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# Polydopamine film coating on polyurethane foams as efficient “sunscreen”.

## Application to photocatalysis under UV irradiation

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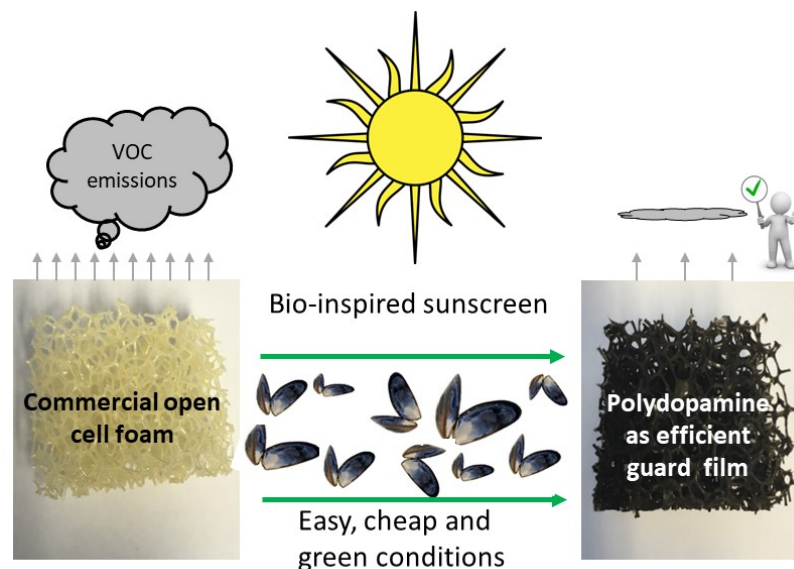
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### Graphical abstract



### Abstract

Polyurethanes are used in a large variety of commercial and technical applications, due to their high tensile strength, chemical resistance, good process ability and good mechanical properties. In particular, polyurethane open cell foams appear as ideal candidates to design

original photoreactors. However, due to their high sensitivity to UV light, polyurethane foams can be not used directly as structured photocatalytic supports. In this work, we show that a simple thin polydopamine film coating on the foam surface plays a “sunscreen” role, protecting the polyurethane foam from UV<sub>A</sub> or UV<sub>C</sub> degradation and inhibiting volatile organic compounds’ emanation. Furthermore, when loaded with TiO<sub>2</sub> particles, these functionalized foams allowed developing an efficient photocatalytic system for the degradation of formic acid in water and the mineralization of acetaldehyde, *n*-heptane, toluene and acetone in air.

**Keywords: Polydopamine, Open cell foam, Polyurethane, Volatile Organic Compound, UV, Photocatalysis.**

## **1. Introduction**

Polyurethanes (PUs) are used in a large variety of commercial and technical applications, due to their high tensile strength, chemical resistance, good process ability and good mechanical properties [1–3]. In particular, open cell polyurethane foams (OCPUF) are known as remarkable elastomers and are essentially used as filters in cooker hoods, aquariums, mattresses or vacuum cleaners. Based on a polydopamine coating strategy [4], we have shown the great interest of using OCPUF as a soft structured catalytic support (S<sub>2</sub>CS) for various catalytic reactions [5-10].

One of the main disadvantages of PU-based materials, however, is their high sensitivity to light, in particular to UV light. This is a major limitation, which relates to their use for outdoor applications or under UV radiation. PUs indeed undergo significant structural changes upon exposure to UV radiation, which cause deterioration of their physical and mechanical properties [11-15]. For instance, a polyurethane made with an aromatic isocyanate will yellow upon exposure to UV light due to physical and chemical modifications of its surface. Although various analytical techniques or spectroscopies such as Fourier-Transform Infra-Red spectroscopy (FT-IR), scanning electron microscopy (SEM), or X-ray photoelectron spectroscopy (XPS) have been used to study the accelerated weathering degradation of PU systems, the exact mechanism of photolytic degradation of PU remains, to our knowledge, unsure [11-19].

In this work, we show that a polydopamine (PDA) guard film prepared by a simple eco-friendly dip-coating methodology in water efficiently protects OCPUF from UV radiation. For that purpose, pristine OCPUF and PDA-coated OCPUF (OCPUF@PDA) samples were compared before and after UV irradiation by FT-IR spectroscopy and on-line measure of volatile organic compounds emanation by gaseous chromatography and ATD-MS. Based on the interesting “*sunscreen*” properties of PDA, we next used OCPUF@PDA loaded with TiO<sub>2</sub> nanoparticles (NPs) for photocatalytic applications.

For photocatalytic applications and water treatment, the catalyst is usually dispersed in an aqueous solution and used in slurry reactors. This type of reactors however generates major drawbacks: (i) the catalyst particles must be separated from the liquid phase, which involves a time and energy consuming process and (ii) the pressure drop is not negligible. To avoid these costly filtration/separation and catalyst recovery steps, the active phase can be anchored on a suitable support and used in fixed or fluidized bed reactors. In this context, Jain and Pradeep [20] used the bactericidal properties of silver nanoparticles anchored on a polyurethane foam for obtaining a logarithmic abatement of 5 over Escherichia Coli-contaminated water at a water flow rate of 0.5 L/min. However, the silver nanoparticles were directly coated on the foam by possible interactions with the nitrogen atoms of the polyurethane. As another example, Yamamoto and Imai [21] prepared foam-based photocatalysts with the synthesis of anatase titania nanoparticles and open cellular structure by calcination of polyacrylamide gels containing titanyl sulfate and urea. The titania foams showed, under UV<sub>A</sub> illumination, disappearance rates that were 2.5 and 4 times greater than those shown by fluffy commercial TiO<sub>2</sub> P25 for methylene blue decomposition in water and gas phase acetaldehyde removal, respectively. The performances were attributed to the high accessibility and the high transparency of UV light due to an open cellular structure with wide channels and thin walls. Using the photocatalytic oxidation of 1,8-diazabicyclo[5.4.0]undec-7-ene in water as a model reaction, Ochuma et al [22] evidenced the interesting performances of a TiO<sub>2</sub>-coated alumina reticulated foam monolith inserted inside an annular photo-reactor compared to a slurry reactor. From these works, it clearly appears that there is an interest in developing a photo-reactor based on OCPUF@PDA materials. In this context, we present a new photoreactor based on OCPUF@PDA@TiO<sub>2</sub> foams, which we have tested for water and air treatment.

