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Development of a fluorescence-based method for evaluation of self-cleaning properties of photocatalytic layers

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ABSTRACT

A new method for determination of self-cleaning activity of photocatalytic surfaces is proposed. It is based on the deposition of a transparent solid layer comprising terephthalic acid over the photocatalytic surface (three types of titania films on glass were used as test samples). When such a system was irradiated, among the other degradation products also a hydroxyterephthalic acid was formed due to a reaction between photoexcited TiO_2 and terephthalic acid. Hydroxyterephthalic acid is a highly fluorescent molecule and it was detected by HPLC-FLD or spectrofluorimeter. This direct method of following quantitatively the formation of an oxidation product was found to be accurate, highly sensitive and reproducible, therefore, it represents a promising option to be considered in standardization efforts in the field of photocatalysis.

1. Introduction

TiO_2 photocatalysis as one of the most studied advanced oxidation methods in the last three decades for pollutant removal in water and air has, on the contrary, experienced the more successful transfer from research to application when self-cleaning surfaces are concerned rather than water or air remediation [1,2]. This is because the only major drawback of TiO_2 photocatalyst material, which is a negligible absorption of photons with the wavelengths above 400 nm, is the least important in self-cleaning applications. The fast kinetics of photocatalytic degradation is not absolutely needed in this case. Additionally, a self-cleaning effect of a titania thin film is not only based on photochemical degradation and mineralization of adsorbed organic dirt on the surface, but also on the photoinduced superhydrophilicity of the titania surface, enabling that the residual organic as well as not well-adhered inorganic dirt is easily washed away by rain water for example. This process is characterized by high quantum yields already at low illumination levels [2] and therefore, such surfaces function well under sunlight and normal weather conditions.

In spite of successful application of TiO_2 photocatalysis in the field of self-cleaning surfaces, an ideal method for determining the self-cleaning efficiency of the products (photocatalyst films on different supports) is still not available. Currently, the two standard methods are based on (i) photobleaching of methylene blue aqueous solution in contact with thin solid catalyst layer, and on (ii) photodegradation of a solid fatty deposit (e.g. stearic acid) over catalyst layer. The first one is focused on an aqueous-solid system and as such it is not the most appropriate one for characterization of self-cleaning surfaces, where solid-solid and solid-air interfaces dominate. Methylene blue can be bleached via both oxidation and reduction process, but the former is favored at aerobic and neutral/alkaline conditions [3]. Chin and Ollis [4] studied the decolorization of some organic dyes on Pilkington Activ^{TM} glass in a solid-air system, which was, however, a slow process. The second method (mineralization of a fatty acid) also suffers from the slow oxidation (degradation) process of a solid fatty deposit, which could be followed directly by FT-IR analysis, but is usually measured indirectly by water contact angle (CA) measurements [5]. Measuring of the indirect quantity (CA) is another drawback of such photocatalytic evaluation. Due to the measurement technique, such method cannot be used for evaluation of hydrophobic photocatalytic surfaces and for porous substrates or substrates with a rough surface.

Recently, Mills et al. [6–8] reported about a new method to determine self-cleaning efficiency, which is based on the entrapment of an organic dye in a solid polymer matrix deposited over the photocatalyst layer. Upon illumination, the dye is reduced by the photogenerated electrons to the form of a different colour (resazurin reduction) [6,7] or to the bleached form (2,6-dichloroindophenol reduction) [7,8]. This method therefore allows a fast analysis of reduction products by visual inspection (qual-

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Abbreviations: CA, contact angle; TPA, terephthalic acid; HTPA, hydroxyterephthalic acid; CM, coumarin; TTIP, titanium(IV) tetraisopropoxide; HEC, hydroxyethyl-cellulose; EAA, ethyl acetoacetate; HBA, 4-hydroxybenzoic acid.

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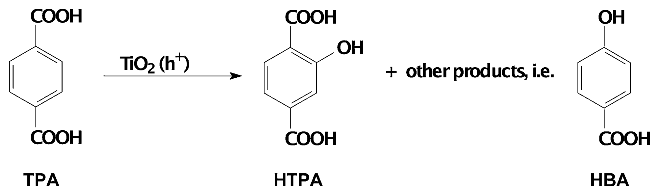

Fig. 1. Formation of a fluorescent HTPA in a reaction between photogenerated holes and TPA.

itatively) or UV–vis spectroscopy (a difficult way of quantitative analysis), but it does not directly resemble the photocatalytic oxidation process, which usually takes place in the destruction of organic pollutant under aerobic conditions. The presence of oxygen can also cause the instability of a reduction product and its re-oxidation back to the initial form of the dye. In addition, a sacrificial electron donor, e.g. glycerol, is needed to capture photogenerated holes for a balance of the redox process. This method is excellent from the qualitative point of view because one can easily observe colour changes of a fast reduction process, but on the other hand a dye layer over the photocatalyst surface with its visible spectral absorbance represents a screen for the photocatalyst, especially in the case of visible-light active photocatalysts.

