of these PET structures were coated with three TiO\(_2\) layers, deposited by dip-coating technique at a rate of 1.5 mm s\(^{-1}\) and dried at 50 °C between layer depositions. The monoliths were placed in the interannular space of the reactor and irradiated overnight to eliminate possible initial inactivation effects. Lamps were powered for stabilization at least 30 min before the tests (Portela et al., 2007). The reactor has an
internal diameter of 5.1 cm and the lamp diameter is 1.6 cm. The reactor has a 368 cm$^3$ catalytic bed with 1820 cm$^2$ of catalytic surface.

A series of experiments under continuous flow conditions were run in order to compare the photocatalytic (with TiO$_2$) with the photolytic (without TiO$_2$) activity for real indoor air disinfection using both UVA and UVC radiation of two different intensities. The feasibility of simultaneous photocatalytic disinfection and detoxification during the test with the 8 W UVA lamp was explored. Blank experiments without irradiation were performed as well, in order to study the effect of the presence of reactor, lamp, monoliths and TiO$_2$, and to evaluate the adsorption of bacteria on the reactor packing and walls. The experiments were run in a laboratory room of 46 m$^2$ used by 5 people. During the experiments, windows and door were closed in order to avoid the interference of airflows transferring bacteria, fungi and VOCs. Temperature and relative humidity were monitored and oscillated between 22-26 °C and 20-40%, respectively. The flow characteristics during the samplings are collected in Table 1.

### 2.2. Biological characterization

The air was sampled with an air impactor through two 219-hole sieved head plates and over 90 mm Petri dishes at a flow rate of 180 L min$^{-1}$. According to preliminary tests, the sampling volume was adjusted to 1800 L in the case of bacteria and 750 L in the case of fungi, in order to have adequate sensitivity avoiding plate saturation.

The Petri dishes attached to the sampler heads contained growth medium for bacteria or fungi. Bacterial samples were collected using Nutrient Agar (3 g meat extract, 10 g peptone, 5 g NaCl and 15 g agar in 1 L distilled water, pH = 7.2-7.4) and incubated at 37 °C for 48 h. Fungal samples were collected using Malt Extract Agar (malt extract and agar, 20 g of each in 1 L distilled water, pH = 5.5 ± 0.2) and incubated at 28 °C for 48 h. Every test was repeated three times with each one of the two sampling heads.
After incubation, the colonies were counted. The concentration of microorganisms in the air, expressed in CFU m\(^{-3}\), was calculated using Eq. 1

\[
[bioaerosol] = \frac{n_c}{Ft}
\]  

(1)

where \(F\) and \(t\) are the flow rate and the sampling time, respectively, and \(n_c\) the colony counts after positive hole correction. \(n_c\) for a multiple-hole impactor with 219 jets can be calculated from Eq. 2 (Hinds, 1999):

\[
n_c = n_f \left(\frac{1.075}{1.052 - f}\right)^{0.483} \quad \text{for } f < 0.95
\]  

(2)

where \(n_f\) is the number of CFUs or filled impaction sites and \(f = n_f/219\).

The colonies were then isolated for identification. Fungi identification, based on the morphology of the colonies and their microscopic features, was made using an Olympus SZH10 Research Stereo microscope and an Olympus Vanox AHMT3 microscope, both with a Color view III 5 MegaPixel digital color camera incorporated. Bacteria identification was performed by molecular biology techniques (PCR and sequenciation). Bacterial DNA was extracted as described by Bell et al. (1998). The 16SrRNA gene of every colony was amplified using the PCR with universal primers for bacteria (27F and 1492R) (Weisburg et al., 1991). The PCR products were purified (JetQuick, Genomed kit) and sequenced directly as described by Moore et al. (1999). Sequences were automatically analyzed on an ABI model 377 sequencer (Applied Biosystems) and compared with the National Center for Biotechnology Information databases using the Basic Local Alignment Search Tool to identify the closest related sequences.
2.3. Chemical characterization

The photocatalytic experiments were carried out feeding the reaction with the real air from the laboratory. VOC samples were collected using stainless steel tubes containing Tenax TA as adsorbent and connected to a pump (Gillian LFS-113-DC) that forced the air to pass through the reactor set up. The tubes were placed in the reactor outlet under the influence of irradiation or without irradiation. The temperature and relative humidity were the same than in the biological test. The experimental device was cleaned for 120 min before sample acquisition to ensure steady state conditions. Reference samples from the laboratory indoor air were taken in all the experiments. The VOCs were desorbed and analyzed by means of an ATD (Turbo Matrix 650, Perkin-Elmer) connected to a GC/MS (6850 network GC system/5973, network mass selective detector, Agilent) equipped with a HP-5MS column. Most representative compounds of different nature (aromatic, aliphatic, terpenes, aldehydes, among others) were selected for calibration. The compounds were identified using a reference mass spectra library (NIST-02) or reference compounds and quantified by external standard.