## 2. Experimental

### 2.1. Materials and methods

Commercial compounds were used as received. Dopamine hydrochloride, Tris base, were purchased from Alfa Aesar. Titanium (IV) oxide, anatase (99.9% - AB208992) was purchased from Sigma. TiO<sub>2</sub> NPs present a specific surface and size of 100-220 m<sup>2</sup>/g and 30-50 nm, respectively. Polyurethane open cell foams were purchased from FoamPartner. Their characteristics are: (i) strut size: 220 μm; (ii) window size: 779 μm; (iii) cell size: 2500 μm; (iv) density: 0.027-0.033 and (v) hydrodynamic porosity: 0.94-0.97. The samples (0.150 g - 7g) were used without prior treatment. The solutions are prepared with water purified by Synergy® Water Purification System (Millipore). Polydopamine-coated open cell polyurethane foams (OCPUF@PDA) and the samples loaded with TiO<sub>2</sub> particles (OCPUF@PDA@TiO<sub>2</sub>) were prepared according to our reported procedures [5-6].

Scanning electron microscopy was performed with a Hitachi S800 FEG microscope at the “Centre Technologique des Microstructures” (CTμ) at the University of Lyon. Samples of foams were observed by SEM under an accelerating voltage of 15 kV. Elemental analyses were performed with an EDS-SDD detector (SAMx) with an active area of 30 mm<sup>2</sup>.

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) measurements were performed by the Plateforme Analytique of the Institut Pluridisciplinaire Hubert Curien (UMR CNRS 7178), Strasbourg, France.

FT-IR spectra were recorded with a Bruker Vertex 70 spectrometer at a resolution of 4 cm<sup>-1</sup> after 128 scans.

Photodegradation studies of OCPUF foams under UV<sub>C</sub> irradiation were performed at the Institute for Research on Catalysis and Environment of Lyon (IRCELYon). Gaseous chromatography coupled to a photoionization detector (GC/PID), gaseous chromatography coupled to a plasma emission detector (GC/PED), gaseous chromatography coupled to a pulsed discharge helium ionisation detector (GC/PDHID), and thermic desorption coupled to gaseous chromatography and mass spectrometry (ATD/GC/MS) were used for analysis.

Photodegradation studies of formic acid in water were conducted in the UV-RER/ANEMO laboratory.

Photodegradation studies of Volatile Organic Compounds (VOCs) in air were conducted by Ultra Traces Analyses Aquitaine (Pau, France) in agreement with the French AFNOR XP B44-013 standard test. Details about the airtight chamber and the methods used can be found

in reference [23]. GC-FID, PID and FID-methanizer from AIRMOTEC were used for the determination of VOCs and CO<sub>2</sub>, respectively.

## **2.2. Photodegradation studies of foams under UV<sub>A</sub> irradiation**

OCPUF and OCPUF@PDA samples were irradiated in air with an 8 W fluorescent UV<sub>A</sub>-365 nm lamp for 200 h. The lamp has a polychromatic emission spectrum in the range of 300–540 nm, with the peak wavelength at 365 nm, and a light intensity of 1165 μW/cm<sup>2</sup>. FT-IR spectra were recorded before and after irradiation.

## **2.3. Photodegradation studies of foams under UV<sub>C</sub> irradiation**

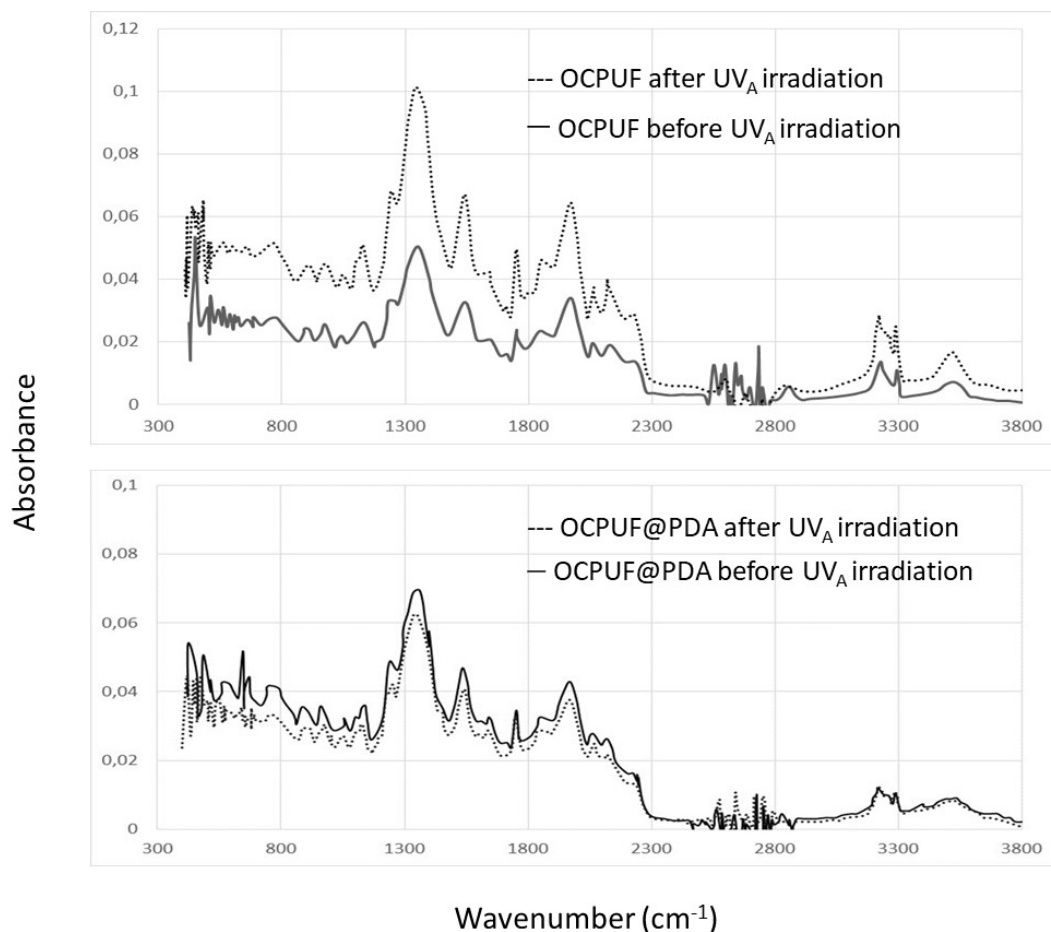
OCPUF, OCPUF@PDA, and OCPUF@PDA@TiO<sub>2</sub> samples were irradiated for 16 h with a 95 W Philips TUV PL-L UVC-253.7 nm lamp introduced inside the annular hole. GC/PID was used for detecting the VOCs such as formaldehyde, acetaldehyde, acetone, toluene and heptane, and GC/PED for CO<sub>2</sub> measurements. Concentrations of formaldehyde, acetaldehyde, acetone, toluene and heptane were measured by GC/PDHID. In addition, gas samples collected at the end of UV<sub>C</sub> irradiation with an AirToxics cartridge were analysed by ATD/GC/MS for VOC analysis.

