

PET as a Support Material for TiO₂ in Advanced Oxidation Processes

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ABSTRACT: The use of polyethylene terephthalate (PET) as a support material for TiO₂ films in advanced oxidation processes (AOPs) for water treatment was investigated. A green, low-cost immobilization procedure was developed and the amount of deposited photocatalyst ranged from 0.036 to 0.202 mg per cm² PET. Photocatalytic activity of the films was evidenced by degrading paracetamol solutions under UV radiation. The highest kinetic constants were observed for at least 0.09 mg TiO₂ per cm² PET. Scan electron microscopy (SEM) and energy-dispersive X-ray (EDX) analyses indicated 0.15 mg TiO₂ per cm² PET as enough to provide complete covering of the PET support. Characterization analyses were also performed with a film after 30 h of use in a UV/TiO₂/O₃ reactor. According to SEM analyses, the photocatalyst was not detached from the PET support, while EDX and gravimetric data indicated the possibility of the TiO₂ to have been contaminated by compounds present in the solution during the treatment. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40175.

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INTRODUCTION

In the search for new strategies in water and wastewater treatment, growing attention has been given over the past few decades to the so-called advanced oxidation processes (AOP),¹ which can be used to promote the degradation of contaminants by means of highly reactive molecular and radical species.

UV/TiO₂ heterogeneous photocatalysis is one of the most studied AOPs so far and is based on the action of UV light on the semiconductor TiO₂: photons with enough energy can excite electrons in the structure of TiO₂, resulting in the formation of pairs of electrons in the conduction band and positively charged “holes.” During the process, reactants can also be adsorbed onto TiO₂ particles.² The electron-hole pairs can either simply recombine or react with molecules present in the solution, e.g., water and organic compounds, starting a series of reactions with production of OH· and other radical or molecular intermediates. Ideally, such degradation processes are expected to provide complete mineralization of the contaminants, i.e., their conversion to CO₂ and H₂O.

In AOPs TiO₂ photocatalyst has been used in aqueous medium either in the dispersed form^{3,4} or immobilized on the surface of support materials.^{5,6} Its use as an aqueous dispersion is expected to be energetically more efficient since, within certain limits, greater area of the photocatalyst is available. However, its use in the immobilized form shows the advantage of eliminating the need to separate the dispersed TiO₂ particles from the solution when the treatment is finished.⁷

In recent years, the use of TiO₂ immobilized on the internal surface of PET bottles has been studied in closed, stationary systems for water disinfection⁸ and arsenic removal.⁹ The promising results found make even more relevant the search for information regarding the characterization and new applications of PET/TiO₂ films. In addition, the use of PET as a support material for TiO₂ may represent a matter of interest from both economical and environmental perspectives, since PET is a low-cost, recyclable material found in a large variety of residues, and its mechanical properties, e.g., flexibility, may allow its shape to be easily adjusted to a number of applications in different reactor configurations.

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In this work, the preparation, characterization, and use of flat PET/TiO₂ films in UV/TiO₂-based AOPs was investigated. A novel procedure for the deposition of TiO₂ onto PET surfaces obtained from plastic bottles was developed and the different films obtained were used in kinetic studies regarding the degradation of paracetamol solutions in UV/TiO₂ (bench-scale) and UV/TiO₂/O₃ (pilot-scale) systems.

The immobilization procedure developed can be considered environmentally friendly, since small amounts of chemicals are used and almost no residues are generated. It also shows the advantage of low-energy consumption by not involving heating steps, while temperatures up to some hundreds of degrees Celsius may be required, especially when glass supports are used.^{6,10} To enhance the adsorption of TiO₂ particles onto PET surfaces, the use of alkaline surface modification of PET and thermal treatment above 200°C has also been reported.¹¹

Paracetamol (*N*-(4-hydroxyphenyl)acetamide), also named acetaminophen, is an emerging contaminant with antipyretic and analgesic properties, largely used worldwide, commonly adopted as an alternative for the use of sodium diclofenac and acetylsalicylic acid. Since the early 1990s growing attention has been given to the environmental contamination caused by substances whose presence in a great number of aqueous systems had not yet been detected, among which paracetamol can be cited.¹² Because of the lack of parameters concerning the disposal of such compounds, they have been named “emerging contaminants”, including pharmaceuticals and personal care products (PPCPs), which can be introduced in the water cycle by improper disposal of solid residues or industrial, domestic and hospital effluents.¹³ In the year 2000, a total amount of 400 tons of paracetamol were prescribed only in England.¹⁴ Some information regarding this compound is presented in Table I.

