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# Characterization of self-cleaning glasses using Langmuir–Blodgett technique to control thickness of stearic acid multilayers Importance of spectral emission to define standard test

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#### Abstract

The photocatalytic properties of commercialized self-cleaning glasses have been evaluated by the degradation of stearic acid  $C_{17}H_{35}COOH$  (SA), selected as a model molecule representative of fatty dirt. The relative amount of SA has been determined by measuring the FTIR peak area in the range 2752 and 2992 cm<sup>-1</sup> corresponding to the C–H stretching bands. In order to estimate the thickness of one layer, the deposit of SA has been performed using the Langmuir–Blodgett (LB) method, which allows obtaining organized monomolecular layers of amphiphilic organics on a substrate. The thickness of one SA layer, obtained by Langmuir–Blodgett deposition, has been correlated to the FTIR signal. The photocatalytic degradation of a SA layer of a controlled thickness was carried out in a double jacket Pyrex reactor equipped with a UV Philips HPK 125 lamp. The photocatalytic degradation rate of the SA layer with different thicknesses was determined. The SA degradation rate was investigated under UV-A and UV-B irradiations to determine the influence of the photon wavelength range on efficiency.

Keywords: Stearic acid; Photocatalytic degradation; Irradiation wavelength; Self-cleaning glass; Langmuir–Blodgett; Fatty acid

# 1. Introduction

Titanium dioxide (TiO<sub>2</sub>) films have been used for several applications, such as air and water purification [1,2], and recently self-cleaning materials [3–5]. Fujishima et al. in Japan and Saint Gobain vitrage company have been the first ones to patent methods to deposit transparent, abrasion-resistant and photocatalytically efficient TiO<sub>2</sub> thin films onto glass surfaces [6,7].

Recently several self-cleaning glasses have been successfully commercialized, such as Bioclean [8], Hydrotech TM [9], Activ TM [10], sold by Saint Gobain, TOTO and Pilkington Glass, respectively.

Self-cleaning glazing are based on the photocatalytic property and also on hydrophilicity of these thin films of TiO<sub>2</sub> deposited on the surface of the glasses [10]. Under UV solar irradiation, free oxidative radicals are produced on the surface of TiO<sub>2</sub> in the presence of oxygen and water molecules [11]. These species are able to degrade organic stains adsorbed at the surface into volatile molecules. The photocatalytic performances of such self-cleaning surfaces have been estimated by their ability to degrade model pollutants such as polycyclic aromatic hydrocarbons [12] or fatty acids [13–16,17]. The photocatalytic degradation of fatty acids deposited on UV-irradiated TiO<sub>2</sub> films, corresponds to

$$C_{n-1}H_{2n-1}COOH + \frac{3n-2}{2O_2} \rightarrow nCO_2 + nH_2O$$

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The hydrophilic properties of thin films  $TiO_2$ , which were early discovered in 1986 by Nihon Itagarasu K.K. Company [18], play also an important role on self-cleaning properties as thoroughly described by Fujishima and co-workers [19].

Several groups in USA [3,14,17], Japan [6,19], France [12,15], UK [10,16] have thoroughly studied, since more than 10 years, the self-cleaning properties of TiO<sub>2</sub> thin-film, the including effect of different parameters such as humidity, temperature, thickness of fatty acids layers and light intensity. All these studies showed the efficiency of TiO<sub>2</sub> thin film in the removal of thick layers of fatty acids or of other stains. Actually, the results in the literature concerning the photocatalytic activities of deposited titania can vary in a large range from a removal rate of 1.9 nm/h of a layer of stearic acid deposited on Activ<sup>TM</sup> commercial glass using an intensity of 6.9 mW/cm<sup>2</sup>, to about 60 nm/h of palmitic acid using a TiO<sub>2</sub> thin layer with an intensity of 1 mW/cm<sup>2</sup>.

The objectives of the present paper (i) a better understanding of the kinetics of removal of fatty acids layers obtained by using Langmuir Blodgett method and (ii) the determination of the influence of light intensity and of the wavelength on the kinetic, to better define a standard test.