## **3. Results and discussion**

### **3.1. UV<sub>A,C</sub> irradiation of OCPUF, OCPUF@PDA and OCPUF@PDA@TiO<sub>2</sub>**

The behaviour of OCPUF, OCPUF@PDA and OCPUF@PDA@TiO<sub>2</sub> foams under UV<sub>A</sub> and UV<sub>C</sub> irradiation was studied by FT-IR spectroscopy and GC measurements. The PDA content ranges typically from 3 to 5 wt.% for OCPUF@PDA and ICP-AES analyses revealed an average Ti loading of 5112 ± 52 mg/kg for OCPUF@PDA@TiO<sub>2</sub>.

The vibrational changes in the FT-IR spectra of both OCPUF and OCPUF@PDA after UV<sub>A</sub> irradiation can be seen in Figure 1; important changes are observed in the FT-IR spectrum of OCPUF while no evident IR differences are observed for the foam coated with PDA film.

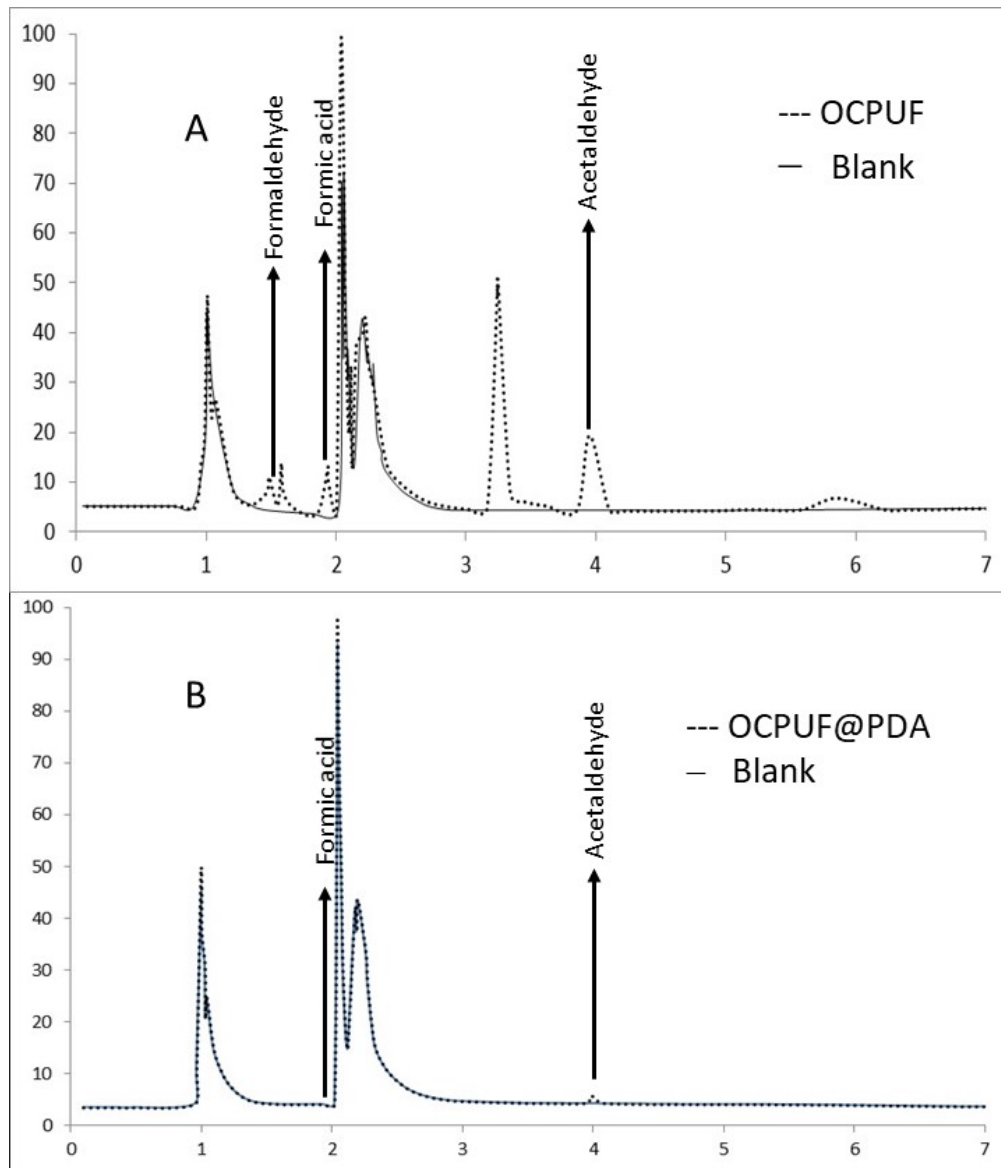


**Figure 1.** FT-IR spectra before and after  $UV_A$  irradiation for both OCPUF and OCPUF@PDA. 400 to  $3800\text{ cm}^{-1}$

According to Rosu *et al.* [24], the differences between the spectra before and after irradiation reflect the structures that were formed or lost during the UV irradiation. These results unambiguously show that UV radiation modified the chemical structure of OCPUF, but not that of OCPUF@PDA. As the polyurethane photo-degradation mechanism is complex, and as this work only focusses on the possible “*sunscreen*” properties of PDA for open cell foam, the latter is not discussed here and the reader is invited to consult references [15-17] for more information on this topic, as well as the excellent work of Rosu *et al.* [24] for a complete analysis of the FT-IR difference spectrum in the  $1000\text{-}3700\text{ cm}^{-1}$  region.

Figure 2 shows the gas chromatographs obtained for annular samples of OCPUF and OCPUF@PDA after 16 h under 95 W  $UV_C$  irradiation. It can be seen that OCPUF releases a lot of VOC including formaldehyde, formic acid, and acetaldehyde under  $UV_C$  irradiation, whereas OCPUF@PDA releases almost none compared to the blank (Figure. 2B: dotted and full lines are superimposed). Table 1 gives the quantification of the emitted VOC for all

samples. It is remarkable to note that only 50 ppb of formaldehyde and 450 ppb of acetaldehyde were detected for OCPUF@PDA.