Based on some disadvantageous features of self-cleaning characterization mentioned above, we introduce a novel method for determination of self-cleaning efficiency of the photocatalyst surfaces within the present work. It is based on the homogeneous entrapment of a sodium salt of terephthalic acid (TPA) in the polymer host to form a transparent thin solid layer over photocatalyst surface, i.e. commercial and sol–gel produced TiO_2 film on glass, and on highly sensitive fluorescence detection of the one of TPA oxidation products (hydroxyterephthalic acid = HTPA) (Fig. 1). This method represents a step forward due to the following desirable characteristics for the self-cleaning tests: (i) it comprises solid–solid and solid–air interfaces, (ii) the slow oxidation process can be traced in a short time scale on account of a highly sensitive and accurate fluorescence detection, (iii) it is a direct method to follow photocatalytic oxidation process, (iv) it is a quantitative method based on HPLC-FLD or spectrofluorimeter analysis, (v) the TPA layer itself is photostable and highly transparent for visible and UVA radiation.

TPA has been used as a raw material in polymer industry and due to its extensive applications has become an environmental pollutant [9]. There are quite many publications describing the use of TPA in photocatalysis as a fluorescence probe [10–18], but all of them deal with the solid–liquid system (where TPA is present in the liquid alkaline phase), which is not a good method to test self-cleaning efficiency, but is more appropriate to follow hydroxyl radical mediated photocatalytic oxidation process in an aqueous phase. It is well accepted that under conditions of diluted TPA solution, the highly fluorescent product HTPA is formed in the reaction between TPA and hydroxyl radical, which is the most famous reactive species generated in aqueous photocatalysis. In the solid system, which is our case and where TPA is much more concentrated and adsorbed on the photocatalyst surface, the more probable mechanism of TPA oxidation is a direct one with photogenerated holes [10,16,19]. However, the exact mechanism of the reaction is still under the discussion. To the best of our knowledge, this is the first published work on the use of TPA in a solid system to determine self-cleaning activity of the underlying photocatalyst surface.

Table 1
Characteristics of TiO_2 thin films prepared.

Characterization	Film D	Film C
Crystalline phase	Anatase	Anatase
BET surface area [$m^2\,g^{-1}$]	5.5	75
Size of primary particles [nm]	19	10
Macroscopic density of the deposited TiO_2 layer [$g\,cm^{-3}$]	4.3	2.2
Surface roughness [nm]	0.95	1.87
True absorption of UVA radiation by the thin film samples at 365 nm (area density of TiO_2: 100 $\mu g\,cm^{-2}$) [%]	9	9.5

2. Materials and methods

2.1. Chemicals, preparation of sols and deposition of photocatalytic films

The following chemicals in this study were used as purchased: coumarin (CM), 7-hydroxycoumarin, TPA, 2-bromoterephthalic acid from Alfa Aesar, Cu powder (200 mesh) and NaOH from Aldrich, methyl stearate, titanium(IV) tetraisopropoxide (TTIP), 2-methoxyethanol, acetic acid, hydroxyethyl-cellulose (HEC), 4-hydroxybenzoic acid (HBA) from Fluka, tetraethoxysilane from J.T. Baker, Pluronic F-127 from Sigma, ethyl acetoacetate (EAA) from Riedel-de Haen, acetonitrile from Fischer Scientific, 96% ethanol from Itrij, *n*-hexane from Carlo Erba. Self-cleaning window Pilkington Activ^{TM} was kindly provided by Pilkington. All aqueous solutions were prepared by using highly pure water from the NANOpure system (Barnstead).

HTPA was synthesized from 2-bromoterephthalic acid according to the procedure described by Field and Engelhardt [20]. The recrystallization of a crude product was done from the ethanol solution. The purity of the obtained crystals was confirmed by ^1H NMR spectra and by measuring the melting point. ^1H NMR spectrum of the pure product still shows a small amount of terephthalic acid (2.5 at.%) as an impurity. The obtained melting point of the pure product was 324–327 °C, while the literature value is 320–322 °C [21].

The detailed procedures of TiO_2 film preparation with a thorough material characterization are already described in our previous publications [22,23]. Summarizing the preparation route, transparent TiO_2-anatase films deposited on both sides of SiO_2-precoated soda-lime glass slides (25 mm × 70 mm) were produced by a sol–gel processing route from TTIP, EAA and 2-methoxyethanol. In this way, a sol D was prepared. The procedure for the preparation of the sol C was basically the same as for sol D, the only difference was that the triblock copolymer Pluronic F-127 was dissolved in the sol D after the addition of 2-methoxyethanol. The films were deposited from a TiO_2 sol using a dip-coater and they were subsequently heat-treated at 500 °C. The thicknesses of the TiO_2 films were increased by repeating the dipping and heat-treatment cycles. The amount of the catalyst on a glass slide was determined by weighing. The names of the TiO_2 samples are composed of two characters: (1) D or C = the symbol of titania sol; (2) 1 or 2 = number of dipping-heating cycles. In Table 1, their most important physicochemical characteristics are collected.