A potential approach to obtain a well-defined thickness of the pollutant layer at the glass surface is the Langmuir–Blodgett (LB) method [20,21]. The LB technology is based on the properties of amphiphilic molecules. These molecules are constituted of an hydrophobic tail and an hydrophilic (polar) head group, having for result the capacity to form an organised monomolecular film after spreading and compression of the molecules at an air/water interface. This interfacial film can be then transferred regularly and homogeneously onto a solid support after dipping it through the compressed monolayer maintained at a constant surface pressure (Fig. 1).

The total thickness of the deposit can be controlled by the number of deposited layers. Fatty acids are amphiphilic molecules [22], Stearic acid (SA), a  $C_{18}$  carboxylic acid with



Fig. 1. Principle of Langmuir-Blodgett technology.

18 carbons has been chosen, as a model molecule for photocatalytic degradation by UV-irradiated titania on self-cleaning glasses.

# 2. Experimental

#### 2.1. Reactants

Stearic acid (purity 97%) was purchased from Acros Organics (France). Buffer solutions were prepared with ultra-pure water (resistivity 18.2 M $\Omega$ ) obtained from a Milli-Q four-cartridge purification system (Millipore, France). Chloroform of analytical grade was provided by Normapur (France). All other reagents were of analytical grade.

# 2.2. Substrates

The self-cleaning glass SCG, Bioclean, was provided by Saint Gobain Recherche (France) [23]. The employed photocatalyst is titanium dioxide (TiO<sub>2</sub>) in its nanocrystalline anatase form. TiO<sub>2</sub> anatase was deposited on a 4 mm thick float glass as a thin film (typically 15–20 nm) by an atmospheric pressure chemical vapour deposition (APCVD). A barrier layer of silica is necessary between the soda-lime silicate glass substrate and the deposited titanium dioxide layer to prevent alkaline metal ion migration between these two layers.

The titania-free glass sample, Planilux, was provided by Saint Gobain Recherche (France).

# 2.3. Substrate pre-treatment

Before use, the substrates were washed with a detergent (Gigapur 05 2%, purchased from Shimitek, France), rinsed with pure water and dried under filtered air flow. Especially for SCG, deposited  $TiO_2$  has been irradiated with a UV-lamp (254/365 nm) during 1 h. This pretreatment is very important to obtain a good transfer of the monomolecular film onto the solid support. The LB deposition must be carried out just after UV-irradiation of the glass sample to guarantee a good reproducibility of the deposited layer thickness.

#### 2.4. Langmuir–Blodgett LB films

Interfacial film formation and LB deposition were carried out with a computerised KSV 3000 LB trough (KSV, Finland) enclosed in a filtered air dry flow cabinet to avoid dust deposition, as previously described [24]. All the LB films have been prepared at ({ Laboratoire de Génie Enzymatique et Biomoléculaire, at University of Lyon 1.

A CaNa7 solution (pH7) was prepared with NaCl  $10^{-2}$  M, CaCl<sub>2</sub>  $10^{-4}$  M in ultra-pure water and the pH was adjusted at 7 with a NaHCO<sub>3</sub> 0.5 M solution. This solution was used as a subphase and was thermostated at  $20 \pm 0.5$  °C in the LB trough. The surface area of the LB trough was 772.5 cm<sup>2</sup>. A solution of stearic acid in chloroform at  $2 \times 10^{-3}$  M was spread onto the subphase to form an interfacial film. Spreading experiments at the air/solution interface were performed



Fig. 2. Experimental setup of the Pyrex photoreactor for stearic acid degradation.