**Figure 2.** Gas chromatograms obtained for OCPUF and OCPUF@PDA after 95W UV<sub>C</sub> irradiation for 16 h

Concerning the OCPUF@PDA@TiO<sub>2</sub> sample, although the performance and robustness under hard mechanical solicitation and under photocatalytic conditions have been already demonstrated [5-6], no evaluation of possible VOC emission from OCPUF@PDA@TiO<sub>2</sub> under UV irradiation had been done yet. The results are presented in Table 1.



**Table 1.** GC/PDHID quantification of the emitted VOC by OCPUF, OCPUF@PDA and OCPUF@PDA@TiO<sub>2</sub> after 16 h under 95 W UV<sub>C</sub> irradiation

Residence time (min)	VOC	OCPUF	OCPUF@PDA	OCPUF@PDA@TiO <sub>2</sub>
1.06		x <sup>a</sup>	-	x
1.20		x	-	-
1.37		x	-	-
1.48	Formaldehyde	1.1 ppm	0.05 ppm	0.1 ppm
1.58		xx	-	-
1.94	Formic acid	5638 <sup>b</sup>	428 <sup>b</sup>	7069
2.25		x	-	-
2.52		x	-	-
2.90		x	-	-
3.30		xx	-	x
3.55		x	-	-
3.97	Acetaldehyde	38.2ppm	0.45ppm	1.1ppm
5.91		x	-	x
7.65	Acetone	0.1ppm	-	-

<sup>a</sup> x signify that the presence of a VOC was detected but not quantified. <sup>b</sup> Formic acid has not been quantified, but the area of the pic is given for information.

The immobilised TiO<sub>2</sub> NPs on OCPUF@PDA seem to not increase the rate of OCPUF degradation under UV<sub>C</sub> irradiation. Indeed, at the exception of formic acid, the VOC emissions of OCPUF@PDA@TiO<sub>2</sub> are close to those observed with OCPUF@PDA. In other words, the PDA film, which protects OCPUF does not seem to be degraded by the TiO<sub>2</sub> NPs under UV irradiation.

From these results, it is clear that OCPUF materials without a protective coating are not suitable for use in a photocatalytic system. However, we can claim that a polydopamine film coating efficiently protects OCPUF from UV<sub>A</sub> or UV<sub>C</sub> degradation and strongly inhibits organic compounds emanation. In this context, and encouraged by our previous work on OCPUF@PDA@TiO<sub>2</sub> [5-6], we next studied the use of OCPUF@PDA@TiO<sub>2</sub> as a macroscopic soft structured catalytic support (S<sub>2</sub>CS) for the development of a pilot flow photo-reactor for both water (acid formic) and air (VOCs) treatment.

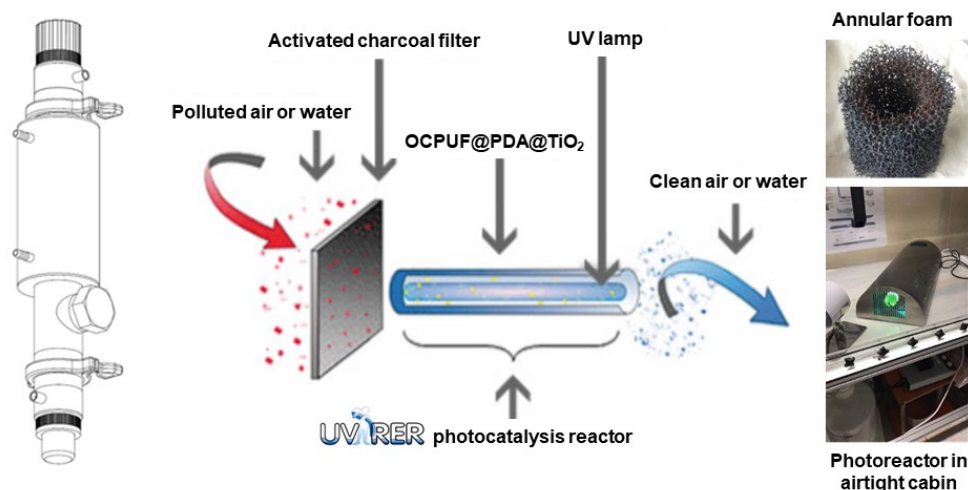
### 3.2. Photocatalytic reactor based on OCPUF@PDA@TiO<sub>2</sub> materials

