

# Absorption and Photocatalytic Degradation of VOCs by Perfluorinated Ionomeric Coating with TiO<sub>2</sub> Nanopowders for Air Purification

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## Abstract

In this work, we propose a transparent multilayered perfluoropolymeric coating as immobilization method for TiO<sub>2</sub> nanoparticles, and evaluate its suitability in the gas phase photocatalytic degradation of six different volatile organic compounds. The use of TiO<sub>2</sub> nanoparticles as photocatalyst for gas and water purification has been widely discussed in literature. Yet, several issues remain open, starting from the need for an immobilization system – to avoid nanoparticles dispersion in the treated media, while at the same time offering high

photoactivity by making nanoparticles fully accessible to activating radiation and to pollutants. Here, a transparent multilayered perfluoropolymeric coating was made of a layer of TiO<sub>2</sub>-containing perfluorosulfonic acid polymer on a layer of perfluorinated amorphous polymer. The use of perfluoropolymeric materials overcomes the possible degradation of the polymeric immobilization system due to UV radiation and UV-activated TiO<sub>2</sub>. Moreover, the ionomeric perfluorosulfonic layer, which actually held the nanometric TiO<sub>2</sub>, worked as selective membrane for pollutants absorption and catalyst preservation, depending on the interactions between the superacidic polar heads of the ionomer and the pollutants, in particular those capable of hydrogen bonding. Gas-phase photocatalytic degradation tests were performed using pentane, methanol, 2-propanol, toluene, dichloromethane and pyridine as reference volatile organic pollutants, thus ranging on different polarity properties. Results indicate performances comparable to other approaches reported in literature and show a strong influence of both atmospheric conditions (namely, humidity) and pollutant nature – polarity, proticity – on the actual kinetics of photodegradation, also depending on the interactions regulating the affinity between the ionomeric layer of the coating and pollutants. The high potential of the coating in the photodegradation was confirmed by the observed values of the photoabatement rates: all approximately above 10<sup>-5</sup> s<sup>-1</sup> and maximum for alcohols (1.4 × 10<sup>-4</sup> and 1.7 × 10<sup>-4</sup> s<sup>-1</sup> in dry and humid conditions, respectively).

**Keywords:** Photocatalysis; Gas phase; Volatile Organic Compounds; Titanium dioxide; Fluorinated PFSA coating

## **1 Introduction**

Air pollutants have influence on comfort and life, and volatile organic compounds (VOCs) can generate adverse effects on human health by causing illnesses from sick building syndrome (SBS) (1-7) to cancer (8). Thus, many people are nowadays victims of poor air quality and efficient technologies for VOC abatement are highly required (9). Most standard depollution systems are based on filtration and absorption, requiring periodic replacement (10). However, these systems showed that absorbed pollutants can produce secondary VOCs, thus producing supplementary risks for the human health (11).

Many advanced technologies like biological methods (biofilter, biotrickling filter, membrane bioreactor and bioscrubber) (12), plasmachemical systems (13) and advanced oxidation processes (14) for a quick and inexpensive removal of VOCs from air have recently been developed. Among these techniques, photocatalytic oxidation arises as a safe and advantageous method for the complete degradation of contaminants by exploitation of solar radiation (15-18). Titanium dioxide,  $\text{TiO}_2$ , thanks to its high photocatalytic activity, nontoxicity, chemical stability, and relatively low cost, is certainly the most studied photocatalyst and, actually, the focus of numerous well-established applications (19-22). UV activation of  $\text{TiO}_2$  can induce the formation of strongly oxidizing reagents, such as  $\text{OH}\cdot$  radicals (redox potential  $\text{OH}\cdot/\text{H}_2\text{O} = +2.27$  eV vs. the SHE) and  $\text{O}_2^-\cdot$  superoxide ions (redox potential  $\text{O}_2/\text{O}_2^-\cdot = -0.28$  eV vs. the SHE), which can cause the decomposition of pollutants present in air or water; in case of highly adsorbed pollutants, direct oxidation at the hole site of  $\text{TiO}_2$  photocatalyst is also favored (22-24).

Several issues pertinent to the use of  $\text{TiO}_2$  as photocatalyst in the form of conventional powders emerged during preliminary applications: for example, inefficient light exploitation, stirring difficulties during reaction, complex catalyst separation after reaction as well as concerns about the safe use of nanosized compounds (25-27).  $\text{TiO}_2$  immobilization inside a UV transparent solid

matrix can overcome the aforementioned disadvantages (28-31). However, the exposure of TiO<sub>2</sub> to UV light generates free radicals, which can degrade hydrogenated and partially halogenated polymers, such as polyvinyl chloride, polystyrene, polyvinyl alcohol, and polyethylene (32-35). The compatibility of fluorinated materials in the presence of TiO<sub>2</sub> was also studied and perfluoropolymers resulted extraordinarily stable toward UV-activated TiO<sub>2</sub> photodegradation (36). In particular, amorphous perfluoropolymers showed the highest chemical stability and, due to their high UV transparency and high gas permeability, emerged as best candidate class of materials for the fabrication of TiO<sub>2</sub>-embedding matrices (37,38). Recently, a multilayered perfluorinated coating based on amorphous and low-crystalline fluoropolymers with immobilized TiO<sub>2</sub> was applied in a continuous photocatalytic apparatus for water remediation (39). In this application, the multilayered coating comprised an ionomeric layer of perfluorosulfonic acid (PFSA) polymer in order to optimize the interaction between the catalyst and the polluted aqueous solution (39).

Although TiO<sub>2</sub>-mediated photocatalysis is the subject of a very large number of research studies, it is difficult to find a comprehensive account addressing a large number of pollutants: in general, only one model reactant is considered, which is not necessarily representative of the actual photocatalytic efficiency of the material against other pollutants. Moreover, while several immobilization methods have been proposed to produce stable photocatalytic coatings for water purification (40-42), in gas phase photocatalysis the catalyst nanoparticles are generally spread on a suitable support, or alternatively produced by sol-gel and applied by spraying or dipping (42-45). This poses some questions on the actual stability of the coating and on the potential dispersion of nanoparticles in the treated air effluent, with related health concerns, and opens the way to scientific research on reliable and efficient methods of catalyst immobilization.

In the present work, the photocatalytic activity of a TiO<sub>2</sub>-containing perfluorinated coating was tested against six different gas-phase VOCs, chosen for their environmental effects and for screening a broad range of polarity properties. The selected pollutants are pyridine, pentane, methanol, 2-propanol, toluene, and dichloromethane. Pyridine is highly polar, has alkaline behavior and, despite its wide use as industrial solvent, it is extremely harmful to human organs, such as liver, kidney, nerve system, and eyes, causing nausea, headache, insomnia, and other disorders (46,47). Pentane is a completely apolar hydrocarbon and it is a colorless toxic liquid used in establishing the octane rating for gasoline, thus being released by gasoline evaporation (48). Dichloromethane is a colorless, highly volatile toxic chlorohydrocarbon, widely used as solvent; as it belongs to chlorinated VOCs, it is often used as model molecule to investigate the behavior of this class of pollutants (49). Methanol is a polar alcohol which can cause damage to several organs, particularly to the optic nerve, and currently there is a great interest in making methanol manufacturing more environmentally friendly because it is massively produced from syngas for application as hydrogen and energy carrier (50). 2-propanol is an alcohol with lower polarity than methanol and it is also well known to cause ocular surface irritation, epithelial keratitis and occasionally corneal abrasion (50). Finally, toluene belongs to the class of aromatic hydrocarbons and it is a model compound which provides useful information for its treatment and for dealing with more complicated organic pollutants (51).