with 200 or 300 µL of SA using a microsyringe. After a 15 min period of chloroform evaporation, the interfacial films were compressed symmetrically at a rate of  $5 \text{ mm min}^{-1}$  (compression rate 7.5 cm<sup>2</sup> min<sup>-1</sup>). The surface pressure ( $\pi$ ) was measured using a platinum Wilhelmy plate attached to a sensitive balance with an accuracy of  $\pm 0.3$  mN m<sup>-1</sup> à voir avec CG. The SA monolayer compressed at a surface pressure of  $30 \text{ mN m}^{-1}$  was transferred onto the substrate by the vertical dipping method with a deposition rate of  $10 \text{ mm min}^{-1}$ . Self-cleaning glass plates  $(28 \text{ mm} \times 28 \text{ mm} \times 4 \text{ mm})$  were used as supports. The substrate was clamped parallel to the barriers and immersed into the subphase just before the spreading procedure. During the transfer of the first layer, the polar groups of the stearic acid were oriented toward the substrate, whereas, they were oriented oppositely in the second layer. Several SA-LB films were prepared on SCG substrate with a different number of deposited monolayers: They were constituted of one, three, five and seven LB layers of SA. The transfer ratio (TR), calculated for each layer deposition from the interfacial film area removed, reflects the efficiency of the transfer process. After transfer of stearic acid LB films onto a TiO<sub>2</sub> self-cleaning surface, it was possible to correlate the FTIR SA areas of the signal of methyl and methylene groups of the hydrocarbon chain to the total thickness of the multilayer of SA obtained by LB deposition.

#### 2.5. Photoreactor and light source

Photocatalytic degradation experiments were carried out in a specially designed Pyrex reactor with a double jacket for water circulation to maintain a fixed temperature. Its capacity was 100 mL. A circulating-water cell equipped with Pyrex optical filters was used both to remove IR radiations thus preventing any heating and to select the desired wavelengths ( $\lambda \ge 290$  nm). The UV source was a Philips HPK 125 W lamp with an emission spectrum ranging from 200 to 600 nm with a maximum of energy at 365 nm and main secondary radiations at 254, 317, 400 and 435 nm. The experimental setup is shown in Fig. 2. The side of the self-cleaning glass is always plate supporting titania exposed to the lamp. The radiant flux is measured using a VLX-3W radiometer with 3 detectors: CX-365 (355–375 nm), CX-312 nm (280-320 nm) and CX-254 (254 nm). The overall intensity value corresponds to the sum of three values obtained with each cell. The use of a grid enables one to decrease the intensity of the light to the intensity value selected. The glass sample is placed at 63 mm from the lamp and receives a overall radiant flux adjusted at  $5.4 \,\mathrm{mW \, cm^{-2}}$  by using a grid. All these tests were carried out in presence of a small recipient containing water in order to maintain a saturated humidity in the reactor.

Blank experiments were performed with Planilux (glass free of TiO<sub>2</sub>) in the same UV irradiation conditions for light intensity (5.4 mW cm<sup>-2</sup>) and wavelength range ( $\lambda \ge 290$  nm) as used for degradation test with SCG.

#### 2.6. FTIR spectroscopy analysis

The quantitative analysis of the thickness of SA-LB layers was made by FTIR spectroscopy using a PerkinElmer Spectrum One apparatus. The self-cleaning glass,  $TiO_2$  film on float glass, is transparent to IR beams for wave-number above  $2200 \text{ cm}^{-1}$ , as presented in Fig. 3. The parameters chosen for the FTIR spectrometer were:

- Scan from 4000 to  $450 \, \text{cm}^{-1}$ .
- Number of scan: 32.
- Resolution:  $4 \text{ cm}^{-1}$ .

The reaction rates of photocatalytic degradation process were calculated by using the measured the FTIR SA bands area from 2752 to 2992 cm<sup>-1</sup>. This range corresponds to the signals of the symmetric and asymmetric C–H stretching mode of the CH<sub>2</sub> groups at 2849 and 2916 cm<sup>-1</sup> and to asymmetric stretching mode of the terminal CH<sub>3</sub> group at 2953 cm<sup>-1</sup>.

### 3. Results and discussion

# 3.1. FTIR investigation of the thickness of stearic acid Langmuir–Blodgett films

The Langmuir–Blodgett experiments have been performed for different numbers of SA-LB layers to obtain a direct relation between FTIR SA area and the number of SA-LB layers. One, three, five and seven LB layers have been deposited on each side of the self-cleaning glass substrate. FTIR spectra have been recorded to estimate SA area as a function of the number of



Fig. 3. FTIR spectra obtained from Bioclean self-cleaning glass supporting stearic acid. Th upper curve is related to the blank test.