#### 3.2.1 Developed pilot photoreactors

The photoreactors were developed by UV-RER/ANEMO. Two kinds of experimental setups were used depending on the type of tests:

- For liquid phase: the system was composed of a central chamber with a 55 W Philips TUV PL-L UV<sub>C</sub> lamp (253.7 nm) embedded in annular OCPUF@PDA@TiO<sub>2</sub> foams. The available volume was of 1.485 L, and the foam volume of 0.215 L with a length of 0.39 m. The system temperature was controlled *via* a heating jacket with circulating water at 21.4 °C (Figure 3)

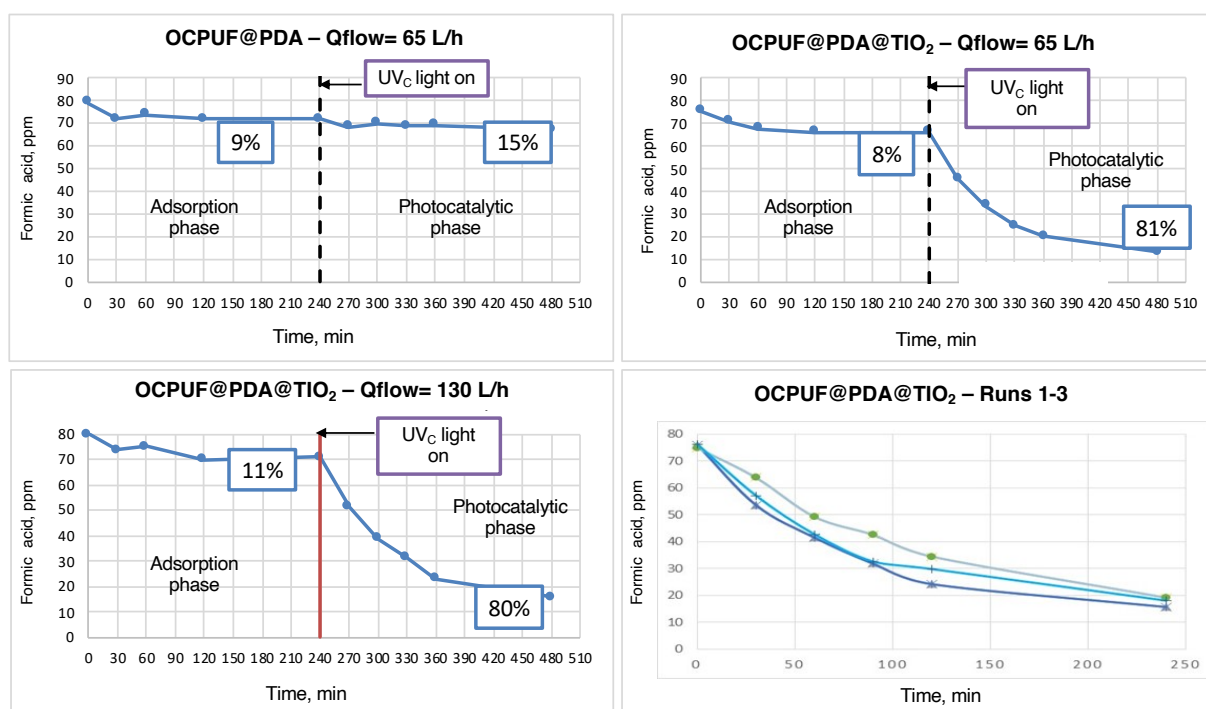
- For gas phase: the system was composed of a central chamber with a 95 W Philips TUV PL-L UVC lamp (253.7 nm) embedded in annular OCPUF@PDA@TiO<sub>2</sub> foams. The total volume was of 1.2 L with a foam-length of 0.44 m. There was no cooling jacket in this case. (Figure 3)