As a reference, a sample of commercial self-cleaning glass Pilkington Activ^{TM} was used in our experiments. According to Mills et al. [24] the Pilkington layer is around 15 nm thick and consists of TiO_2 aggregated particles of sizes around 30 nm.

2.2. Preparation of the organic coating over the titania layer

At first, a solution of sodium terephthalate was prepared by mixing together TPA (500 mg, 0.0031 mol) and aqueous solution of NaOH (31 mL, 0.201 M). Ethanol (96%) was added to obtain 50 mL of the TPA solution. Separately, an aqueous solution of HEC (2 wt.%, 10 mL) was mixed with ethanol (96%, 30 mL). The final coating solution for the deposition onto titania layers was prepared by mixing 10 mL of TPA solution and 20 mL of HEC solution. The solution is stable for months at ambient conditions without degradation and/or precipitation of TPA.

The films of TPA were deposited at 22 °C using a dip-coater with a pulling speed of 10 cm min^{-1}. The layer was dried by a hair dryer immediately after the deposition of the film and in this way a completely transparent coating of TPA was obtained. The thickness of this coating was 1.04 ± 0.01 μm, which was determined by a Taylor–Hobson Talysurf profilometer. The preparation of the coating followed always the same procedure and no differences in the coating thickness and absorption characteristics were noticed on different TiO_2 films, therefore, the reproducibility of the organic film formation was high, at least as much defined as in the case of methyl stearate deposition.

The methyl stearate coatings were prepared from a solution of methyl stearate in *n*-hexane (0.2 M) by dip-coating with a pulling speed of 20 cm min^{-1}.

2.3. Photodegradation of the organic coating

The pure titania films were pre-irradiated in the photochamber (type of the lamps: CLEO 20 W, 438 mm × 26 mm, Philips; broad maximum at 355 nm) for 24 h. The photon flow (Φ_p) in the cell was evaluated by potassium ferrioxalate actinometry [25], and determined to be 5.3×10^{-9} Einstein $\text{cm}^{-2}\,\text{s}^{-1}$. After the pre-irradiation, the organic layer of TPA or methyl stearate was deposited as described in the previous chapter. Then the films were positioned back in the photochamber on places with the same UVA intensities and were irradiated for a certain time in air at 25 °C.

In case of TPA films, washing of the TPA layer was the next step. A mixture of ethanol/water (1:1 volume ratio) was used for this purpose. To obtain reproducible results, always the same ratio between the volume of the extracting solvent and the deposited area was taken (0.25 mL of the ethanol/water solvent was used to wash 1 cm^2 of area covered by the TPA layer). The solution collected was usually analyzed directly by HPLC or spectrofluorimeter, only in case of the experiments, where the degradation products and their concentrations were determined, the sample preparation followed a different route. In this procedure the solution extracted was firstly dried and then re-dissolved in the ethanol/acidified water (HCl, pH 2) mixture, so that the concentration of the solutes was increased for 10 times.

The used films were heat-treated at 400 °C before depositing the TPA layer again.

2.4. Analytical procedures

Transmittance spectra (200–800 nm spectral range) of deposited layer of TPA over a borofloat glass were recorded on HP 8453 UV–Vis spectrophotometer.

The extracted mixture of the TPA, HEC and their oxidized products in the ethanol/water solvent were analyzed by HPLC-FLD or by spectrofluorimeter. The HPLC analyses were made on HP 1100 Series chromatograph, coupled with a DAD and/or FLD detector. The chromatographic separations were run on the BIA Separations C8 column (Kromasil, 250 mm × 4.6 mm, 5 μm) using a 41:18:41 mixture of 0.1% H_3PO_4 in water, acetonitrile and deionized water as the eluent (isocratic elution). The flow rate was 1.0 mL min^{-1}. The injection volume was 50 μL. The elution of TPA was monitored by a DAD detector at 288 nm and the elution of HBA at 256 nm, while HTPA was monitored by a fluorescence detector (FLD) with the excitation wavelength at 325 nm and emission wavelength positioned at 440 nm. The calibration curves were performed for the solutions of TPA, HBA and HTPA. The fluorescence of the washed samples (without chromatographic separation) was also measured by a spectrofluorimeter (PerkinElmer LS-5B) with excitation bandwidth set at 15 nm and emission bandwidth set at 5 nm. The position of absorption wavelength (λ_{EX}) was at 294 nm for alkaline or neutral solutions or 307 nm for acidic solutions, while the fluorescence spectra were recorded between 350 and 550 nm.