## **2 Materials and methods**

### **2.1 Coating materials**

Aquivion<sup>®</sup> D83-06A (AQ) and Hyflon<sup>®</sup> AD60 (AD)(Solvay Specialty Polymers) were employed for the preparation of the photoactive coating. AQ is a melt-extruded ionomeric branched

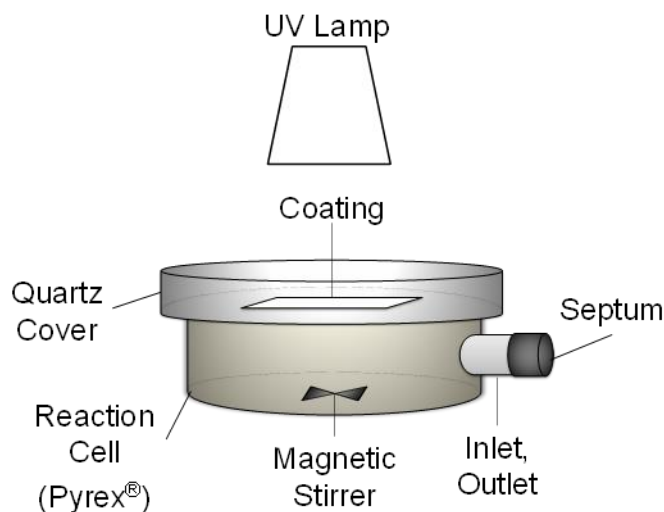
copolymer, obtained from tetrafluoroethylene (TFE) and a sulfonyl fluoride vinyl ether (SFVE),  $F_2C=CF-OCF_2CF_2SO_2F$ : the starting material is in the acidified form, in a 6% solution of 1-propanol (40%), 2-propanol (40%) and water (20%). Namely, AQ was the PFSA polymer employed for embedding the catalyst particles. AD is a random copolymer of TFE and 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD), characterized by outstanding chemical stability, low refractive index (equal to 1.327) and  $T_g$  of 130°C (38). For the experimental tests, AQ was used as received and AD was dissolved in solution by using Galden<sup>®</sup> HT110 (Solvay Specialty Polymers) as solvent. Galden<sup>®</sup> HT110 is a PFPE-based solvent with boiling point of 110°C and formula as follow:  $CF_3O(CF_2CF(CF_3)O)_p(CF_2O)_nCF_3$  ( $p+n = 2-3$ ;  $p/n = 20-50$ ). Nanometric powder of commercial titanium dioxide P25 (75% anatase, 25% rutile, Evonik<sup>®</sup>) with a band gap between 3.05 and 3.15 eV was employed as a photocatalyst (52).

## 2.2 Photocatalytic apparatus

The photochemical apparatus consisted of a Pyrex<sup>®</sup> glass reactor (internal volume: 145 ml) covered with a quartz glass, irradiated with a Ultra Vitalux<sup>®</sup> lamp (Fig. 1 and Fig. S.I.-1 in the Supporting Information). The insertion of pollutants and water, as well as for the collection of gas samples for GC-MS analyses, was performed through a septum positioned at half cell height. The reactor contained a stirring device for the homogenization of gases inside the reactor. Tests were performed in batch conditions.

The lamp employed is well known in photocatalytic tests, since it is a widely used broad spectrum lamp. The UV irradiation intensity was 21 mW/cm<sup>2</sup>, as measured by means of a UM-10 Konica Minolta radiometer. Tests were performed both at high temperature (85°C) and at room temperature (approx. 20°C): the temperature profile in the reactor was monitored by means

of a thermocouple, in order to ensure a constant temperature throughout the whole test duration.



**Figure 1.** Experimental apparatus.

### 2.3 Photoactive coatings production

The deposition of an enduringly stable photoactive coating on the quartz cover of the reactor was obtained by applying a first layer of AD, followed by thermal curing and application of a second layer of AQ, containing the photocatalyst nanoparticles. A 10 wt% solution of AD in Galden® HT110 (53) and a 6% solution of AQ in a hydroalcoholic solvent (water/*i*-propanol/*n*-propanol 20:40:40) containing 0.6 wt% of dispersed active nanometric TiO<sub>2</sub> (*i.e.*, 10 wt% of TiO<sub>2</sub> on AQ content) were employed. The former acted as inner hydrophobic fluorinated primer, in contact with glass, and the latter as outer photoactive layer. Both polymeric AD and AQ layers were chemically stable toward the degradation effects due to UV light and TiO<sub>2</sub> photocatalytic activity (37).

The fine dispersion of TiO<sub>2</sub> in the hydroalcoholic AQ solution was obtained by ultra-sonication for 40 min at room temperature in order to homogenize the catalyst into the ionomeric mixture.

The AD layer was thermally cured for 1 h under N<sub>2</sub> flux and 1 h under vacuum at 50°C, and then after adding the AQ layer, the whole coating was thermally cured for 1 h under N<sub>2</sub> flux at the same temperature. Since P25 photocatalyst can suffer conversion to rutile phase only at high calcination temperatures, we assumed that the thermal curing of AQ polymeric layer did not affect TiO<sub>2</sub> phase and band gap (54). The average weights of the AQ and AD layers were 12±3 mg and 25±3 mg, respectively, and the size of the photoactive coatings on the quartz cover of the reactor was 3.5×3.5 cm<sup>2</sup>. Overall, the multilayered photocatalytic coating resulted adherent to the internal surface of the quartz cover of the reactor and it was in direct contact with the gaseous pollutants.

For benchmarking purposes, two photoactive coatings made of a single layer of pure fluoropolymer containing TiO<sub>2</sub> were prepared: one AQ-based and one AD-based coating. The former was thermally cured for 1 h under N<sub>2</sub> flux at 50°C, and the latter was thermally cured for 1 h under N<sub>2</sub> flux and then for 1 h under vacuum at 50°C.

## 2.4 Model reactants for photocatalysis tests

As previously mentioned, tested pollutants were chosen with increasing dipole moment and on the basis of their environmental interest (Table 1). The volumes of the volatile liquid pollutants injected in the reactor in order to obtain the reference gas-phase concentrations of 5000 and 2000 ppm are reported in Table 1.

**Table 1.** Chemical formula, polarity and volumes of liquid VOC pollutants injected in the reactor in order to obtain reference gas-phase concentrations of 5000 and 2000 ppm.

Name	Chemical Formula	Dipole Moment (D)	5000 ppm V (μl)	2000 ppm V (μl)
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Pentane	C <sub>5</sub> H <sub>12</sub>	0	3.7	1.5
Toluene	C <sub>7</sub> H <sub>8</sub>	0.37	3.4	1.4
2-propanol	C <sub>3</sub> H <sub>7</sub> OH	1.56	2.5	1.0
Dichloromethane	CH <sub>2</sub> Cl <sub>2</sub>	1.60	2.1	0.8
Methanol	CH <sub>3</sub> OH	1.70	1.3	0.5
Pyridine	C <sub>5</sub> H <sub>5</sub> N	2.21	2.6	1.0

## 2.5 Coatings characterization

All the photoactive coatings were first characterized by static contact angle measurements with different liquids (*i.e.*, water, *n*-hexadecane, squalane, *n*-perfluorohexane) and their surface energy was calculated on the basis of the theory of equation of states. The contact angle instrument used in this analysis is Data Physics OCA 150 and the software is SCA20 version 2.3.9. build 46.

The X-ray photoelectron spectroscopy (XPS) spectra were obtained by using an M-probe spectrometer manufactured by Surface Science Instrument. The spectra were excited with monochromatic X-ray emission Al K $\alpha$  radiation (1486.6 eV). A spot size of 300×300  $\mu$ m and pass energy of 29 eV was used. *1s* level hydrocarbon-contaminant carbon was taken as the internal reference at 284.6 eV. Fittings were performed using pure Gaussian peaks, Shirley's baseline, and without any constraints.

The photocatalytic activity of the TiO<sub>2</sub>-embedded perfluorinated ionomeric coatings was evaluated by monitoring ratio between the concentration of each pollutant at different times of irradiation and its initial concentration *via* GC-MS analysis. An Agilent GC-MS system 6850-5975C with a Poraplot U column was used throughout.