**Figure 3.** Pictures and schematic representations of the UV-RER photoreactors used for air and water treatment

### 3.2.2. Formic acid degradation in water

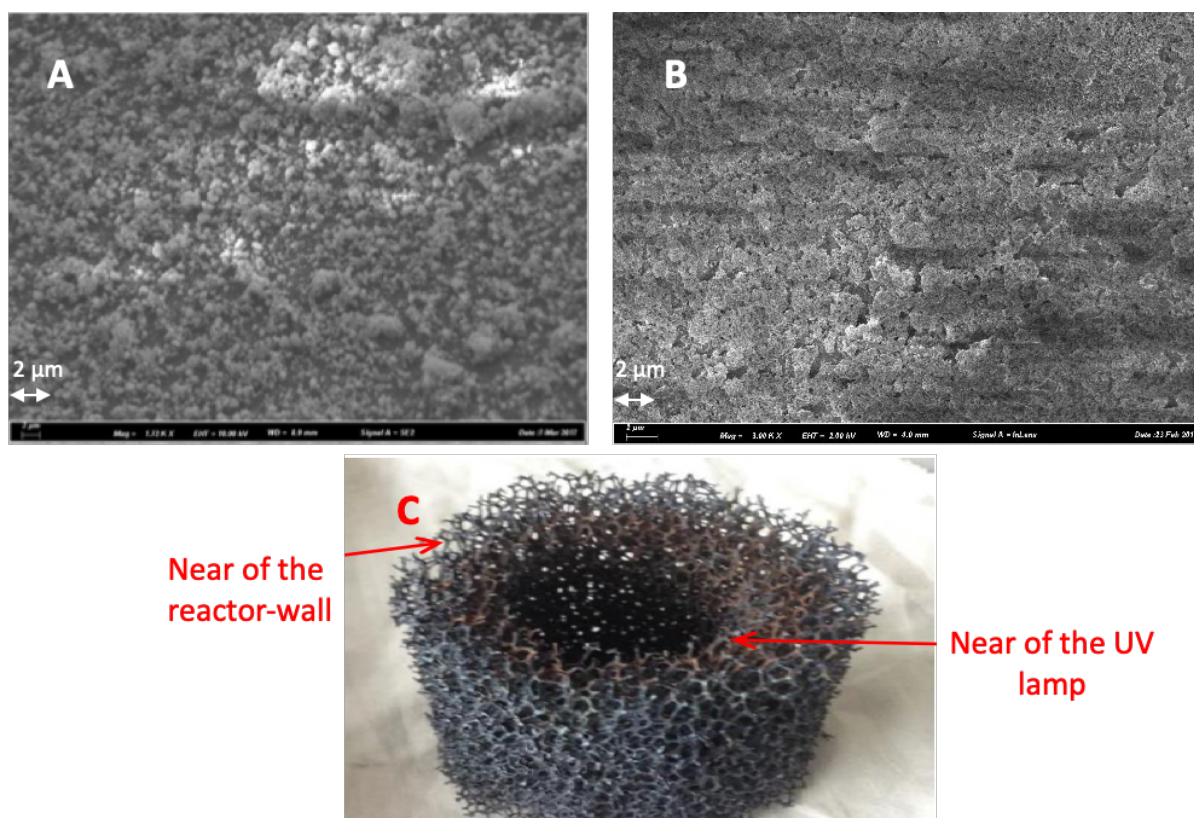
The degradation of formic acid solutions (80 ppm) in water (8 L) was studied with the UV-RER photo-reactor garnished with annular OCPUF@PDA@TiO<sub>2</sub> foams presented above (Figure 3). Two mass flow were considered: 65 and 130 L/h, which corresponds to contact times of 52 s and 25 s, respectively. With a UV<sub>C</sub> light power of 55 W, the maximum temperatures recorded were of 30 °C and 29.8 °C, respectively. At the beginning of each experiment, the foam and system were saturated by the pollutant for 240 min (adsorption phase), then the system was switched on, and the degradation of formic acid versus time was followed by GC (Figure 4).



**Figure 4.** Abatement of formic acid versus time with OCPUF@PDA and OCPUF@PDA@TiO<sub>2</sub>.

As can be seen in Figure 4, the adsorption phase gives similar results with OCPUF@PDA or OCPUF@PDA@TiO<sub>2</sub> with an abatement of 8-9% after 240 min, and does not seem to be significantly affected by the flow rate (9 vs. 11% of formic acid abatement). When the device is on, only the photo-reactor filled with OCPUF@PDA@TiO<sub>2</sub> foams allows to degrade the formic acid. This result show (if needed) that the TiO<sub>2</sub> is necessary for a photocatalytic action. Again, the mass flow does not significantly affect the reaction rate; 80-81% of formic acid degradation is obtained in both cases. Accordingly, we can assume that a chemical regime is established. In other words, in agreement with the works of Edouard *et al.* [25-28], Giani *et al.* [29] and Richardson *et al.* [30], due to the high mass transfer properties of the open cell foams, no apparent mass transfer limitation is observed. Finally, as can be seen from the graph in the right bottom corner of Figure 4, an OCPUF@PDA@TiO<sub>2</sub> foam could be used three times with a fresh formic acid solution, displaying the same apparent activity under similar conditions (same flow) for each run. Consequently, it is reasonable to assume that no important leaching nor major deactivation process occurred. In agreement with that, ICP-AES analyses of the foams before (5112 mg/kg) and after test (5004 mg/kg) show no titanium leaching. However, SEM images of the foam surface revealed a net morphological change of the foam surface (see Figure 5), that may be attributed to a kind of surface abrasion by the

mass flow and more probably to the temperature near of the UV lamp, which may soften the OCPUF during the photocatalytic runs.



**Figure 5.** SEM images of OCPUF@PDA@TiO<sub>2</sub> before (A) and after test (B), and picture of the annular foam after test (C)