Just like many other PPCPs, paracetamol has frequently been found in effluents from sewage treatment plants. It has been detected in concentrations ranging from 0.13 to 26.09 µg L⁻¹, average 10.194 µg L⁻¹,¹⁵ and from 29 to 246 µg L⁻¹, average 134 µg L⁻¹ in this kind of matrix.¹⁶ Up to 10 µg L⁻¹ has been observed in natural waters in the United States.¹⁷ UV and UV/TiO₂,¹⁸ O₃,^{19,20} UV/H₂O₂,¹⁹ UV/O₃, Fenton process,²⁰ anodic oxidation,^{20,21} and ozonation catalyzed by metals²² are some examples of AOPs used in paracetamol degradation studies.

Both adsorption and mass transfer processes play a key role in the degradation kinetics in TiO₂-based treatments. For this reason, in this work the covering of PET surfaces by the photocata-

lyst is related to the kinetic constants observed. Information regarding the characterization of the PET/TiO₂ films before and after use is presented and discussed.

EXPERIMENTAL

Chemicals and Solutions

Paracetamol was used in its solid form, pharmaceutical grade (>99%). TiO₂ (P-25) was used with the composition 80% anatase, 20% rutile, as received from supplier (EVONIK). HPLC grade methanol (VETEC) was used in the chromatographic analyses. Paracetamol solutions were prepared with distilled water. For the preparation of any other solutions and mobile phases, ultrapure water (18.2 MΩ cm at 25°C) was used. PET surfaces (28 cm × 9 cm) were obtained from soft drink bottles.

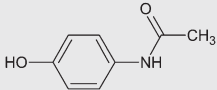
Instrumentation

Reactors. Bench-scale experiments were performed in the reactor represented in Figure 1(a,b). A Petri dish with 5-cm inner diameter was used as the reaction chamber, in which 15 mL of paracetamol solution (2 mg L⁻¹) were stored during each degradation essay. The TiO₂ films were cut to fit the circular bottom of the Petri dish but a piece of each film (1-cm height) was cut out to allow a small stir bar (0.4-cm length) to be positioned in the reaction chamber, to provide homogenization of the solution (250 rpm). The films remained completely covered by the solution during each essay. A UV lamp (length 25 cm, nominal Power 8 W) (PHILIPS) with maximum emission at 254 nm was positioned over the reaction chamber, 4.0 cm above the liquid surface.

Pilot scale experiments were carried out in the UV/TiO₂/O₃ reactor represented in Figure 1(c). Horizontally positioned, the reaction chamber (5 cm × 100 cm × 22 cm) was built with stainless steel. The solution under treatment (paracetamol 2 mg L⁻¹; 8 L) enters the reactor by the slightly higher extremity. Up to four UV lamps (length 90 cm, nominal Power 30 W) (PHILIPS) with maximum emission at 254 nm were used. The lamps were positioned on the top of the reactor, 6 cm above the surface of the liquid, while TiO₂ films were placed in the bottom of the reactor, 0.5 cm below the surface of the liquid. When leaving the reaction chamber, the solution returns to the reservoir from where it is continuously pumped. An ozone generator (SUPERZON) delivers ozone in the bottom of the reservoir.

Instrumental Analysis. The thickness of the films was measured by using a manual, digital micrometer (MITUTOYO). For this purpose, five samples (2 cm × 6 cm) were cut from different regions of the PET/TiO₂ film, and the thickness was measured

Table I. Physical and Chemical Properties of Paracetamol

Chemical structure	Properties	
	Chemical formula	C ₈ H ₉ NO ₂
	Molecular weight	151.16 g mol ⁻¹
	Visual aspect	White powder
	Solubility	12.7 g L ⁻¹ in water; soluble in ethanol
	Aqueous solution pH	5.5–6.5
	pK _a	9.38