The degradation of methyl stearate was studied by measuring the water CA at room temperature using a horizontal microscope with a protractor eyepiece. To this aim, a Contact Angle Meter (CAM-100), KSV Instrument, Ltd. Finland, was used. Specimens were taken out of the illumination chamber for CA measurements after irradiation for different times. The data reported herein correspond to the stable value of the angles obtained by averaging three repeated measurements.

3. Results and discussion

As one of our previous publications [23] deals with a photocatalytic degradation of CM in aqueous solutions and measuring fluorescence of the fluorescent oxidation product (7-hydroxycoumarin), first trials of solid–solid photocatalysis were done on the deposition of CM over titania surface. The titania layer with deposited CM molecules (solid–solid interaction) was irradiated and the fluorescence of the surface (solid phase) was measured using the spectrofluorimeter. No fluorescence of the solid film was detected and the reason was probably a quenching of absorbed energy by the neighbouring molecules in the solid phase. Therefore, a washing of the irradiated layer to a liquid phase was a next trial and the fluorescence of the liquid sample was measured. Using an additional washing step, we were able to detect a fluorescence of photoproduced 7-hydroxycoumarin in a liquid phase.

A new problem occurred, because CM molecules were slowly photodegraded even in absence of TiO_2 under UVA radiation. Although no 7-hydroxycoumarin (no fluorescence) was formed in such experiments, the low photostability of CM presented a big obstacle to implement the novel idea. Therefore, TPA was chosen, the molecule, which reacts with hydroxyl radicals in a similar way as CM and its oxidation product – HTPA – is also an excellent fluorescent compound, easily detected by fluorimetry. Indeed, the TPA was proved to be stable under UVA radiation in absence of a photocatalyst, whereas in presence of TiO_2 and UVA radiation a defined fluorescence occurred.

Deposition of TPA over the substrate led to a hazy coating due to the crystallization and aggregation of TPA on the surface after the evaporation of the solvents. To prevent the non-controlled aggregation of TPA, the HEC was taken as a host polymer to entrap TPA molecules homogeneously. To increase the solubility of TPA in solvents, such as water, the neutralization of TPA to sodium salt of TPA was carried out. The ethanol as a second solvent enabled a deposition of a uniform layer of TPA over the substrate. After many trials, an optimized TPA solution was obtained and used for a deposition of TPA layers. The UV–vis transmission spectrum of a deposited layer of TPA on the borofloat glass is presented in Fig. 2(A).

It can be observed that the transmittance of the borofloat glass above 300 nm was not highly affected by the additional layer of TPA (low haze, almost no absorption of radiation). This is advantageous in comparison with the methods that are based on dye inks, which all cause some filtering of the incoming radiation in UV and vis range.

The amount of deposited TPA using the described conditions was approximately 5.0 μg cm^{-2}. 2.5 mL of the water/ethanol solvent effectively washed the whole layer of TPA from the surface of 10 cm^2. An additional extraction volume of the solvent and a usage of an ultrasound bath contributed just 4–5% to an overall efficiency of the extraction. As it was already mentioned, a layer of

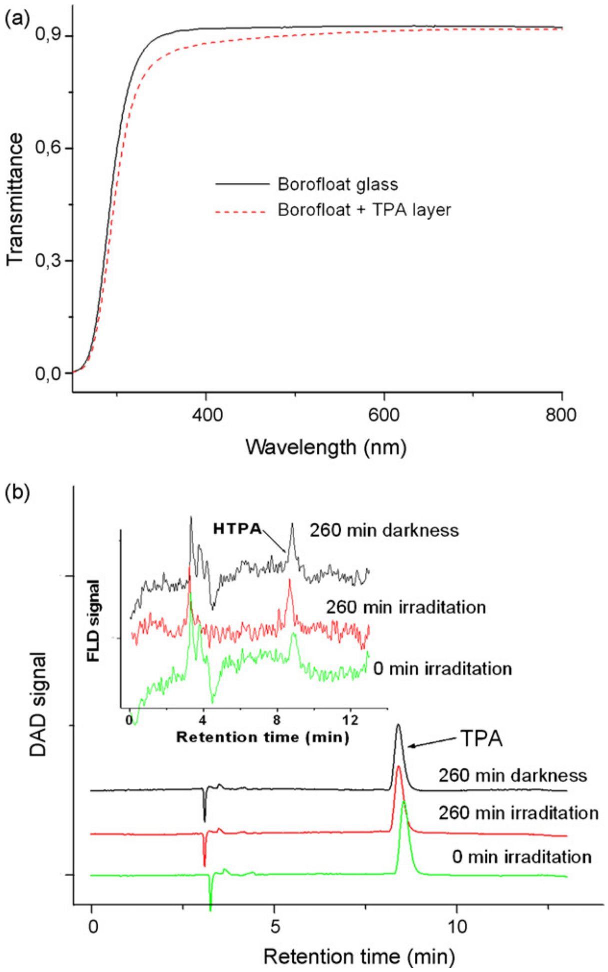

Fig. 2. (A) Transmittance of a borofloat glass and a borofloat glass with deposited TPA layer. (B) Chromatograms showing the TPA peak (DAD detector, 288 nm) and HTPA peak (FLD detector, excitation wavelength at 325 nm and emission wavelength at 440 nm) before and after the 260 min of irradiation in absence of a photocatalyst.