Table 1 FTIR areas of FTIR signals of SA as a function of the number of SA LB layers

Total number of SA LB layers <sup>a</sup>	2	6	10	14
FTIR SA initial area (cm <sup>-1</sup> )	0.132	0.370	0.606	0.882
TR (transfer ratio)	1.07	0.92	0.88	0.84
Corrected area (cm <sup>-1</sup> ) <sup>b</sup>	0.123	0.401	0.689	1.048
Area of one monolayer $(cm^{-1})$	0.062	0.067	0.069	0.075

<sup>a</sup> Number of SA LB layers for both sides of substrates.

<sup>b</sup> Corrected area corresponds to FTIR initial area × transfer ratio (TR).

deposited layers, as previously described [25]. The results are shown in Table 1 and Fig. 4.

Considering that one layer deposited by the Langmuir– Blodgett method corresponds to one monomolecular layer of SA, the layer thickness mainly depends of the hydrocarbon chain length. Consequently, it is possible to estimate the FTIR response of one monomolecular layer. As one molecule of stearic acid  $CH_3(CH_2)_{16}COOH$  contains 16  $CH_2$  groups and one  $CH_3$ group, the equivalent FTIR response of one SA monomolecular layer in the range of the CH-stretching vibration of the hydrocarbon chain was calculated.

As shown in Fig. 4, the scaling line is linear. Consequently, the FTIR SA area of one LB layer could be determined from the slope of this line. It corresponds to an area of  $0.072 \pm 0.005 \text{ cm}^{-1}$ . Hence, we can deduce the correlation between FTIR SA area and the thickness of one SA LB layer.

According to Sawunyama et al. [26], the thickness of 5 layers of SA deposited by the Langmuir-Blodgett technique corresponds to 12.5 nm considering that all the molecules are vertically aligned. Ulman [20] reports that the thickness of a vertical monolayer of SA-LB is 2.5 nm. Similarly, Mills et al. [16] admit that the thickness of one monolayer of SA-LB is 2.5 nm, and consequently that a thickness of 17 nm corresponds to 6.8 layers of SA. Bonnerot et al. [27] have transferred the LB layers of behenic acid (C22 fatty acid) onto CaF2 substrates. The results of this study show that the axes of the molecular chains, perpendicular to the substrate for the first layer, would progressively tilt to reach a final limit angle of 23°. However, the work of Kimura et al. [28] shows that the first LB layer of SA is quite vertical, while the following layers are tilted at an angle of about  $30^{\circ}$ , with respect to a vertical axis of the substrate surface after transfer on a germanium plate. Therefore, as the exact orienta-



Fig. 4. Scaling of FTIR SA area integrated between 2572 and  $2992 \text{ cm}^{-1}$  as a function of the number of deposited SA-LB layers.



Fig. 5. Two limit cases of the orientation of the fatty acid chains for monomolecular layers deposited by the Langmuir–Blodgett method.

tion of the SA chains on the  $TiO_2$  plate is unknown, two limit cases have been considered, as presented in Fig. 5.

Each limit case corresponds to a given orientation for all the fatty acid chains. The orientation is either vertical (case 1) or tilted with an angle of about 30° with respect to the vertical axis of the substrate surface (case 2). Considering both arrangements of the fatty acid molecules on the self-cleaning glasses, the SA area from FTIR ( $S_{\rm FTIR}$ ) can be correlated to the overall thickness of the LB film (e) expressed in nm. In our case, one monolayer of SA corresponds to a mean FTIR area of  $0.072 \pm 0.005$  cm<sup>-1</sup>. The monomolecular layer thickness (*l*) is 2.5 nm for vertical chains ( $l_v$ ) or 2.16 nm (2.5 cos 30°) for tilted ones ( $l_t$ ). Therefore, the SA-LB film global thickness can be calculated as followed

for vertical monolayers, the thickness equals :

$$e_{\rm v} = \left(\frac{S_{\rm FTIR}}{0.072}\right) \times 2.5\tag{1}$$

for tilted monolayers, the thickness equals :