Photocatalysis (**Pc**) tests were performed in the presence of the photoactive coating under UV irradiation. Since humidity influences the hydration of the PFSA-based ionomeric layer in the photocatalytic coating, **Pc** tests were performed at 85°C, and at two relative humidities (RH): in

dry conditions at ~20% RH (**Pc-D** test) and in wet conditions with content of water corresponding to a 5-fold saturated air, namely 500% RH (**Pc-W** test).

The absorption properties of the coating were evaluated in dark tests (*i.e.*, **Abs** tests) in the presence of the photoactive coating. Three different **Abs** tests were performed for each pollutant: at room temperature (RT) in dry conditions (**Abs-RTD** test), at 85°C in dry conditions (**Abs-85D** test) and at 85°C in wet conditions (**Abs-85W** test). Absorption in wet conditions was slightly enhanced at RT with respect to what observed at 85°C, being the observed kinetic constants equal to 9.6 and  $7.3 \times 10^{-6} \text{ s}^{-1}$ , respectively (see Supporting Information). In the following, only room temperature absorption will be shown for the sake of simplicity: this condition was chosen as it provides the worst benchmark for photocatalysis tests, being a higher share of decrease in pollutant concentration ascribed to absorption rather than to photocatalysis.

It is worth underlining that absorption tests reflect the ability of the coating as a whole to absorb the pollutant, facilitating its diffusion towards the photocatalyst nanoparticles embedded in the coating, rather than the pollutant direct adsorption on the surface of the photocatalyst.

Finally, photolysis tests were also carried out by treating the pollutants under UV irradiation in the absence of the photoactive coating (*i.e.*, **PI** tests). All measured data of concentrations of pollutants in time are reported in the Supporting Information.

Absorption, photocatalytic and photolytic reactions were considered to follow pseudo-first order kinetics (correlation coefficient  $R^2 > 0.9$ ) which enabled the direct comparison of the apparent rate constants ( $k_{app}$ ), calculated as follows:

$$\ln C/C_0 = -k_{app} t$$

where  $C$  and  $C_0$  are the pollutant concentration at time  $t$  and at the beginning of the test, respectively, and  $t$  is reaction time.

### 3 Results

#### 3.1 Photocatalytic coating assembly and preliminary characterization

In this work, two amorphous perfluoropolymeric materials were considered for the fabrication of a photocatalytic coating tested on the TiO<sub>2</sub>-catalyzed abatement of pollutants in gas phase: ionomeric AQ and high-T<sub>g</sub> AD, which is a TFE-TTD copolymer. Both fluoropolymers can be used in this application because they are characterized by high transparency, particularly in the UV region, and complete stability toward UV radiation and reactivity of UV-activated TiO<sub>2</sub>. In the early stage of this research, three different photocatalytic coatings with embedded TiO<sub>2</sub> were prepared for comparison: a single layered coating of AQ, a single layered coating of AD and a multilayered photoactive coating obtained by depositing an AQ layer on an AD layer (AQ-AD coating).

**Table 2.** Static contact angle with different liquids (water, *n*-hexadecane, squalene and *n*-perfluorohexane) on different coatings and their corresponding surface energies.

Photoactive coating	Static contact angle <sup>a</sup>				Surface energy (mN/m)
	water	<i>n</i> -hexadecane	squalene	<i>n</i> -perfluorohexane	
AQ-based	62°±3 <sup>ob</sup>	29°±1°	40°±2°	9°±1°	33.0
AD-based	110°±2°	54°±1°	59°±2°	12°±4°	16.5
AQ-AD multilayer	45°±3 <sup>ob</sup>	28°±1°	34°±4	8°±1°	39.5

a. static contact angles were measured after exposing the samples to an environment at 20% RH for 6 h.  
b. immediately after the curing treatment, both AQ- and AQ-AD-coatings showed a contact angle equal to 85°±3°, corresponding to a surface energy of 26.0 mN/m (±0.3 mN/m).

These photocatalytic coatings were characterized by static contact angle measurements with four different liquids: water, *n*-hexadecane, squalene, and *n*-perfluorohexane (Table 2). The AD-

based coating showed the lowest wettability with a surface energy around 16.5 mN/m, due to high hydrophobicity and to the most marked oleophobicity in the series. The single layered AQ-based coating and the multilayered AQ-AD coating freshly extracted from the N<sub>2</sub> atmosphere of the curing treatment, hence fully dry, resulted similar, with a surface energy for both equal to 26.0 mN/m. However, after exposing the coatings to a slightly moisturized environment (RH = 20%), the AQ-AD coating revealed a surface energy higher than that of the single layered AQ-based coating: 39.5 and 33.0 mN/m, respectively (Table 2). These different wettabilities can be ascribed to a quicker absorption of humidity in the multilayered coating, due to the surface-oriented assembly of the polar sulfonic moieties driven by fluorophilic interactions between the AD layer and the fluoropolymeric AQ backbone.

**Table 3.** Surface composition (at%) of the components of AQ-AD multilayered coating embedding TiO<sub>2</sub> photocatalyst.

Samples	Amount (at%)							Ti/S	CF/C <sub>tot</sub> <sup>a</sup>
	F	O	C	S	N	Si	Ti		
AQ	54.8	8.7	32.6	1.6	1.2	1.1	-	-	0.69
AD	52.7	17.1	30.2	-	-	-	-	-	0.92
TiO <sub>2</sub>	-	48.5	34.1	-	-	-	17.4	-	-
AQ-AD multilayer	55.8	6.8	33.5	1.9	1.6	-	0.4	0.21 <sup>b</sup>	0.75

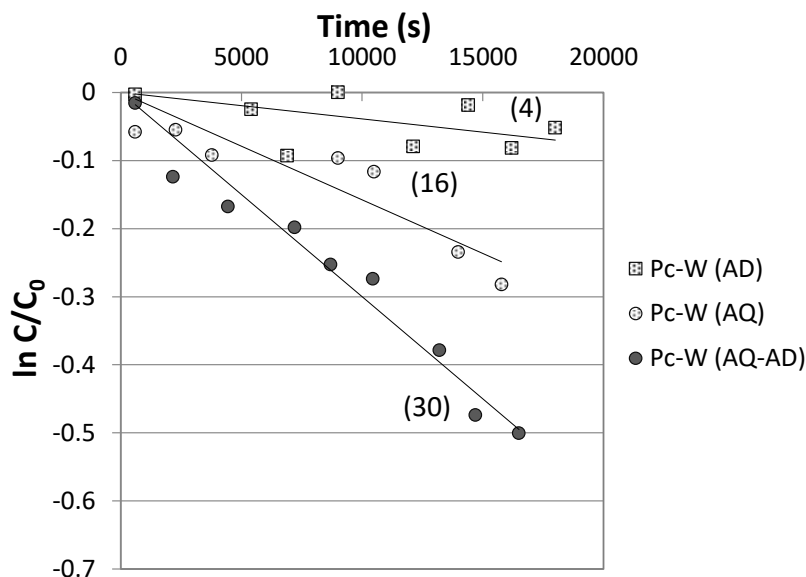
a. CF/C<sub>tot</sub> ratio was obtained by dividing the areas of the deconvolutions attributed to fluorinated moieties on C 1s region by the total area of all the deconvolutions in the same region (see Fig. S.I.-2 in the Supporting Information).

b. 1.04 is the Ti/S ratio based on the composition of the starting solution with 6% of AQ in hydroalcoholic solvent containing 0.6 wt% of nanometric TiO<sub>2</sub>.