3. Results and Discussion

3.1. Bactericidal activity during the first set of experiments

Results of blank, photolytic and photocatalytic tests are shown in Table 2. Bacterial concentration in control samples varied from 50 to 200 CFU m\(^{-3}\). Bacteria elimination values are the mean values of six repetitions. As expected, the incorporation of the photoreactor with the lamp to the air sampler in the dark did not modify the bacterial concentration measured. Nevertheless, when PET monoliths, with or without TiO\(_2\), were incorporated to the experimental device, there was a slight reduction in the bacteria concentration in the reactor head, below 10%, attributed to adsorption on the monolith walls.
Both UVA and UVC irradiation significantly reduced the concentration of bacteria. As shown in Fig. 2a, the photolytic bactericidal effect of UVA irradiation was not competitive with that obtained with UVC, which reduced the presence of bacteria in the air with an efficiency of 70 and 80% when the lamp power was 8 and 16 W, respectively. Logically, in the range studied higher irradiance enhances the photolytic activity for both types of radiation.

The bactericidal effect promoted by the presence of the photocatalyst significantly increased the disinfection attained with UVA irradiation to values similar to the UVC, which indicates that photocatalysis with UVA radiation may be competitive with UVC photolysis for bacteria reduction in air. Taking into account the high total flow selected and therefore the low residence time during the performance of the tests (t_r = 0.12 s), the results obtained are very promising. No beneficial effect of the photocatalyst was observed in the case of UVC radiation. In this case the presence of TiO_2 seems to be detrimental for the disinfection capacity. The absorption of radiation by the photocatalyst could be responsible for the lower photolytic rate.

SEM images and EDX analysis of the photocatalyst after the tests (Supplementary Material) revealed the presence of adsorbed bacteria and rests of organic matter on the surface. Although the mechanism of bacterial photocatalytic degradation is still not clear, some experimental work has been performed by other authors to clarify this issue. Matsunaga et al. (1988) proposed that direct photochemical oxidation of intracellular coenzyme A caused respiration difficulties that led to cell death. Later, Saito et al. (1992) proposed that the TiO_2 photochemical reaction caused disruption of the cell membrane and the cell wall. Sunada et al. (1998) found that endotoxins were destroyed under photocatalytic conditions. Maness et al. (1999) concluded that TiO_2 photocatalyst damaged the lipid membrane. Subsequently, essential functions that rely on intact cell membrane architecture, such as respiratory activity, were lost, and cell death was inevitable.
3.2. Bactericidal activity during the second set of experiments

Regular repetitions of the disinfection experiments reported above were performed under the very same experimental conditions. After several coincident results, a sudden decrease of the reactor efficiency was observed with both UVA and UVC radiation and this low efficiency was maintained in further repetitions. The experimental procedure was checked in an attempt to explain this efficiency decrease: brand new lamps were used; temperature, humidity and irradiation of these lamps were measured and found to be similar to the values obtained during the first set of experiments; new Nutrient Agar was prepared; the air samplers were checked and then substituted by the model SPIN AIR V2 (IUL S.A., Barcelona, Spain), which works with lower air flow (100 L min\(^{-1}\)) and, according to tests performed in the laboratory, is more precise (Sánchez-Muñoz et al., 2011). The efficiency values were always low, as shown in Fig. 2b, even with UVC lamps, with around 30% of bacterial destruction against the 60-80% found in the previous tests.

Fresh photocatalysts were prepared with new TiO\(_2\) sol synthesised with new reagents and the same low efficiency values were obtained. The photocatalytic activity of the new monoliths was tested under UVA radiation for trichloroethylene (TCE) photocatalytic elimination in the experimental set-up described elsewhere (Suárez et al., 2008). The results showed normal values of around 80% degradation. Additional experiments were performed between January and June changing the location of the photoreactor in the building and the results did not improve significantly. The only difference observed between the first and second set of experiments was the low amount of CFUs collected during the experiments of the second set, 20-80 against 50-200 CFU m\(^{-3}\) collected during the first set of experiments. Therefore, it must be concluded that the photoreactor disinfection efficiency was affected by the type or concentration of microorganisms in order to explain the contradictory results. Unfavourable outdoor environmental conditions, like a cold winter with high rainfall and snow, could be responsible for the low concentration of bacteria observed in the second
set of experiments and possibly for a different distribution of bacteria species, prevailing species more resistant to the photochemical treatment than before.