### 3.2.3. VOC degradation in air

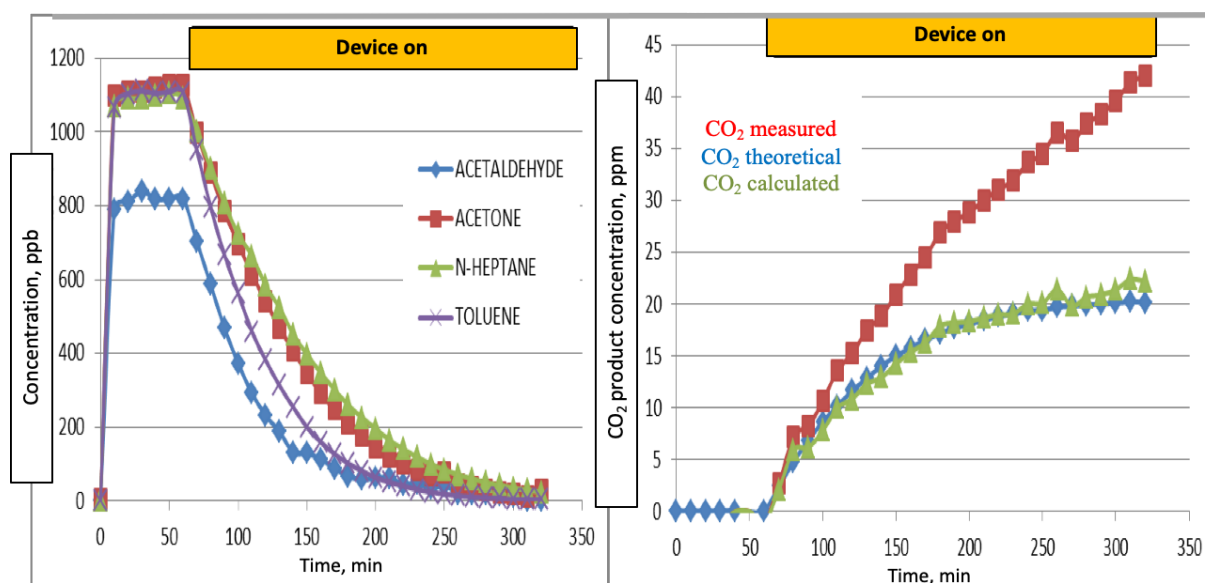
The efficiency of the developed OCPUF@PDA@TiO<sub>2</sub> photo-reactor was assessed according to the French XP B44-013 AFNOR standard test in a closed chamber (1.2 m<sup>3</sup>) with air in recirculation at the ppbV level under controlled conditions representative of indoor air. The device was evaluated for the mineralization of a mixture of four representative VOCs (acetaldehyde, acetone, *n*-heptane and toluene). The degradation rate allowed the determination of the Clean Air Delivery Rate (CADR), while the mineralization efficiency was determined from CO<sub>2</sub> analysis.

A validation test of the closed-chamber was made before the photocatalytic experiments in order to control the leaks, the possible release of VOCs from the chamber materials and the stability of VOC concentration without the photocatalytic device for 24 h (less than 10% variation). The chamber was equipped with an external fan (minimum flow 120 m<sup>3</sup>.h<sup>-1</sup>), and a

relative humidity and temperature probe. Online connection of the analytical systems to the chamber allow automatic sampling.

A control experiment run with the device-on but without VOC revealed the formation of formaldehyde (70 ppbV) and benzene (11.9 ppbV) after 23 h. A comparison of the CO<sub>2</sub> concentrations measured with the empty chamber and with the photo-reactor, revealed a more important production with the latter, probably in reason of the mineralization of the produced formaldehyde and benzene. This increase in CO<sub>2</sub> concentration (namely CO<sub>2</sub><sub>blank</sub>) is around of 20 ppm after 300 min. These results are in good agreement with the test carried out in their airtight chamber (*vide supra*) (Table 1). For the empty chamber (without photo-reactor), the small increase of CO<sub>2</sub> concentration (around 10 ppm) is due to infiltration of outside air into the chamber.

A typical test consisted in adding a standard mixture from pure liquid commercial solutions with a micro-syringe through a septum into the chamber at 250-1000 ppbv concentration for each compound. The external fan was switched on only during pollutant homogenization and switched off after homogenization, *i.e.*: when the photocatalytic device was started. Continuous VOCs and CO<sub>2</sub> analyses, as well as temperature and relative humidity evolution were followed before the pollutants addition and during the complete photocatalytic test. The results were compared by following the pollutant's concentrations versus time (Figure 6) and by calculating the clean air delivery rate (CADR; Figure 7 and Table 2) for each individual VOC and the total VOCs (see for instance [23]).



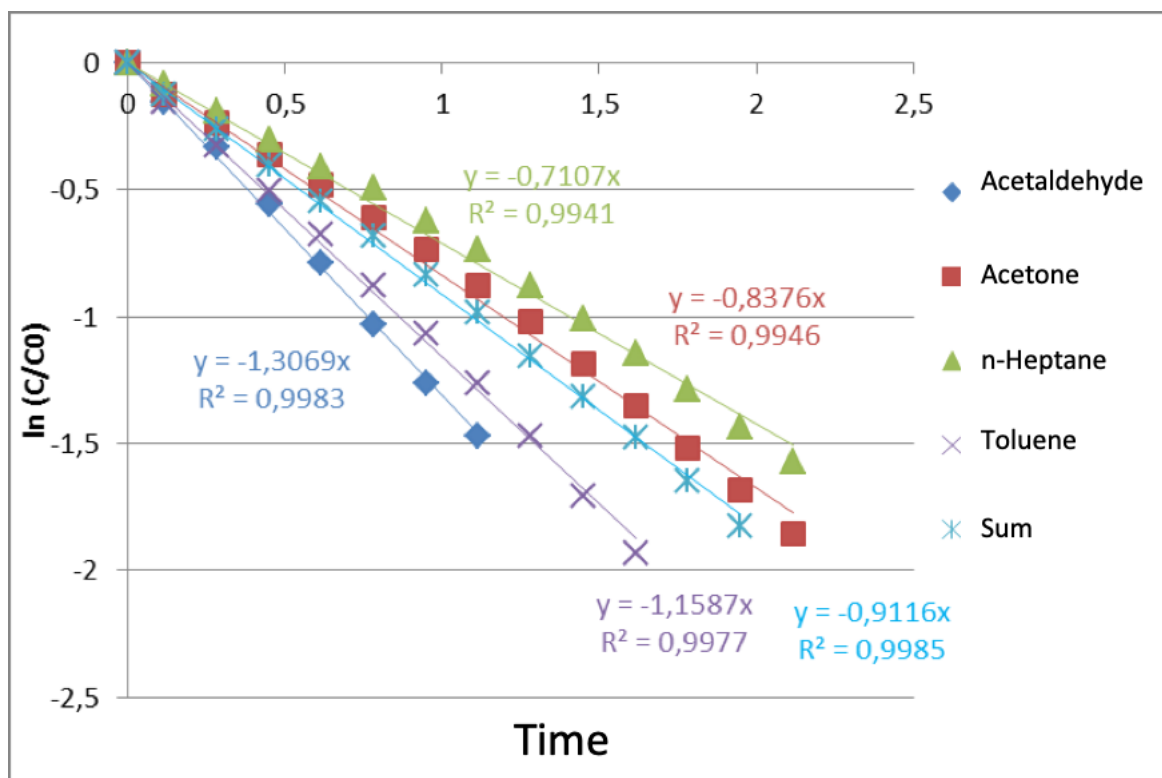
**Figure 6.** VOCs (left) and CO<sub>2</sub> (right) concentration vs. time