XPS data reported in Table 3 show that the highly fluorinated nature of AQ and AD is preserved in the multilayered coating. Moreover, the presence of sulfur in both pure AQ (1.6 at%) and AQ-AD multilayer (1.9 at%) confirmed that the deposition process prevented the mixing of the two fluoropolymers and maintained the ionomeric moieties on the surface of the final coating. The

Ti/S ratio, correlated to the amount of TiO<sub>2</sub> per PFSA group in the AQ layer, on the surface of the AQ-AD multilayered coating showed a value equal to 0.21. This value resulted significantly lower than 1.04, which is the value obtained from the composition of the starting solution of AQ containing the dispersion of nanometric TiO<sub>2</sub>. This behavior can be explained supposing that the TiO<sub>2</sub> migrated preferentially in the bulk of the AQ layer of the coating, rather than staying on the surface, or, alternatively, that part of TiO<sub>2</sub> was dispersed during the deposition process. The high resolution spectrum in the Ti 2*p* region of the AQ-AD coating embedding TiO<sub>2</sub> (Fig. S.I.-3D) showed a typical pattern ascribable to pure nanometric TiO<sub>2</sub>, ascertaining the idea that the photocatalyst was not influenced by the surrounding environment made of the PSFA-based polymer.

The photocatalytic properties of the three coatings were also compared: this was done by monitoring the abatement of pentane in wet conditions under UV exposure with an initial concentration of the pollutant equal to 5000 ppm. Pentane was chosen within the pollutants list because it resulted particularly resistant to photocatalytic abatement in preliminary tests and, therefore, it was a suitable reference molecule for performances differentiation. Moreover, as it will be discussed in greater detail in the next paragraph, the apolar character of pentane is at the basis of its negligible affinity toward the AQ layer, therefore its absorption is very low and independent on coating hydration. Thus, all the differences observed in this specific test (Fig. 2) can be ascribed to the actual influence of relative humidity on the photocatalysis mechanism, and not on pollutant absorption.



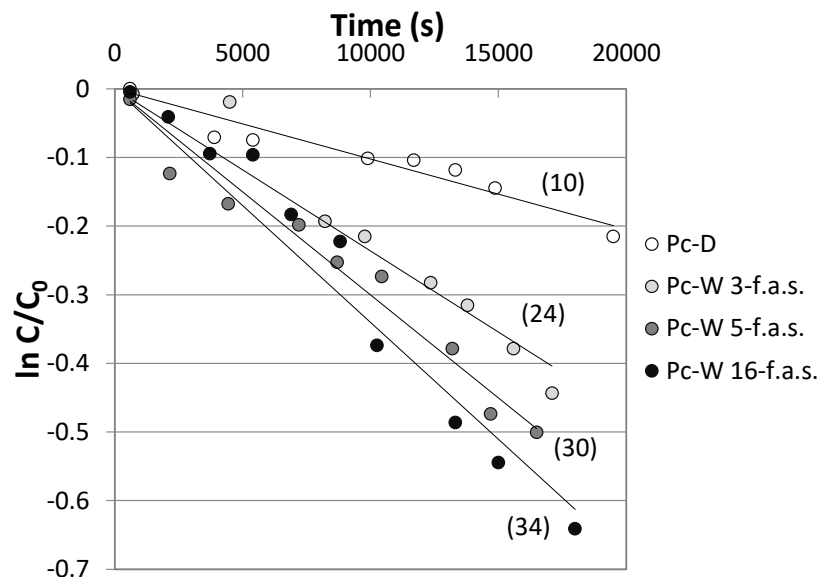
**Figure 2.** Photocatalytic abatement of pentane in wet conditions (**Pc-W** test) with three different photoactive coatings with embedded TiO<sub>2</sub>: AQ-based coating (dotted circle), AD-based coating (dotted square) and multilayered AQ-AD coating (grey circle). Apparent rate constant values ( $k_{app}$ ) are reported in brackets (values  $\times 10^{-6} s^{-1}$ ).

As reported in Figure 2, the most performing pentane photocatalytic abatement was obtained by employing the multilayered AQ-AD coating: in wet conditions a rate constant equal to  $30 \times 10^{-6} s^{-1}$  was measured. Single layered AQ coating showed intermediate activity ( $16 \times 10^{-6} s^{-1}$ ), while AD-based coating nearly inhibited photodegradation ( $4 \times 10^{-6} s^{-1}$ ). The ionomeric nature of the PFSA AQ polymer favored both the direct oxidation of highly absorbed molecules at TiO<sub>2</sub> hole sites and the hydroxyl radical mediated degradation of weakly absorbed pollutants on the coating surface. In the multilayered AQ-AD coating the pollutant absorption was furtherly facilitated by the preferential orientation of the ionomeric AQ moieties toward the surface induced by the underlying AD layer. In the AD-based coating both the high hydrophobicity and the

oleophobicity of the amorphous AD fluoropolymer almost blocked the direct oxidation pathway and only a weak degradation of the pollutant due to hydroxyl radical reactivity was observed. Based on contact angle measurements and pentane abatement results, the multilayered AQ-AD photoactive coating resulted the most promising for further development and, therefore, the study of RH influence on oxidation rate and the tests on photodegradation of other pollutants were focused on this multilayer coating system.

### **3.2 Effect of relative humidity**

The hydration level of the PFSA ionomer-based layer, *i.e.* AQ layer, embedding TiO<sub>2</sub> catalyst can widely influence the permeation rates of pollutant molecules in the multilayered AQ-AD coating (55,56). Moreover, the role of water molecules in the mechanism of photo-induced oxidation catalyzed by TiO<sub>2</sub> is widely recognized (57-59). Since in gas-phase reactions the water content can range from dry to wet conditions depending on the reaction environment, a preliminary evaluation of the effects of environmental humidity on VOC abatement rates was performed. Also in this case, pentane was employed as target pollutant: a dry condition with ~20% RH and three different wet conditions were selected, with water additions corresponding to 3-fold, 5-fold and 16-fold air saturation. The oversaturated conditions were considered because part of the water can be absorbed by the AQ layer during the reaction.



**Figure 3.** Photocatalytic abatement of pentane in dry (white) (**Pc-D**) and wet conditions (**Pc-W** tests) with three different water contents: 3-fold (light-grey), 5-fold (dark-grey) and 16-fold (black) air saturation (labeled as 3-, 5- and 16-f.a.s., respectively). Apparent rate constant values ( $k_{app}$ ) are reported in brackets (values  $\times 10^{-6}\text{s}^{-1}$ ).

In dry conditions (**Pc-D** test) pentane was photocatalytically decomposed with a  $k_{app}$  equal to  $10 \times 10^{-6} \text{ s}^{-1}$ , which was the lowest observed apparent rate constant in the tests at different RHs (Fig. 3). The increase in atmospheric humidity progressively increased the photodegradation rates: in conditions of 3-fold, 5-fold and 16-fold air saturation, the  $k_{app}$  were  $24 \times 10^{-6}$ ,  $30 \times 10^{-6}$  and  $34 \times 10^{-6} \text{ s}^{-1}$ , respectively (Fig. 3). Humidity enhanced the hydration of polar ionic moieties of AQ and, thus, it improved the availability of water-filled ionic cluster channels surrounded by fluoropolymeric AQ phase (60-62). As a consequence, the hydration of AQ ionic clusters increased the absorption of the pollutants inside the ionic layer and the degradation was performed by both bulk and surface  $\text{TiO}_2$  photocatalyst particles. Based on this principle, the  $\text{TiO}_2$ -catalyzed photoabatement of pentane resulted approximately from 2.5 to 3.5 times more