TPA deposited over a normal glass (not photocatalytically active) is photostable. Even after 260 min of irradiation no decrease in the concentration of TPA and an extremely weak fluorescence signal was observed (Fig. 2(B)), similarly to non-irradiated samples.

Further on, the photocatalytic degradation of the TPA layer over titania film was studied. C1 film was chosen for preliminary test. One of the chromatograms in Fig. 3 shows the FLD signal of TPA sample irradiated for 3.5 min. According to the presented chromatogram, there is only one fluorescent peak, which is attributed to the HTPA. This was confirmed also by a synthesized standard of HTPA.

The next question arising from the structural point of view is the mechanism of the initial photocatalytic degradation of TPA in the solid HEC matrix. The initial oxidation of a TPA molecule can possibly occur in two different ways: either through a direct charge transfer from the irradiated TiO_2 photocatalyst or by an attack of primary photogenerated hydroxyl radical. In the former case, a photo-Kolbe reaction probably takes place leading to 4-hydroxybenzoic acid = HBA (analogy to a degradation of phthalic acid, which was studied by Taborda et al. [26]). In the latter case, an unstable OH-adduct of TPA is first created that immediately transforms, after addition of a triplet oxygen molecule ($^3O_2$) and a subsequent elimination of hydroperoxyl radical ($HO_2^{\bullet}$), into hydroxyterephthalic acid = HTPA, which is later on monitored by fluorescence. There is an unavoidable question of the participation of hydroxyethyl-cellulose (HEC) matrix in the overall photocatalytic reaction. It is possible that radical groups formed photocatalytically on HEC could also mediate oxidation of TPA as well as of its primary degradation products HTPA and HBA (analogically to the processes observed for cyclodextrine complex of naphthalene [27]). One can suppose that oxidation events of such organic radicals can take place at longer distances from the irradiated TiO_2 surface than the direct charge transfer and OH-attack mentioned above. In the similar way, radical forms of TPA could react with HEC to form other products than HTPA and HBA. This would explain the observation that less HTPA plus HBA are formed than TPA degraded as mentioned below.

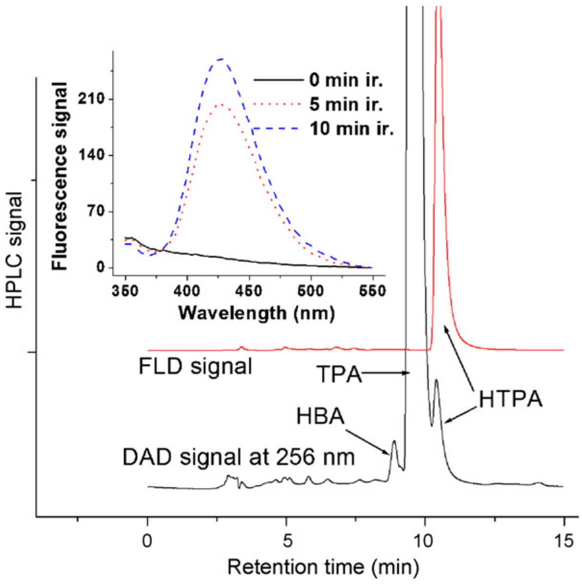

Fig. 3. Photocatalytic degradation of TPA on C1 film and formation of HTPA and HBA. Chromatograms showing the TPA, HTPA and HBA peaks (HPLC-DAD and HPLC-FLD signal) after 3.5 min of irradiation on C1 titania film. The extracted solution was 10 times concentrated before the analysis. Inset: Fluorescence of non-irradiated, 5 min- and 10 min-irradiated sample C1 measured by spectrofluorimeter (λ_{EX} = 294 nm).

To get a better insight into the initial degradation products, the solutions containing mixture of reactant and products after the photocatalytic experiment were 10 times concentrated before the HPLC analysis. The chromatogram (DAD detection) of such a solution (photocatalytic film C1, irradiated for 3.5 min) shows two major additional peaks beside TPA, which could be detected by DAD detector in UVC range (Fig. 3): at 8.8 min and 10.7 min retention times. The peak at 10.7 min belongs to HTPA, while the second peak, at 8.8 min, represents HBA, which was proved with the standard compound as well. This product is a molecule arising from a direct hole transfer (photo-Kolbe reaction), where the decarboxylation of the TPA occurred.