Bacterial identification was done in order to know which species were resistant to the photocatalytic treatment in our experimental conditions. There is a great variability of species found in the air and sometimes very few species coincide from one year to another, which made it very difficult to identify the resistant and non-resistant species and compare one experiment to another. Apparently, the results showed that species (accession number, maximum identity - degree of correspondence between two subsequences -) like *Staphylococcus pasteuri* (FR839669.1, 100%), *Staphylococcus saprophyticus* (JN409469.1, 100%), *Micrococcus luteus* (HQ220044.1, 100%), *Acinetobacter radioresistens* (FJ608261.1, 100%), *Kocuria rosea* (JN084149.1, 100%), *Naxibacter haematophilus* (EU554441.1, 100%), *Bacillus endophyticus* (JN585716.1, 100%) were resistant to our UVA photocatalytic treatment. *M. luteus* (FJ229461.1, 99%) was also resistant to UVC photocatalysis together with *Stenotrophomonas maltophilia* (JF427723.1, 100%), *Arthrobacter luteolus* (GU188881.1, 100%), *Curtobacterium flaccumfaciens* (JN378724.1, 100%), *Staphylococcus hominis* (JN644561.1, 100%), *Acinetobacter sp* (HQ449642.1, 97%) and *Macrococcus equi pericus* (NR_044926.1, 100%).

Some of these species have special properties that could explain their resistance to the treatment. For instance, *Bacillus sp.* are spore-forming bacteria, which make them able to resist harsh conditions like heat, desiccation, radiation or disinfectants. The dormant spores are able to survive thousands if not millions of years (Atri and Foster, 2002). *M. luteus* can be found in human skin, water, dust and soil and their cells can live for long periods (Greenblatt el al., 2004). Evidences support the view that this specie (and related members of the genus) has numerous adaptations for survival in extreme nutrient-poor environments; this trait will assist in the bacteria persistence and its dispersal in the environment. *C. flaccumfaciens* is very
resistant to drying and can remain viable for up to 24 yr stored in the laboratory. It has been known to survive in soil for at least two winters (EPPO/CABI, 1997).

Our group is currently working on new photoreactor configurations in order to repeat and improve the efficiency results. But from our point of view, it is very important to point out that the differences found between the first and second set of experiments show that the scientific community should be very careful when talking about indoor air microbial characterization and disinfection in realistic conditions.

### 3.3. Fungicidal activity

The analysis of the indoor air showed the presence of several fungal species, mainly of the genera *Cladosporium, Alternaria, Aureobasidium, Penicillium, Mucor* and yeasts, which are commonly found in indoor air and food (Samson, 2004). The photocatalytic treatment was not able to significantly reduce the amount of any of the fungi detected in both set of experiments. One reason could be related to the fungal ability to form a high number of spores that are difficult to eliminate due to the complex composition of their cell walls. The presence of spores in the photocatalytic surface has been observed by SEM (Supplementary Material). Moreover, only few studies have dealt with fungal photocatalytic inactivation (Lonnen et al., 2005; Sichel et al., 2007b) and long irradiation times were required. For example, Vohra et al. (2006) using filters coated with TiO$_2$ saw that the photocatalytic destruction of fungal spores was 78% after 24 h, around 91% in 36 h and as much as 48 h were required to achieve complete inactivation of *A.niger* spores. Experiments varying several factors like residence time, light intensity or catalyst dosage are being performed in order to increase the efficiency of fungi elimination.
3.4. VOC elimination

Samples for VOC analysis were taken at three different photocatalytic experiments using UVA radiation. Figure 3 shows an example of the chromatograms obtained for the inlet and outlet of the reactor. Data obtained with control samples were similar to those given from the air passing through the reactor with the light off, indicating that VOCs come from the indoor air and not from the experimental device. The chromatograms show the presence of many VOCs similar to those founded by Hippelein et al. (2004). Aromatic compounds such as toluene and xylene, siloxanes (octamethylcyclohex siloxane, decamethylcyclopentasiloxane or dodecamethyl cyclopentasiloxane), aliphatic hydrocarbons such as tetracetane, pentadecane, or hexadecane, and hexanol were some of the most representative compounds detected. Comparing both chromatograms, a noticeable decrease of peak intensity with UVA photocatalysis can be observed.

Figure 4 shows the average efficiency of the three samplings for the different VOCs detected along to the initial concentration $C_0$ for calibrated compounds. For uncalibrated compounds, the conversion was obtained considering the integration of the area under the curve. Conversions above 80% are generally reached for most of the VOCs. Aromatic and aliphatic compound represent near 75% of the total VOCs detected.