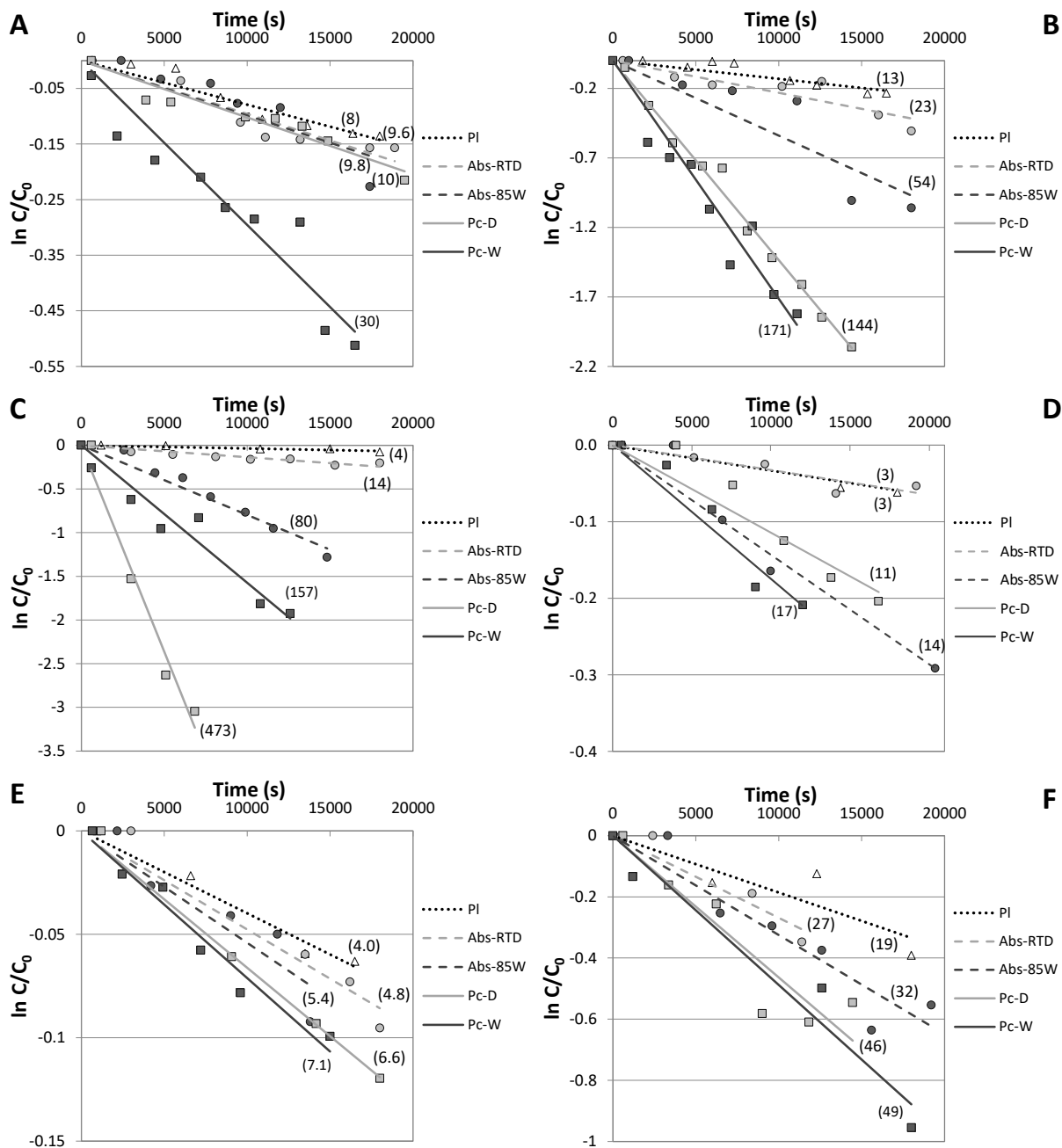
efficient in wet conditions than in dry conditions. However, the improvements due to high RH almost reached stability passing from 5-fold to 16-fold water saturation: despite an augmentation of 3 times in water content, the photodegradation rate increased only by 13%.

The addition of water corresponding to a 5-fold supersaturation of the reaction environment, namely 500% RH, was employed as optimized condition in the photocatalytic abatement tests with toluene, 2-propanol, dichloromethane, methanol, and pyridine. Absorption rates in this condition were also evaluated.

### **3.3 Absorption and photocatalysis**

The photocatalytic performances of the multilayered AQ-AD photoactive coating were evaluated by comparing the abatement of several pollutants, such as pentane, toluene, 2-propanol, dichloromethane, methanol, and pyridine, in a condition of 5-fold water oversaturation of the reaction environment. In the multilayered AQ-AD assembly, the AQ layer resulted directly exposed to the reactor chamber. Thus, it was expected that the gaseous pollutants were adsorbed on the AQ layer and diffused within it until reaching the embedded TiO<sub>2</sub> photocatalyst particles. Perfluorinated ionomers with strongly acid sulfonic moieties, like AQ, can exhibit phase-transfer capabilities related to the continuous water phase clusters formed inside the hydrophobic fluorinated matrix (63). Molecular oxygen can also penetrate into the photoactive coating due to the high gas permeability of AQ and AD polymers (64). In the presence of UV light and oxygen, the pollutants can be oxidized by photoactivated TiO<sub>2</sub> particles achieving their mineralization or generating partially oxidized intermediates and by-products. Alternatively, the degradation of weakly adsorbed pollutants can be obtained by strongly oxidizing species, like hydroxyl radicals

and superoxide ions, which are generated by UV-photoactivation of  $\text{TiO}_2$  in the presence of water (65).

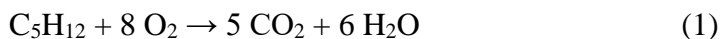


**Figure 4.** Photolysis (white triangle, linearized with dotted line), absorption in dry (light grey circle, linearized with light grey dashed line) and wet (dark grey circle, linearized with dark grey

dashed line) conditions and photocatalytic abatement in dry (light grey square, linearized with light grey solid line) and wet (dark grey circle, linearized with dark grey solid line) condition of pentane (**A**), methanol (**B**), 2-propanol (**C**), toluene (**D**), dichloromethane (**E**) and pyridine (**F**). Apparent rate constant values ( $k_{app}$ ) are reported in brackets (values  $\times 10^{-6}\text{s}^{-1}$ ). In Fig. 4-C the value of Pc-D ( $473 \times 10^{-6}\text{s}^{-1}$ ) is overestimated due to competitive synthesis of propene.

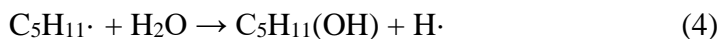
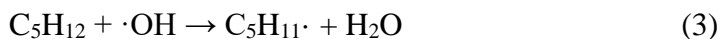
Degradation reactions and absorption phenomena appeared to follow pseudo-first order kinetics, enabling the comparison of the corresponding apparent rate constants ( $k_{app}$ ).

Pentane,  $\text{C}_5\text{H}_{12}$ , was tested as apolar volatile hydrocarbon pollutant and its mineralization reaction is shown below (eq. 1):



Due to the lack of affinity between apolar hydrocarbons and ionomeric AQ layer, it was expected that pentane absorption in the photocatalytic layer would be hindered, without significant variations ascribable to coating hydration. Experimental data confirmed this behavior (Fig. 4A). Pentane absorption in dry conditions at room temperature (**Abs-RTD**) as well as in wet conditions at  $85^\circ\text{C}$  (**Abs-85W**) showed low apparent kinetic rate constants with similar values:  $9.6 \times 10^{-6}$  and  $9.8 \times 10^{-6}\text{s}^{-1}$ , respectively. Thus, the hydration of the photocatalytic layer resulted nearly irrelevant on absorption rates of pentane. Moreover, pentane photolysis (**PI**) and photocatalysis in dry condition (**Pc-D**) showed very similar  $k_{app}$  equal to  $8 \times 10^{-6}$  and  $10 \times 10^{-6}\text{s}^{-1}$ , respectively. The photolytic mechanism, therefore, remained dominant also during the photocatalytic degradation test of pentane in dry conditions because the contact between pollutant molecules and photocatalyst particles was prevented by the actual absence of pentane absorption. The photocatalytic abatement of pentane in wet conditions (**Pc-W**) followed a

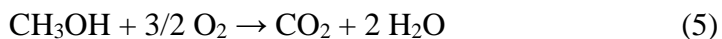
different mechanism, related to the presence of water in AQ layer and the subsequent formation of strongly oxidizing species by UV-activation of TiO<sub>2</sub>. In similar conditions, Shang *et al.* observed the formation of alcohol intermediates during the photocatalytic oxidation of alkanes with TiO<sub>2</sub> as photocatalyst (66,67). A similar scenario can also be envisioned in our case, considering the formation of oxidizing species at the TiO<sub>2</sub> surface and their transport through the coating to the coating/atmosphere interface, where they react with pentane. The free-radical synthesis of hydroxylated species derived from pentane can be summarized in the following scheme, in which H<sub>2</sub>O<sub>ads</sub> represents water molecules adsorbed in the ionomeric layer and adsorbed on photocatalyst particles and h<sup>+</sup> photogenerated holes on TiO<sub>2</sub> surface (eq. 2-4):



Once these polar alcoholic intermediates are formed, their absorption in the ionomeric layer becomes highly facilitated, allowing the direct contact with photoactivated TiO<sub>2</sub> particles. As a consequence, the apparent kinetic rate constant of the photocatalytic abatement of pentane in wet conditions (**Pc-W**) resulted the highest of the series (Fig. 4A):  $30 \times 10^{-6} \text{ s}^{-1}$ .