$$e_{\rm t} = \left(\frac{S_{\rm FTIR}}{0.072}\right) \times 2.16. \tag{2}$$

These relationships enable to express the deposited film thickness in nm. During the photocatalytic degradation of the LB film, the FTIR SA area is measured at different UV irradiation times. These FTIR SA areas obtained in  $cm^{-1}$  are calculated in nm by using Eqs. (1) or (2). Two limit angle values of this film thickness are obtained as a function of the UV irradiation time. The removal rate for both limit series of film thickness is determined from the degradation curve by drawing the SA-LB film total thickness as a function of the UV irradiation time.

The both removal rates ( $r_i$ ) of the SA-LB film in nm min<sup>-1</sup> can also be directly calculated from the removal rate obtained

in  $\text{cm}^{-1} \text{min}^{-1}$  for the vertical chains  $(l_v)$  and the tilted chains  $(l_t)$ , as followed:

$$r_{i} (nm \min^{-1}) = \left(\frac{r_{i} (cm^{-1} \min^{-1})}{0.072}\right) \\ \times l_{i} (l_{v} = 2.5 \text{ and } l_{t} = 2.16nm).$$
(3)

From the both limit removal rates obtained as a function of  $(l_i)$ , an average could be calculated, as followed:

$$r(\operatorname{nm}\operatorname{min}^{-1}) = \frac{[r_{v}(l_{v}) + r_{t}(l_{t})]}{2}.$$
(4)

#### 3.2. Photocatalytic degradation of stearic acid

The same UV radiant flux and wavelength range were used for photochemistry and photocatalysis tests indicating that the photochemistry contribution is negligible, as observed on the  $TiO_2$ -free, Planilux by glass.

The correlation between FTIR SA area and the thickness of a SA layer deposited by the Langmuir–Blodgett method can be assimilated, as previously suggested by Mills et al. using a deposition by dip-coating [16], in order to determine the thickness of a layer deposited by another method.

The SA photochemical degradation rate is very slow, 0.013 and 0.011 nm min<sup>-1</sup> for vertical and tilted chains respectively, and can be neglected.

The photocatalytic degradation of the stearic acid LB film has been performed in the Pyrex photoreactor for each number of deposited LB layers. Only one side of the self-cleaning glass is covered with TiO<sub>2</sub>. The SA film on the other side of SCG has been cleaned with acetone. The TiO<sub>2</sub> side with the SA film has been directed towards the UV lamp and the FTIR investigation of the LB film thickness has been performed. The correlation between FTIR SA area and SA-LB film thickness at different times of UV irradiation enables one to estimate the efficiency of the self-cleaning phenomenon by quantifying the SA degradation rate, expressed in nm min<sup>-1</sup> (Eq. (3)). The degradation results measured by FTIR spectroscopy (cm<sup>-1</sup>) and converted in thickness (nm) are presented in Fig. 6 for 3, 5 and 7 deposited LB layers, respectively.

The SA layer thickness decreases proportionally with the UV irradiation time. Whatever the number of deposited layers, the



Fig. 6. Photocatalytic degradation of stearic acid LB films for vertical and tilted chains ( $I = 5.4 \text{ mW cm}^{-2}$ ,  $\lambda \ge 290 \text{ nm}$ ).

degradation rate of deposited LB layer remains constant. Similarly, the degradation rate is independent of the initial thickness of SA. These results are in agreement with those ref. [16]. The constancy of the photocatalytic rate indicates a zero kinetic order. This is in line with a full coverage ( $\theta = 1$ ) in fatty acid as explained by the apparent zero order at high reactant concentration. The value of SA-LB film degradation rate is around of  $0.004 \pm 0.001$  cm<sup>-1</sup> min<sup>-1</sup>. By using Eq. (3), the degradation rate of SA-LB layer (3, 5 or 7 layers) is  $0.14 \pm 0.04$  nm min<sup>-1</sup> for vertical chains and  $0.12 \pm 0.03$  nm min<sup>-1</sup> for tilted chains. Fig. 6 shows the photocatalytic degradation for each SA-LB layer in both SA chains orientations. The difference between both degradation rates is comprised in the experimental error limits. Therefore, Eq. (4) could be used to obtain the medium value of the degradation rate:  $0.13 \pm 0.03$  nm min<sup>-1</sup>, i.e. 0.08  $\mu$ mol/h, for a SA layer deposited onto the self-cleaning glass. By comparison with the amount of fatty acid deposited on glass by a finger print (from 0.0015 to 0.0045 µmol) which has been determined in our laboratory, this indicates that ca. 1-2 min only would be necessary to remove this finger print.