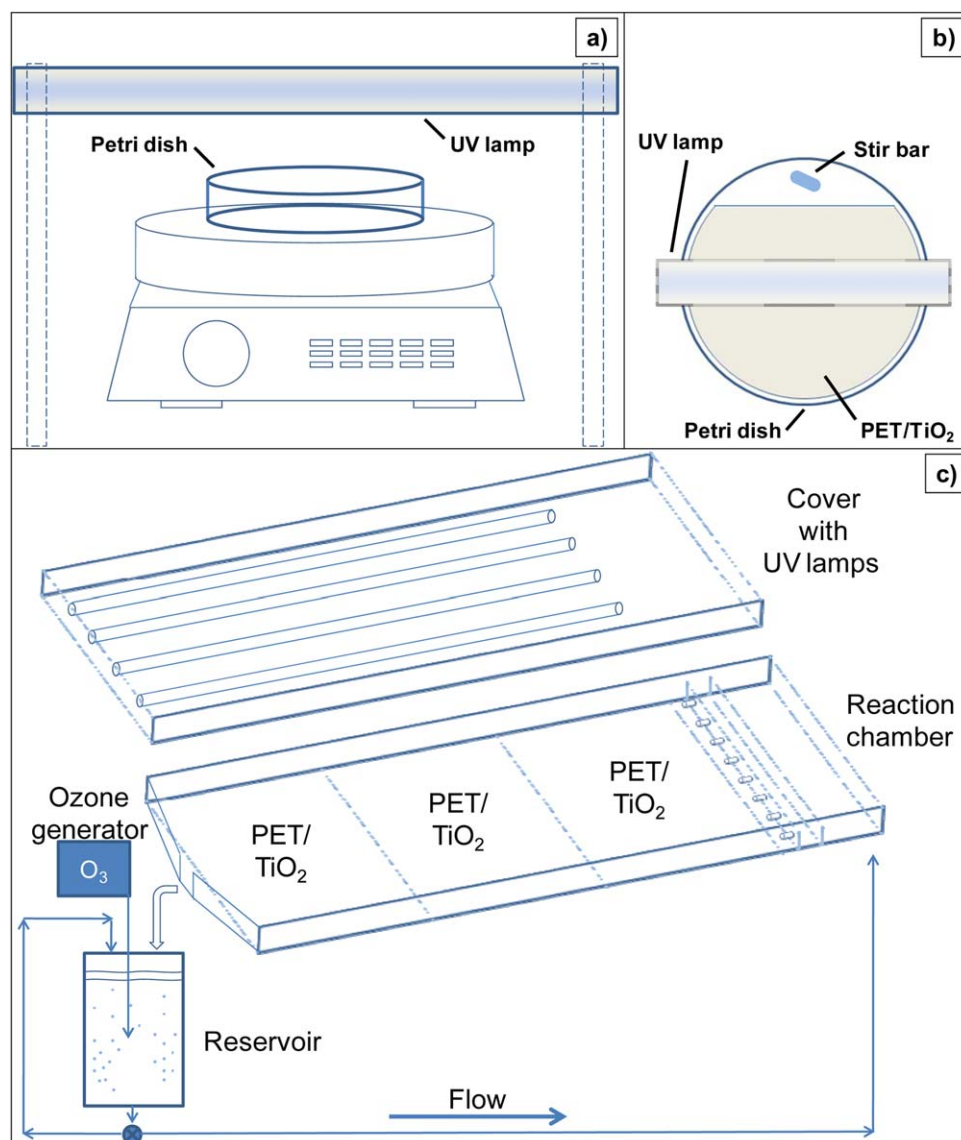


Figure 1. Front (a) and top (b) views of the bench-scale reactor; pilot scale UV/TiO₂/O₃ reactor (c) used in the degradation experiments. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in five different spots of each sample. The same procedure was performed with the PET surfaces without TiO₂, so the average values calculated in both cases could be used to estimate the film thickness due to TiO₂ deposition.

For the quantitation of the immobilized TiO₂, 100-cm² samples of the PET/TiO₂ films were weighted with an electronic analytical balance (TECNAL), after which the TiO₂ was removed from the support by washing with water and detergent, without using any abrasive material to avoid any PET loss. The PET supports were rinsed with distilled water and allowed to dry for 24 h at room temperature, after which they were weighted again.

Pt-metalized samples of PET support and PET/TiO₂ films were analyzed by scan electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX), with a Vega-Tescan instrument (BRUKER). EDX analyses were performed all over the

surfaces of samples obtained from the films, to provide average values to each sample.

The absorbance of the paracetamol solution was monitored throughout the bench-scale experiments by UV–vis spectroscopy, with a Cary instrument (VARIAN). Absorbance values were considered proportional to the concentration of absorbing species, according to Beer's law. For each measurement, the sample (3.5 mL) was collected from the reactor chamber and immediately transferred to a quartz cuvette (optical path 1 cm) and the absorbance was measured at 200 nm. The sample was then returned to the reactor.

Immobilization Procedure

The photocatalyst was immobilized on the PET surfaces according to the procedure described below, adapted from Meichtry et al. (2007).⁸ A TiO₂ aqueous dispersion (2% m v⁻¹) was

prepared by using 5 g of the photocatalyst to a final volume of 250 mL. The mixture was acidified to pH 2.5 with perchloric acid before use. For 10 min, the dispersion was homogenized with a magnetic stirrer until TiO_2 was no longer accumulated in the bottom of the flask. After that, ultrasound bath was used for 20 min to provide better separation of suspended TiO_2 particles.

The immobilization procedure was carried out as follows: the TiO_2 dispersion was transferred to a glass recipient (20-cm length \times 20-cm width \times 5-cm height), resulting in a liquid layer with ~ 1 cm height. Each PET surface was then manually immersed in the dispersion for about 10 s, removed, and left to dry vertically positioned for 2 h at room temperature, protected from direct air flow. The dispersion was then homogenized with a magnetic stirrer and ultrasound bath, prior to another immobilization step. Different films were obtained just by varying the number of times the immobilization step was carried out. The films were then named accordingly, thus resulting in the films "1 \times ," "5 \times ," "10 \times ," "15 \times ," and "20 \times ."