Methanol permeability in PFSA membranes has been widely studied for application in direct methanol fuel cells (68-71). It was demonstrated that methanol readily diffuses into PFSA polymers with permeation rates inversely proportional to the hydration of the membrane: in water-swelled PFSA specimens, almost no preferential absorption was observed between water and methanol (72-75); conversely, water sorption resulted favored in dry PFSA specimen (76,77). Moreover, mechanistic studies on the photocatalyzed oxidation of methanol suggest that, depending on water presence and O<sub>2</sub> concentration, direct or indirect oxidation reactions

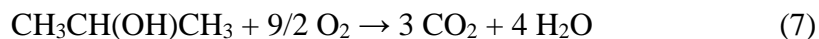
can competitively occur (78). Formate and formaldehyde intermediates are considered as the primary products of direct and indirect oxidation reactions, respectively (78). The complete oxidation reaction of methanol is here reported (eq. 5):



Methanol photodegradation through the multilayered AQ-AD photoactive coating was evaluated taking into account the effects of hydration of the photocatalytic layer due to atmospheric humidity. The facilitation of methanol absorption due to hydration of the PFSA component of the photocatalytic layer was experimentally confirmed by determining the corresponding apparent kinetic rate constants (Fig. 4-B): in dry conditions at room temperature (**Abs-RTD**) a value of  $23 \times 10^{-6} \text{ s}^{-1}$  was observed, which raised to  $54 \times 10^{-6} \text{ s}^{-1}$  in wet conditions at  $85^\circ\text{C}$  (**Abs-85W**). An analogous, although less pronounced, humidity-related increase was also observed in methanol photocatalytic reaction constants (Fig. 4-B):  $k_{app}$  at  $85^\circ\text{C}$  resulted equal to  $144 \times 10^{-6}$  and  $171 \times 10^{-6} \text{ s}^{-1}$  in dry (**Pc-D**) and wet (**Pc-W**) conditions, respectively. The hydration of the photocatalytic layer significantly influenced methanol absorption rate and, hence, the overall photocatalytic performances of the multilayered photoactive coating. Comparing direct and indirect oxidation reactions of methanol, the direct route was favored by the ready diffusion of this pollutant, which easily permeated inside the ionomeric AQ layer encountering the photocatalyst particles on which the abatement occurred. Because of the properties related to the carboxylic nature of formate, such as high polarity, high solubility in water and low vapor pressure, these intermediates of methanol direct oxidation remained absorbed in the bulk of the ionomeric layer, proceeding to a complete mineralization. Thus, detection of formate traces was not possible by GC-MS sampling of the gas-phase reaction environment during methanol photocatalytic abatement. Traces of monohydrated formaldehyde,

namely methanediol,  $\text{CH}_2(\text{OH})_2$ , were detected during the photocatalytic tests in wet conditions (**Pc-W**), confirming that the presence of water favored the indirect route of methanol oxidation.

2-propanol belongs to the class of alcohols and, due to the shortness of its carbon-based chain, its permeation in PFSA membranes is expected to be similar to that of methanol (79,80). Moreover, 2-propanol abatement is an interesting issue because it is a typical volatile organic pollutant present in urban atmosphere and particularly in indoor environments (81,82). There is agreement in the literature that the main gaseous products in  $\text{TiO}_2$ -catalyzed photooxidation of 2-propanol under UV light irradiation are acetone as intermediate (eq. 6) as well as  $\text{CO}_2$  and  $\text{H}_2\text{O}$  as final products (eq. 7) (83,84):



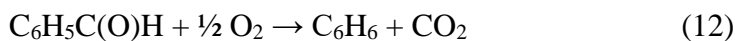
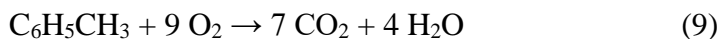
The formation of acetaldehyde and isopropyl formate traces has been also reported (82).

Gas-phase 2-propanol abatement by means of the multilayered AQ-AD photoactive coating was tested, considering also absorption facilitation due to the marked similarities between methanol and 2-propanol behaviors. Apparent kinetic rate constants of  $14 \times 10^{-6} \text{ s}^{-1}$  and  $80 \times 10^{-6} \text{ s}^{-1}$  were measured for 2-propanol absorption in dry conditions at room temperature (**Abs-85W**) and in wet conditions at  $85^\circ\text{C}$  (**Abs-85W**), respectively (Fig. 4-C). A further increment was observed in wet photocatalysis conditions (**Pc-W**), showing at  $85^\circ\text{C}$  a  $k_{app}$  of  $157 \times 10^{-6} \text{ s}^{-1}$  (Fig. 4-C). During the photocatalytic test at  $85^\circ\text{C}$  in dry conditions (**Pc-D**) an extraordinary high  $k_{app}$  of  $473 \times 10^{-6} \text{ s}^{-1}$  was measured because in these conditions the competitive synthesis of propene due to 2-propanol dehydration (eq. 8) was also favored (Fig. 4-C):



Propene formation was confirmed by GC-MS analysis of gas-phase samples collected during 2-propanol photocatalytic abatement. Hence, the anomalously high value of  $k_{app}$  should not be considered as a result of photocatalytic activity, but rather of propene synthesis.

Toluene is an important constituent of anthropogenic emissions in urban atmospheres and its photo-oxidation is a very demanding reaction that can be considered as a tough chemical test to assess the potential of TiO<sub>2</sub>-based systems in the photo-elimination of organic pollutants (36,85-87). In fact, the complete mineralization of toluene to carbon dioxide and water vapor (eq. 9) passes through the formation of deactivated intermediates, like benzaldehyde (eq. 10), benzoic acid (eq. 11) and benzene (eq. 12), and other highly stable side-products such as hydroxylated benzaldehydes (eq. 13) (86):



The interactions between PSFA membranes and aromatic compounds have been discussed in a limited number of studies about the development of membrane electrolyzers for hydrogenation of aromatic compounds with water splitting (88-90). Mitsushima *et al.* described an electrolyzer for toluene hydrogenation working with a conversion of 95%, under the assumption of a substantial absence of toluene permeation within the PFSA membrane (90). The application of the multilayered AQ-AD photoactive coating to toluene abatement confirmed that toluene absorption in the PFSA layer was hindered in dry conditions (**Abs-RTD**) and a low apparent kinetic rate constant of  $3 \times 10^{-6} \text{ s}^{-1}$  was observed (Fig. 4-D). A  $k_{app}$  increase was observed in

absorption test with water-saturated coating (**Abs-85W**) and it can be ascribed to the favorable repartition of toluene vapor in the hydrated ionic cluster channels of PFSA layer (91):  $14 \times 10^{-6} \text{ s}^{-1}$  (Fig. 4-D). Photocatalytic degradation with the multilayered AQ-AD coating enhanced toluene disappearance, and both tests in dry (**Pc-D**) and wet (**Pc-W**) conditions resulted more performing than the corresponding absorption, although not satisfying:  $k_{app}$  was  $11 \times 10^{-6} \text{ s}^{-1}$  and  $17 \times 10^{-6} \text{ s}^{-1}$ , respectively (Fig. 4-D). The monitoring of toluene photocatalytic oxidation by GC-MS analysis of gas-phase samples detected benzene traces ascribable to decarboxylation of benzoic intermediates (eq. 12). Benzene easily back diffused from the AQ-AD photoactive coating to the reaction environment due to its extremely low affinity toward the PFSA-based catalytic layer. Benzene detection indirectly confirmed the formation of intermediates such as the aforementioned benzaldehyde and benzoic acid during the photocatalytic process by direct oxidation; however, these compounds were mainly retained in the AQ ionic clusters because of their polar interactions. In wet conditions, it was also expected that hydroxylated benzaldehydes, which are characterized by high permeation in the PFSA layer, were synthesized through the hydroxyl radical-mediated oxidation of toluene.