Fig. 4(A) shows the kinetic profile of the degradation of TPA and the formation with subsequent degradation of two main primary products on C1 film on a longer time scale. The zero-order kinetics were observed for TPA degradation, what was expected (solid–solid interface and an multilayer of TPA molecules over the titania surface, similar as in case of stearic acid degradation [5]). The pattern for the formation and also disappearance for HBA and HTPA is comparable. There is an increase of their concentrations after the start of irradiation, reaching a short plateau, which is followed by a slow disappearance. A three-curve-fit according to the simplified kinetic model, which is given below and which describes well only the initial step of TPA degradation, is presented in Fig. 4(B) for the first 3.5 min of irradiation on C1 film. From the initial degradation of TPA and initial formation of HTPA and HBA the yield of conversion of TPA to these two products was evaluated. The calculation cannot be really accurate due to the small differences in TPA concentration

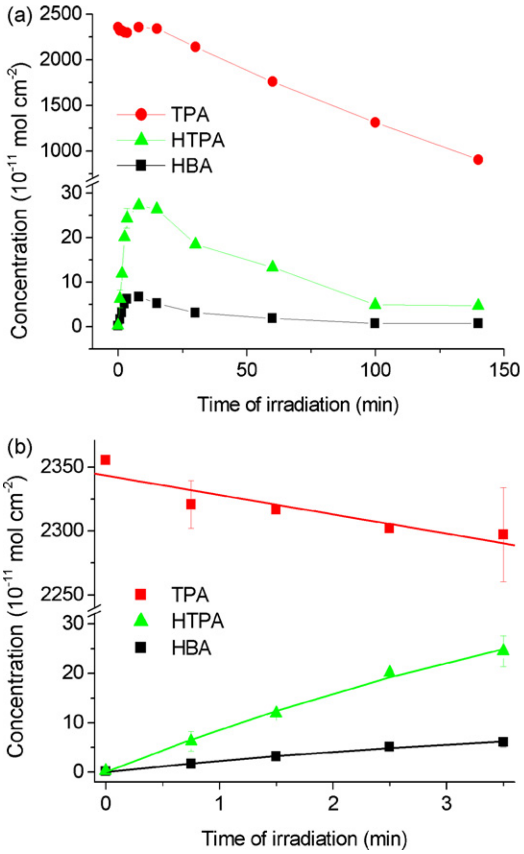

Fig. 4. The kinetics of photocatalytic TPA degradation and consequent HTPA and HBA formation (in moles of the compounds per unit of irradiated area) on a longer (A) and shorter (B) time scale. Sample C1, the analyzing solutions were 10 times concentrated before the HPLC analyses.

after short irradiation time. However, after 3.5 min of irradiation 3.9 nmol of TPA degraded on 11.25 cm^2 C1 film surface, whereas 2.62 nmol of HTPA and 0.73 nmol of HBA formed at the same time. The sum of these two products is 3.35 nmol, representing 86% of the degraded TPA molecules. The difference to 100% can be ascribed to the formation of other products related to HEC transformation (see above) and to the simultaneous degradation of HBA and HTPA to secondary degradation products. The correlative fitting of the curves in Fig. 4(B) resulted in the following kinetic parameters: HTPA formation rate constant = 3.7×10^{-7} M min^{-1} (66%), HBA formation rate constant = 1.0×10^{-7} M min^{-1} (18%), other products formation rate constant = 0.9×10^{-7} M min^{-1} (16%) and TPA degradation rate constant = 5.6×10^{-7} M min^{-1} (100%).

According to the results obtained with C1 film, a fluorescence was a consequence of a photocatalytic reaction. Since HPLC-FLD is a time-consuming analytical method, an analysis of the washed HTPA samples was performed also using a spectrofluorimeter (without preceding separation of the mixture) (inset in Fig. 3). A good correlation between HPLC-FLD and fluorimetric analysis was found for all studied samples and it was concluded that both techniques are appropriate for achieving reliable results. The effect of the solvent and the effect of the pH on the fluorescence intensity and stability were tested using the spectrofluorimeter. The highest fluorescence emission was obtained at alkaline or neutral conditions with ethanol/water mixture as the solvent. λ_{EX} at specified conditions was set to 294 nm and the maximum emission was between 420 and 425 nm. Addition of NaOH to the sample solution did not influence neither the intensity nor the position of absorption (λ_{EX}) or emission wavelength (λ_{EM}). When pure deionized non-buffered water was used as a solvent for HTPA, the fluorescence was the same compared to the samples in water/ethanol mixture at neutral pH. Interestingly, the addition of NaOH changed the fluorescence characteristics of the samples dissolved in pure water. The absorption shifted to longer wavelengths (λ_{EX} was changed from 294 to 335 nm), while the maximum emission was obtained at 410 nm. On the contrary, acidification of the sample led to a dramatic decrease of the fluorescence regardless the solvent used and also the shifts of absorption (λ_{EX} set from 294 to 307 nm) as well as emission (λ_{EM} shifted from 423 to 443 nm) were observed. From these data it can be concluded that the most stable conditions with the highest possible fluorescence intensity at the same time were achieved at neutral or slightly alkaline mixture of water/ethanol at 1:1 ratio. When performing HPLC-FLD analyses, the fluorescence conditions were always the same independently of the sample analyzed (mobile phase dictated the pH and the composition of the solvent). To efficiently separate the HTPA with reversed phase HPLC, the acidification of the mobile phase was necessary. According to our results, the acidification leads to the decrease of the fluorescence, but still its intensity was high enough to perform analyses without problems. However, when studying extremely low efficient photocatalysts the spectrofluorimetric analysis at neutral or alkaline conditions would be preferable due to its lower detection limit compared to reversed phase HPLC-FLD.