The results obtained with initial concentrations of 1100 ppbV reveal a significant photocatalytic activity of this system on the 4 VOCs. A complete degradation of the 4 VOCs is indeed observed with an elimination yield of 99% for acetaldehyde, heptane and toluene, and of 97% for acetone after 4 h. The theoretical (blue curve) and calculated values of CO<sub>2</sub> (green curve obtained after subtraction of the CO<sub>2blank</sub> produced by the system itself, *i.e.*: CO<sub>2calculated</sub> = CO<sub>2measured</sub> - CO<sub>2blank</sub>) are in good agreement, and we can conclude that a complete mineralization of the 4 VOCs occurred.

The CADR represents the “effective” clean air flow rate delivered by the photoreactor based on a well-mixed single zone model. Assuming that the air is well mixed in the chamber and that the contaminant removal mechanisms other than air cleaning (e.g. surface deposition effect and chamber leakage effect) are the same with and without operating photoreactor, the reaction can generally be characterized by a first-order rate constant  $k_n$  when the device is off and  $k_e$  when the device is on. The mass conservation of contaminant in the “pull-down” test can be written as Eq.1 where  $V$  is the volume of the testing chamber (m<sup>3</sup>),  $k_n$  the first-order decay rate constant of the contaminants’ concentration without photocatalysis (possible adsorption on chamber walls and air-cleaner) (h<sup>-1</sup>),  $k_e$  the first-order decay rate constant of the total contaminants’ concentration with the operating air cleaner (h<sup>-1</sup>),  $t$  the time (h) and  $C(t)$  the contaminants’ concentration inside the chamber at time  $t$  (mg. m<sup>-3</sup>) expressed in carbon for the total VOCs. The CADR (m<sup>3</sup>·h<sup>-1</sup>) is calculated from the determination of the slopes of the curves  $\ln(C/C_0) = kt$ , with  $k = k_n$  when the device is off and  $k = k_e$  when the device is on, and  $C_0$  is the initial pollutants’ concentration (Figure 7) [23]. Table 2 summarizes the CADR results for the 4 VOCs at different initial concentrations (or runs).

Eq. 1:

$$\begin{cases} \frac{dC(t)}{dt} = -\left(k_n + \frac{CADR}{V}\right)C(t) \\ \frac{dC(t)}{dt} = -k_e C(t) \end{cases}$$



**Figure 7.**  $k_e$  estimation by linear regression of  $\ln(C/C_0)$  versus time for the 1000 ppbV experiment

**Table 2.** CADR ( $\text{m}^3 \cdot \text{h}^{-1}$ ) for individual and total VOCs at different initial concentrations

	Acetaldehyde	Acetone	<i>n</i> -heptane	Toluene	$\Sigma$ VOC
1 ppmV – run1	1.53	0.98	0.83	1.36	1.07
250 ppbV – run2	2.07	1.36	1.15	1.84	1.53
250 ppbV – run3	1.97	1.31	1.09	1.77	1.42

The efficiency of the photocatalytic system regarding the AFNOR XP B44-013 standard is established. Indeed, a first test with the 4 considered VOCs (with an initial concentration of 1 ppmV) has allowed to establish their complete mineralization with a CADR of *ca.*  $1 \text{ m}^3 \cdot \text{h}^{-1}$ . Moreover, two other tests with initial concentrations of 250 ppbV have confirmed these results with a CADR of *ca.*  $1.5 \text{ m}^3 \cdot \text{h}^{-1}$ . Only formaldehyde is not correctly degraded, as its residual concentration does not go below 70 ppbV. After three runs, the photocatalytic activity seems constant, but an experiment over a long period (several months for instance) would be necessary to confirm or relax this observation. Indeed, it is well known that the

CADR of a photocatalytic system can decrease with time. This possible decrease may result from a diminished efficiency of the lamp and/or the photocatalytic materials.

#### **4. Conclusions**

Thanks to its lightweight, flexibility, good transport properties, low-pressure drop, and large pores that easily let the light go through it, polyurethane-based soft structured catalytic supports appear as ideal candidates to design original photo-reactors. However, due to the disadvantages of PU-based materials (*i.e.*: high sensitivity to light, in particular to UV light), polyurethane foams cannot be used directly. In this work, we show that a polydopamine film coating on the foam plays a “sunscreen” role. This thin film protects the polyurethane open cell foam (OCPUF) from UV<sub>A</sub> or UV<sub>C</sub> degradation and inhibits organic compounds emanation, either in the presence or in the absence of TiO<sub>2</sub> NPs.

Based on these encouraging results, we have developed a UV<sub>C</sub> photo-reactor filled with OCPU@PDA@TiO<sub>2</sub> materials. Although it releases small amounts of formaldehyde and benzene, this device appears to be an efficient photocatalytic system for both the degradation of formic acid in water and the complete mineralization of acetaldehyde, *n*-heptane, toluene and acetone in air. These first photocatalytic results for water or air treatment are very encouraging, and further work will be directed toward the elimination of formaldehyde as well, together with an optimisation the lamp-photocatalytic media assembly, the cooling system, and the mixing of the pollutant in the filter media in order, notably, to increase the Clean Air Delivery Rate.

#### **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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