Numerous methods are reported in literature addressing the degradation of chlorinated pollutants, whose permeation into PFSA membranes is however expected to be negligible (92-95). A study by Sun *et al.* mentions the application of a PSFA coating in an electrocatalytic system for the abatement of chlorinated phenols (96). The use of the multilayered AQ-AD photoactive coating to degrade chlorinated pollutants was thus considered for benchmarking purposes, and dichloromethane,  $\text{CH}_2\text{Cl}_2$ , was chosen because it is a widespread compound that finds many uses in industrial products and processing, such as aerosols, adhesives, dry cleaning, pharmaceuticals, refrigerants, and solvents (97). In the gas-phase photooxidation of dichloromethane, the main

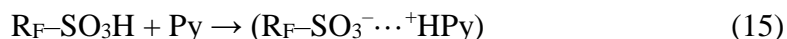


products of complete mineralization are hydrogen chloride, HCl, and carbon dioxide, CO<sub>2</sub> (eq. 14) (97,98):

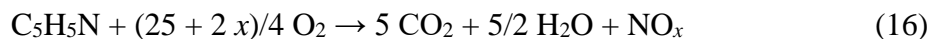


Carbonyl dichloride (*i.e.* phosgene), COCl<sub>2</sub>, carbon monoxide, CO, elemental chlorine, Cl<sub>2</sub>, carbon tetrachloride, CCl<sub>4</sub>, and chloroform, CHCl<sub>3</sub>, are also generated as intermediates or side-products (97,98). Moreover, it is diffusely accepted that the conversion of dichloromethane by photodegradation decreases with an increase in water vapor concentration, because of a competitive adsorption on the active sites of the photocatalyst (93,97-99). Dichloromethane absorption was negligibly improved upon hydration of the PFSA-based coating: in dry conditions at room temperature (**Abs-RTD**) a  $k_{app}$  equal to  $4.8 \times 10^{-6} \text{ s}^{-1}$  was measured, which slightly increased to  $5.4 \times 10^{-6} \text{ s}^{-1}$  in wet conditions at 85°C (**Abs-85W**) (Fig. 4-E). In the photocatalytic degradation of dichloromethane through the multilayered AQ-AD photoactive coating the detrimental effects ascribable to water vapor were not observed, probably owing to the very low degradation obtained in all conditions, and a minimal increase in the photocatalytic rate was detected: the apparent kinetic constants in dry (**Pc-D**) and wet (**Pc-W**) conditions were equal to  $6.6 \times 10^{-6}$  and  $7.1 \times 10^{-6} \text{ s}^{-1}$ , respectively (Fig. 4-E). The PFSA-based phase surrounding TiO<sub>2</sub> particles covered the active sites of the photocatalyst, presumably minimizing the competitive adsorption between water and pollutant. Overall, dichloromethane showed the lowest values of photoabatement rates: it thus resulted significantly resistant to photocatalyzed oxidation, in particular to the oxidative process involving TiO<sub>2</sub> surface-adsorbed hydroxyl radicals. In fact, the improvement in **Pc-W** kinetics with respect to **Pc-D** is analogous to that observed passing from dry to wet absorption, and is therefore to ascribe to an improved absorption rather than to an enhanced photocatalytic mechanism.

Pyridine, being a proton acceptor with high proton affinity, easily interacts with the superacidic groups of PFSA membranes (100). Buzzoni *et al.* studied the absorption of pyridine on dehydrated PFSA membranes, assessing that the following reaction (eq. 15) occurs even in dry conditions (100):



Decomposition of pyridine has been widely studied because this aromatic nitrogenated heterocycle, despite representing a serious hazard for human organs, is broadly used as industrial solvent and is present as building block in a large number of common fine chemicals, agrochemicals, and pharmaceuticals (101-106). Several researches reported its decomposition by pyrolysis as well as by biodegradation (100, 104-110). More recently, TiO<sub>2</sub> heterogeneous photocatalysis has been considered for pyridine mineralization (eq. 16) (100, 104-110):



Pyridine abatement with the multilayered AQ-AD photoactive coating was studied and the absorption of pyridine in the dehydrated as well as hydrated PFSA-based component of the coating was evaluated (Fig. 4-F): the apparent kinetic rate constants in dry conditions at room temperature (**Abs-RTD**) and in wet conditions at 85°C (**Abs-85W**) were  $27 \times 10^{-6} s^{-1}$  and  $32 \times 10^{-6} s^{-1}$ , respectively. Due to the proton acceptor properties and the high proton affinity of pyridine, the interactions between this pollutant and the superacidic groups of PFSA membranes resulted facilitated by hydration of the AQ component of the photoactive coating. In the presence of the dehydrated PFSA-based coating, pyridine was thus the pollutant with the highest absorption rate, while in hydrated conditions it remained second only to methanol. a further decrease in concentration due to pyridine photocatalytic abatement was also observed in both dry (**Pc-D**) and wet (**Pc-W**) conditions at 85°C, showing  $k_{app}$  of  $46 \times 10^{-6} s^{-1}$  and  $49 \times 10^{-6} s^{-1}$ ,

respectively (Fig. 4-F). It is worth noting that pyridine resulted the least stable pollutant toward photolytic abatement compared to the others:  $k_{app}$  of pyridine photolysis (**PI**) was  $19 \times 10^{-6} \text{ s}^{-1}$ .

## 4 Discussion

### 4.1 Mechanisms of coating-pollutant interaction and of photocatalytic degradation

Table 4 summarizes the results of absorption and degradation kinetics presented in the previous section.

**Table 4.** Absorption in dry (**Abs-RTD**) and wet conditions (**Abs-85W**) and photodegradation in dry (**Pc-D**) and wet conditions (**Pc-W**): kinetic constant,  $k_{app}$  ( $\times 10^{-6} \text{ s}^{-1}$ ), and mechanism proposed.

Name	Abs-RTD	Abs-85W	Pc-D	Pc-W	Affinity to coating	Prevailing mechanism
Pentane	9.6	9.8	10	30	Low, not influenced by humidity	Dry and wet: indirect oxidation at coating-atmosphere interface
Methanol	23	54	144	171	High, enhanced by humidity	Dry: direct oxidation on TiO <sub>2</sub> Wet: both direct and indirect oxidation
2-propanol	14	80	473*	157	High, enhanced by humidity	Dry: dehydration of 2-propanol in dry conditions (false positive) Wet: direct oxidation on TiO <sub>2</sub>
Toluene	3	14	11	17	Low, enhanced by humidity	Dry: direct oxidation Wet: indirect oxidation
Dichloromethane	4.8	5.4	6.6	7.1	Low, not influenced by humidity	Dry and wet: direct oxidation
Pyridine	27	32	46	49	High, low	Dry and wet: direct

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The first consideration concerns the immobilization system proposed: indeed, the use of the multilayered AQ-AD photoactive coating overall enhanced the abatement of all the pollutants with respect to single layers, as shown in the preliminary characterization of the coating, particularly in conditions of water oversaturation, which allowed the hydration of the PFSA-based layer. As mentioned in the introduction section, few works in literature present proper photocatalyst immobilization systems and characterize their gas-phase activity; the majority of works are more simply spreading TiO<sub>2</sub> slurries by brush on a substrate. Yet, this practice is not satisfactory, as it poses the issue of nanoparticles dispersion in air, with all health hazards associated. Results here reported present an interesting progress of current photocatalytic systems, because a reliable immobilization method is proposed, which at the same time allows to reach photocatalytic reaction rates comparable to those found in literature for spread coatings (45,82,84).