The removal rate has been determined using a high-pressure mercury lamp (with  $\lambda = 317$  and 365 nm) with a UV-radiant flux equal to  $(5.4 \text{ mW cm}^{-2})$ . Interestingly, Mills et al. [16] report a stearic acid degradation rate of  $1.9 \text{ nm h}^{-1}$  using six 8W blacklight bulbs ( $\lambda = 360 \pm 20 \text{ nm}$ ) with a radiant flux of ( $6.9 \text{ mW cm}^{-2}$ ) for the self-cleaning glass Activ (Pilkington, UK). The SA film initial thickness was 153-187 nm, i.e. 61-75monolayers. This rate discrepancy could be due to the difference in the emission spectrum of the two UV lamps, which are presented in Fig. 7. Considering that both commercialized selfcleaning glasses (Activ and Bioclean) have similar efficiencies, the difference in rates observed indicate that UV-B photons is more efficient than UV-A ones.

The UV–vis spectra of titanium dioxide TiO<sub>2</sub> films deposited on Activ [10] and Bioclean, have the same absorption profile. As shown in Fig. 7, Bioclean has a higher absorbance in UV-B (317 nm) than in UV-A (365 nm). This decreasing absorbance at wavelengths above 360 nm could explain the higher activity of SCG with a Philips HPK125 lamp than with blacklight bulbs. Actually, black light lamps emit about half of photons above 360 nm, which cannot activate TiO<sub>2</sub> thin films.



Fig. 7. UV-vis absorption spectra of Bioclean<sup>®</sup> self-cleaning glass and of a Pyrex optical filter. Emission spectrum of Philips HPK 125 W lamp. Emission spectra of a typical 8W blacklight bulb from [6].

The influence of the wavelength range of the UV irradiation on the self-cleaning glass efficiency has been investigated. In this study, the stearic acid was deposited onto self-cleaning glass surface by spin-coating. The wavelength range has been selected with optical filters in Pyrex for 290–800 nm (UV-A and B) and the Corning 0.52 filter for 340–800 nm (UV-A). Fig. 8 shows the degradation of SA as a function of the nature of the UV radiations for a radiant flux of 5.6 mW cm<sup>-2</sup>.

Under UV-A irradiation 0.52 using the Corning optical filter, SA has been degraded with Bioclean glass at a rate of  $0.10 \pm 0.02$  nm min<sup>-1</sup>, whereas under UV-A and B using a Pyrex optical filter, the rate is equal to  $0.16 \pm 0.03$  nm min<sup>-1</sup> (medium values). However, the UV radiations (UV-A or B) will play a role in the efficiency of self-cleaning glass. The global intensity is of 5.6 mW cm<sup>-2</sup> for both wavelength ranges; nevertheless the radiant flux corresponds to the sum of the values measured with the VLX-3W radiant meter for the UV-A (cell CX-365) and UV-B (cell CX-312).

In order to understand the relationship between the photocatalytic activity of the self-cleaning glass and the UV range (UV-A or -B) used during the UV irradiation, the "yield of efficiency of the emitted photons" has been investigated.

First, the efficient photons rate  $(\varphi n)$  at a given wavelength of the UV irradiation has been calculated by using the following equation:

$$\varphi_n = \frac{\varphi}{N_{\rm A}} \quad \text{and} \quad \varphi = \left(\frac{\Phi}{E}\right) \times S$$
 (5)

with the intensity  $\Phi$  in W cm<sup>-2</sup>, the radiant flux energy *E* in J photons<sup>-1</sup>, and the surface of the substrate.