In the next step, a comparison of photocatalytic degradation of TPA on three different types of TiO_2 thin films was performed. Different films with different characteristics should lead to different, but logical results. This is the reason why films C and D were tested. Their photocatalytic activities have already been evaluated by measuring in situ decolourization of aqueous solutions of Plasmocorinth B azo dye [28] and also by measuring quantum yields of CM degradation and of 7-hydroxycoumarin formation in aqueous solutions [23]. The characteristics of the prepared films are therefore well-known as well as their correlation to photocatalytic activities in aqueous solutions. It is important to notice again that C1 and D2 films were prepared in a completely same way and the only difference was the addition of surfactant in the preparation procedure of films C. The addition of surfactant increased the porosity of the film (surface area) and its surface roughness, which was the main difference between the two types of the catalysts. Accordingly, the conditions of deposition were chosen in a way that almost the same amount of TiO_2 was deposited in both thin films and also almost the same true absorption characteristics in UV region per amount of TiO_2 were measured for these two types of films [[23], Table 1]. It is already known from previous studies [23,28] that these two configurations have exactly the same photocatalytic activities for the degradation of compounds, which do not adsorb on the surface of titania (where it is supposed that the hydroxyl radical and not the direct hole transfer mechanism is the main way of the degradation). Besides these two types of thin films prepared, also a commercial self-cleaning glass Pilkington Activ^{TM} was chosen. The photocatalytic efficiency of Pilkington Activ^{TM} was expected to be one order of magnitude lower or even more compared to our films due to the big difference in the amount of deposited TiO_2. Anyway, Pilkington Activ^{TM} presents a commercial self-cleaning product and therefore, it is important to evaluate the applicability of the novel method for the existing products found in the market.

The first experiment was devoted to the determination of the ratio between HTPA and HBA concentrations. If the ratio between the two different oxidation pathways is the same regardless the photocatalyst used, then the fluorescence could be used as an appropriate way to evaluate photocatalytic efficiency of various samples. The samples were irradiated for a short time. For all three samples the amount of HTPA produced was higher than the amount of HBA. It means that the hydroxylation of the aromatic ring is more pronounced than the decarboxylation of TPA. Unfortunately, the ratio between these two primary products was not constant. For

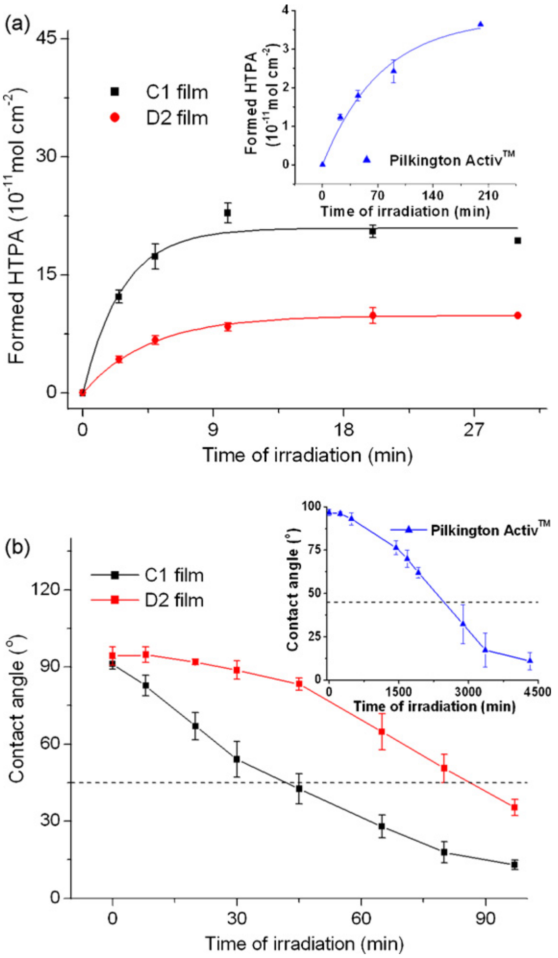

Fig. 5. Photocatalytic efficiency of three different titania films: C1, D2 and Pilkington Activ™. (A) HTPA evolution using the novel method (moles of HTPA per unit area). (B) Methyl stearate degradation by measuring a decrease of CA.

example, n(HTPA):n(HBA) for C1 film was 3.3 ± 0.4, while the same ratio for D2 film was 1.5 ± 0.3 and for Pilkington film it was 1.2 ± 0.2. It seems that the ratio is higher (more HTPA produced relatively to HBA) for more active samples, where TPA degradation was faster.