Concerning the kinetics observed and the mechanisms envisioned, photolysis, direct oxidation and hydroxyl radical-mediated reaction were recognized as predominant routes in the photodegradation process of the pollutants.

Photolysis is unavoidable but it generally provided a rather negligible contribution to the catalyzed processes: only for dichloromethane abatement, the photolytic rate was almost half (around 56%) of the highest photocatalysis apparent kinetic constant.

Direct oxidation was facilitated for pollutants which easily migrate into the PFSA-layer containing the TiO<sub>2</sub> particles. Furthermore, on the hydrated coating the hydroxyl radical-

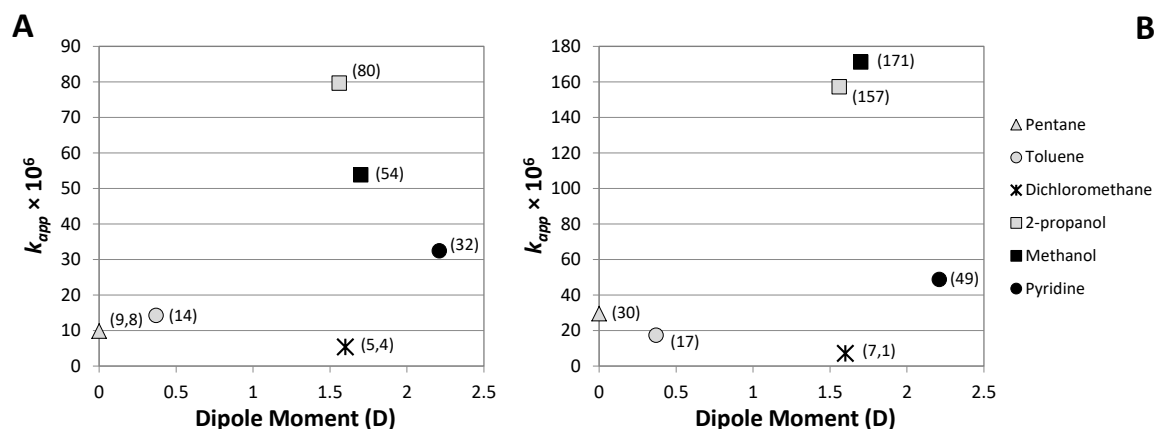
mediated reactions could also occur, and were particularly relevant when the contact between pollutant and photocatalyst was hindered, *i.e.*, in presence of unfavorable PFSA coating-pollutant interactions, as better described in next section. Hence, humidity proved its importance in stimulating photocatalysis by activating hydroxyl radical-mediated reactions which can occur in absence of direct contact of the pollutant with the photocatalyst, or in combination with direct oxidation paths improving the overall efficiency.

In this respect, not only photocatalysis, but also the absorption of pollutants through the ionomer layer seemed to be generally aided by hydration of the coatings: this is particularly true for toluene, whose absorption kinetic constant in dry atmosphere coincides with that for photolysis, therefore indicating a negligible absorption of the pollutant, while in the hydrated coating a 5-fold increase in absorption was obtained. Exception to this behavior are pentane and dichloromethane, which remained recalcitrant to absorption, although coating hydration increased pentane photocatalytic reaction rate – as abovementioned, this should be ascribed to the onset of an indirect photodegradation mechanism, where  $\text{TiO}_2$ -generated hydroxyl radicals migrate to the outer surface of the coating and come into direct contact with the pollutant. Absorption significantly influenced the abatement process because it represents the initial step in which pollutants migrate toward  $\text{TiO}_2$  photocatalyst nanoparticles. Indeed, where absorption was high, also photocatalysis was more efficient, while in absence of absorption photocatalytic degradation resulted very low. This indicates that indirect oxidation at the coating-atmosphere interface is not sufficient to produce a significant pollutant degradation: the cause of this lies in the small contact area, rather than in the weakness of the indirect oxidation mechanism, which conversely is known to be vital to improve photocatalytic efficiency.

The previous considerations highlight the importance of the interactions between each single pollutant and the PFSA coating proposed as immobilization method for TiO<sub>2</sub>: indeed, the chemical nature of the coating determines the likelihood of pollutants absorption, and therefore – as proved above – of an efficient degradation, on the basis of their characteristics, most notably polarity and proticity, as highlighted in next paragraph.

#### 4.2 Effect of pollutant polarity

The investigated pollutants can be classified on the basis of their polarity and their protic behavior: pentane and toluene are apolar and nearly apolar, respectively; dichloromethane is aprotic and weakly polar; methanol and 2-propanol are both protic and polar; pyridine is markedly polar with the nitrogen atom featuring a basic lone electron pair. In Figure 5 the apparent kinetic rate constants of absorption and photocatalytic tests performed by using hydrated coatings (**Abs-85W** and **Pc-W**) are plotted against the molecular dipole moment (expressed in Debye) of the corresponding pollutant.



**Figure 5.** Absorption (A) and photocatalysis (B) rates in the presence of hydrated coating, plotted against the molecular dipole moment of pollutants. Apparent rate constant values ( $k_{app}$ ) are reported in brackets (values  $\times 10^{-6} \text{ s}^{-1}$ ).

Apolarity and aproticity resulted as main features at the base of low absorption and photocatalytic rates; the fastest kinetics were observed on two alcohols, *i.e.*, 2-propanol and methanol. In this respect, a trend inversion can be observed for the two alcoholic pollutants moving from absorption to photocatalysis: 2-propanol was absorbed more readily than methanol, but photodegradation of the latter exploited faster kinetics. This phenomenon can be ascribed to the overall efficiency of the methanol oxidation process, which took advantage of both direct and hydroxyl radical-mediated routes. Pyridine also showed good absorption and photodegradation rates that resulted from the balance between high polarity and Lewis-base features of its nitrogen atom.

The reason for the general behavior highlighted here is related to the chemical characteristics of the PFSA coating, whose polar heads and superacidic character push interactions with pollutants characterized by marked polarity and proticity and capability of hydrogen bonding, such as the alcoholic compounds like methanol and 2-propanol; this in turn enhanced their absorption and subsequent degradation. Hence, to exploit at maximum the advantages of the immobilization system proposed, the preliminary evaluation of the characteristics of pollutants to be degraded is recommended, to envision their possible interactions with the PFSA coating.

#### **4 Conclusions**

This work was aimed at providing a clear understanding of the photocatalytic activity of a perfluoropolymeric TiO<sub>2</sub>-containing coating toward a selection of pollutants typical of indoor environments. The assessment involved the characterization of the coating absorption and photocatalytic efficiency in different relative humidity conditions, in order to have a better picture of its potential activity and of atmospheric conditions that enhance it. The intrinsic chemical nature of each pollutant was commented in regard to its influence on the absorption and photocatalytic reaction rates. Protic compounds were found more prone to absorption in the coating and therefore subject to a faster degradation compared to aprotic ones. Polarity also aided the interaction of pollutant molecules with the coating, increasing their absorption rates, although to a lesser extent. Absorption facilitates pollutants mineralization owing to the multiplication of possible reaction pathways, since not only the molecules can react with oxidizing species created by TiO<sub>2</sub> and diffusing into the coating, but also with TiO<sub>2</sub> particles themselves. It is then possible to conclude that the immobilization system proposed can provide excellent gas phase photocatalytic activity towards polar and protic compounds thanks to enhanced interactions with the ionomer-based perfluorinated coating, reaching reaction kinetics comparable to those obtained with current testing systems, where immobilization is not properly achieved. To our knowledge, it is the first example of efficient gas-phase VOC degradation system where TiO<sub>2</sub> is embedded in a polymeric coating. These conclusions can be used as guidelines for the design of atmospheric purifiers based on the technology presented.

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