The yield of efficient emitted photon ( $\rho$  SCG) during the UVirradiation for the degradation reaction with self-cleaning glass has been calculated in each case of wavelength range according to the following equation:

$$\rho \operatorname{SCG} = \frac{r}{\varphi_n} \tag{6}$$

with the degradation rate r in nm min<sup>-1</sup> and the amount of efficient photons  $\varphi_n$  in Einstein s<sup>-1</sup>.

The values of the yield of efficient emitted photon ( $\rho$  SCG) corresponding to the degradation rate (*r*) in each case of irradiation (UV-A, B) and to amount of efficient photon ( $\varphi_n$ ) are reported in Table 2.



Fig. 8. Photochemical and photocatalytic degradation of SA deposited on Bioclean<sup>®</sup> self-cleaning glass under different UV irradiations (HPK125 lamp with optical filters). Total intensity of  $5.6 \text{ mW cm}^{-2}$ .

Table 2

Yield of efficient photons emitted for different SA degradation rates on Bioclean according to the wavelength range used

Optical filter	Corning 0.52 ( $\lambda \ge 340 \text{ nm}$ )	Pyrex ( $\lambda \ge 290 \text{ nm}$ )
$r \pm 20\% \text{ (nm min^{-1})}$ $\varphi_n \pm 20\% \text{ (Einstein s^{-1})}$ $\rho \pm 20\% \text{ (nm Einstein^{-1})}$	$\begin{array}{c} 0.10 \\ 1.34 \times 10^{-7} \\ 1.2 \times 10^{4} \end{array}$	0.16 $1.26 \times 10^{-7}$ $2.0 \times 10^{4}$

At identical light intensity in our conditions of degradation, the flux of efficient photons emitted in the wavelength range 290-400 nm for Bioclean will be about 1.6 times higher (Pyrex filter, UV-A and B) than that in the 340–400 nm range using the Corning 0.52 filter, UV-A. This result is in agreement with the results observed by Mills et al. [10] using a black light lamp centered at 360 nm (320-400 nm) and a germicidal lamp emitting at 254 nm. Although the near-UV incident light intensity from black light bulbs was 65% greater than that used in the far-UV study, the absorbances of the films were significantly smaller in the near-UV range. This phenomenon has already been mentioned by Brusa and Grela [29] and Emeline and Serpone [30] considering the photocatalytic oxidation of cyclohexane on TiO<sub>2</sub> particles. These authors show that the selectivity depends on the wavelength used and suggest that this behavior could be attributed to the diffusion lengths of electrons and holes which leads to the spectral variation of the ratio of the surface concentrations of electrons and holes. Therefore, y, it appears apparent that the efficiency of  $TiO_2$  thin films are actually governed by energy of photons rather than the light intensity. For standardization tests, it will be not sufficient to work with the same intensity but it is not necessary that the light sources have the same spectral distribution.

# 4. Conclusion

To estimate the efficiencies of the self-cleaning glasses, LB layers of stearic acid have been degraded. The Langmuir–Blodgett technique has the benefit of depositing, layer-by-layer, an organised multilayer deposit at the surface of a self-cleaning object by controlling thickness of the reactant to be removed. SA degradation under UV-B irradiation has been followed by FTIR spectroscopy as a function of the irradiation time. The correlation between FTIR SA Area and the number of LB deposited layer was necessary to determine the overall thickness of SA layers. The degradation rate for a SA-LB film on a UV-irradiated commercialized Bioclean glass has been estimated between two limit values:  $0.12 \pm 0.03$  nm min<sup>-1</sup> for tilted hydrocarbon chains and  $0.14 \pm 0.04$  nm min<sup>-1</sup> for hydrocarbon chains oriented perpendicularly to the surface.

The photons at  $\lambda = 317$  nm (UV-B) than those at  $\lambda = 365$  nm (UV-A). These results are important for a future standardized test, which should be based not only on the same light intensity, but also on the same spectral distribution of photons provided by a unique standard lamp. Actually, for life applications, it must be kept in mind that a realistic test should be done with a UV-lamp adapted to simulate the solar UV-spectrum.

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