The presence of aromatic compounds was related to the road traffic from outdoors. In some cases, benzene was detected in low concentration. Its presence is especially relevant due to the toxic character of this compound. Ethylbencene and xylene are used as additives in paints adhesives and varnish (Claeson et al., 2007). Some aliphatic compounds between C7-C18 were identified, among them, heptane was the one of the VOCs analyzed that presented the lower conversion. Considering the $C_0$ values included in Fig. 4, the heptane initial concentration was one order of magnitude higher than for the other aliphatic compounds. This
fact could be related to its lower reaction rate, but other factors such as its low molecular weight associated to
diffusion limitations can not be rule out. Aliphatic compounds are classic solvents found in several product
used for building construction and renovation. Moreover cyclic terpenes such as $\alpha$-limonene and $\alpha$-pinene
were also identified. These terpenes are added in cleaning products, food industry and, in the latter case, wooden products. The presence of siloxanes has been described in the literature but their origin is unclear (Shields et al., 1996; Schweigkofler and Niessner, 1999). The siloxanes can be released form furniture coatings, deodorants, cosmetic and adhesives (Bosc et al., 2006). The results obtained in this study clearly indicate that under UVA irradiation the TiO$_2$ based material was able to efficiently destroy a large variety of VOCs that include aliphatic and aromatic compounds, terpenes, oxygenated compounds and siloxanes at ppb levels.

4. Acknowledgements

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5. References


Photocatalytic elimination of indoor air biological and chemical pollution in realistic conditions

Figure 1.- Photocatalytic reactor. Biological sampling system (left) and reactor frontal view (right)
**Figure 2.**- Decrease of the number of bacteria in air with the irradiated photoreactor containing PET monoliths without TiO$_2$ (photolysis, white) or coated with TiO$_2$ (photocatalysis, black) in the first set of experiments (a) and the second set of experiments (b).

**Figure 3.**- VOCs present in the indoor air before (black) and after (grey) passing through the 8 W UVA-irradiated photocatalytic reactor with TiO$_2$-coated PET monoliths.
Figure 4.- Mean reduction of concentration of VOCs present in the indoor air with the UVA (8 W) irradiated photocatalytic reactor. $C_0$ is the concentration (mg cm$^{-3}$) at the reactor inlet.
Photocatalytic elimination of indoor air biological and chemical pollution in realistic conditions

Table 1.- Characteristics of the sampling for bioaerosols and VOCs

<table>
<thead>
<tr>
<th></th>
<th>Bacteria</th>
<th>Fungi</th>
<th>VOCs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampling time, $t$ (min)</td>
<td>10</td>
<td>4.17</td>
<td>60</td>
</tr>
<tr>
<td>Sampling system</td>
<td>SAS+Nutrient Agar</td>
<td>SAS+Malt Extract agar</td>
<td>Pump+Tenax tube</td>
</tr>
<tr>
<td>Sampling flow rate, $Q$ (L min$^{-1}$)</td>
<td>180</td>
<td>180</td>
<td>0.215</td>
</tr>
<tr>
<td>Residence time, $t_r$ (s)</td>
<td>0.12</td>
<td>0.12</td>
<td>110.5</td>
</tr>
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</table>
Table 2.- Characteristics of the first set of experiments performed and results obtained for bacteria

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Lamp</th>
<th>PET</th>
<th>TiO₂</th>
<th>Mean bacterial elimination (%)</th>
</tr>
</thead>
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<tr>
<td>No irradiation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lamp blank</td>
<td>off</td>
<td>no</td>
<td>no</td>
<td>0 ± 3</td>
</tr>
<tr>
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<td>no</td>
<td>7 ± 2</td>
</tr>
<tr>
<td>TiO₂ blank</td>
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<td>yes</td>
<td>8 ± 1</td>
</tr>
<tr>
<td>UVA</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>8 W</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Photolysis UVA-8 W</td>
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<td>no</td>
<td>30 ± 26</td>
</tr>
<tr>
<td>Photocatalysis UVA-8 W</td>
<td>on</td>
<td>yes</td>
<td>yes</td>
<td>69 ± 1</td>
</tr>
<tr>
<td>15 W*</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Photolysis UVA-15 W</td>
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<td>no</td>
<td>48 ± 8</td>
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<tr>
<td>Photocatalysis UVA-15 W</td>
<td>on</td>
<td>yes</td>
<td>yes</td>
<td>68 ± 5</td>
</tr>
<tr>
<td>UVC</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>8 W</td>
<td></td>
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<tr>
<td>Photolysis UVC-8 W</td>
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<td>no</td>
<td>70 ± 7</td>
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<td>yes</td>
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<tr>
<td>16 W*</td>
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<td></td>
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<tr>
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<td>no</td>
<td>no</td>
<td>80 ± 5</td>
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<tr>
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<td>yes</td>
<td>yes</td>
<td>76 ± 10</td>
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</tbody>
</table>

* UVC-16 W and UVA-15 W are lamps of commercial power