In Fig. 5(A), a formation of HTPA due to an oxidative degradation of TPA is shown. In order to check the reliability of the analysis, the degradation of the TPA on each film was repeated at least three times and the average signal was later on considered. According to our expectation a formation of HTPA is faster on C1 films compared to D2 films due to a higher surface area of C1 films, although both samples have equal amount of catalyst per unit area. A reaction takes place at solid–solid interface, this is the reason why surface area plays so important role in defining the overall efficiency of the degradation. For both films, C1 and D2, a formation of HTPA with time of irradiation does not follow a linear relationship, but the concentration of HTPA reaches a plateau and after that a decrease of HTPA concentration was observed as in case presented in Fig. 4(A). The difference from Fig. 4(A) is the time scale. We were interested only in the initial kinetics, where the formation of HTPA prevails against its degradation. With the increasing of the HTPA concentration also its degradation rate increases (second degradation step). A plateau is reached, when the rates of formation and degradation of HTPA are of the same size. A fitting of the data according to a simplified kinetic analysis has been performed for the initial degradation (till the plateau). According to Fig. 4(A) and (B) the degradation of TPA followed a pseudo zero-order kinetics and consequently also the formation of HTPA should follow a zero-order kinetics (formation rate constant = k_1). The second suggestion was the pseudo-first order degradation of HTPA (rate constant = k_2). The first-order kinetics of HTPA degradation is not easy to prove, because we deal with extremely small concentrations of an organic compound. However, because its concentration is always small during the experiment (not in excess as TPA) and the concentration of formed holes and/or hydroxyl radicals is constant, it is reasonable to assume the pseudo-first order kinetics for the reaction of HTPA degradation.

Table 2
Self-cleaning efficiency of three different titania films: C1, D2 and Pilkington Activ™. HTPA formation rate constants and the time needed to lower the initial CA to a half value.

Type of the film	HTPA formation rate constant [10^{-9} M min^{-1}]	Time to lower CA from the initial value to 45° [min]
C1	309	42
D2	87	87
Pilkington Activ™	2.1	2460

A simplified kinetic model for HTPA is therefore represented with the Eq. (1):

$$\frac{d\,[\mathrm{HTPA}]}{dt} = k_1 - k_2\,[\mathrm{HTPA}] \qquad (1)$$

After solving the equation the expression (2) is obtained.

$$[\mathrm{HTPA}] = \frac{k_1}{k_2}(1 - e^{-k_2 \cdot t}) \qquad (2)$$

The fitted curves are presented in Fig. 5(A) and the correlation between experimental and fitted data is fairly valid for the initial irradiation time. The HTPA formation rate constants are summarized for all three studied films in Table 2. It has to be pointed out that for their calculation the concentration of HTPA in the solvent after the extraction from the solid film was used. When photocatalytic conversion of TPA to HTPA is concerned, the films C1 were approximately 3 times more active than films D2, while the Pilkington Activ™ was more than 40 times slower in self-cleaning action than both sol–gel based films.

In order to test the novel method, its comparison with a standard method (CA measurements) was carried out. The same films, which were used for fluorescent measurements, were tested. The results are shown in Fig. 5(B). A good correlation is noticed between the novel and the standard method. In order to quantify the data, the time to achieve half decrease of the initial CA was obtained from the curves and the data are collected together with the fluorescence data in Table 2. The correlation between the fluorescence and the CA method is, however, not one to one because the ratio between the two main oxidized products formed was found not to be the same for different photocatalytic surfaces. One has to keep this in mind when evaluating self-cleaning efficiencies by the proposed method. Nevertheless, an obvious advantage of the novel method compared to the standard one is the time of analysis. For example, it takes 2 days for Pilkington Activ™ to get the CA result, whereas the same result could be obtained with the fluorescence method within 3 h of irradiation. Due to its high sensitivity and accuracy, this method can be considered especially useful for surfaces with lower photocatalytic activity that is usually the case in self-cleaning applications.

4. Conclusion

The proposed method has obviously some advantages compared to the standard ones. It is relatively simple, fast and sensitive, the solution of TPA is stable and allows preparation of transparent layers resistant to photolysis under UVA and UVB radiation. The method can be used for any kind of surfaces. It can also be upgraded with a device to measure fluorescence in situ. However, there are still some drawbacks, such as surface dependent ratio of primary oxidation products, and unsolved questions. Especially when dealing with acidic or basic substrates (self-cleaning cement, for example), it is of great importance to know how the pH can influence the formation of HTPA. This is another part of the research, which has to be studied in detail in the future.

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