Degradation Experiments

Throughout the experiments, the *bench-scale* photocatalytic reactor was operated inside a protective box to avoid the incidence of external light on the system and to prevent the UV light from passing to the external environment. The UV lamp was turned off and the protective box was open every time a sample from the solution had to be collected and analyzed. These time intervals were not included in the total time count of the experiment.

The degradation essays performed in the *pilot scale* reactor were conducted until the paracetamol concentration, measured by HPLC, was lower than 10% its initial value, after which the essay was restarted with a new solution to be treated. PET/ TiO_2 "10 \times " films (20 cm \times 9 cm) were immersed under a 0.5-cm layer of paracetamol solution (2.0 mg L^{-1}) flowing horizontally with linear speed of 2.3 m s^{-1} , under recirculation. Two UV lamps ($2 \times 30 \text{ W}$) were used. Ozone was also used as an oxidation agent in this system. For this purpose, an air-ozone mixture was continuously produced by corona discharge (SUPERZON, BRAZIL) and bubbled into the solution.

RESULTS AND DISCUSSION

Photocatalyst Characterization

Visual Aspect of the Films. At first, the originally smooth PET surfaces were carefully scratched with an abrasive material, as an attempt to favor the immobilization of the photocatalyst,^{8,23} but the result was not as expected. The resulting grooves on the PET surfaces provided preferential paths for the TiO_2 dispersion to flow during the immobilization and the films could not be obtained, as the TiO_2 accumulated in a few regions of the support. Films with good homogeneity were obtained when PET supports were used with no modification or any special treatment. Prior to the immobilization procedure the PET surfaces were washed with water and detergent and carefully rinsed with distilled water. A comparative image of the different films obtained is presented in Figure 2.

It can be observed that the opacity of the films increases with the number of immobilization steps and respective increase in the amount of photocatalyst deposited, as shown in "Film thickness, mass, and composition" section.

The efficacy of the immobilization procedure was initially demonstrated by immersing the films for 8 h in a water recirculation system [Figure 1(c)] with linear speed of the liquid $\sim 2.3 \text{ m s}^{-1}$ —the most severe condition to be used in the following degradation tests —, after which no *visual* changes in the film were observed. Film Thickness, Mass, and Composition. Figure 3(a) depicts the quantitation of TiO_2 immobilized per area of PET as a function of the number of immobilization steps performed.

The data presented in Figure 3(a) are in accordance with those from "Visual aspect of the films" section, confirming that the amount of TiO_2 immobilized is increased with the number of immobilization steps. This is expected to enhance the photocatalytic activity of the films, by providing a greater surface area available for the oxidation reactions to take place.²⁴ It can be observed in Figure 3(a) that the increments in TiO_2 mass tend to decrease as more immobilization steps are performed.

The results of EDX semiquantitative analyses of the TiO_2 films are presented in Figure 3(b), which clearly shows that the *relative* amount of Ti deposited on the PET surfaces is increased

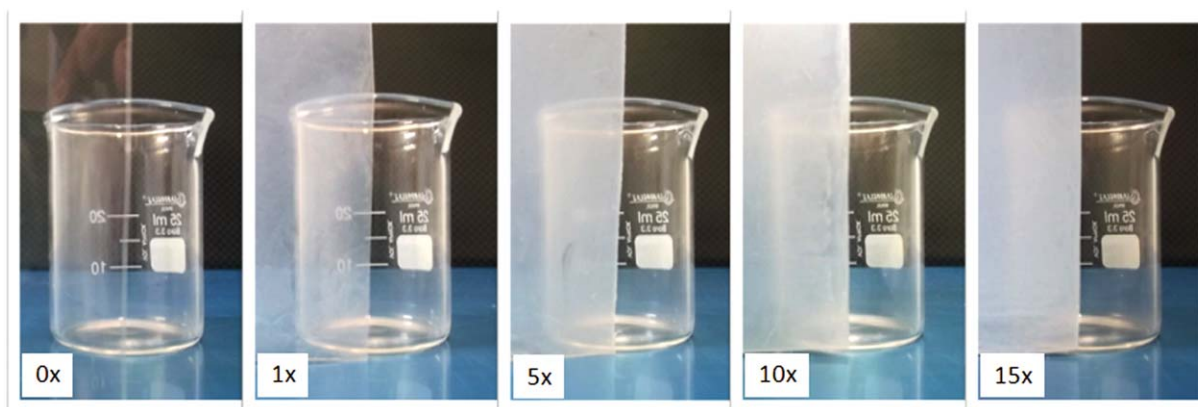


Figure 2. Visual aspect of the different PET/ TiO_2 films. The number in the lower left corner of each picture indicates the number of times the immobilization step was carried out. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

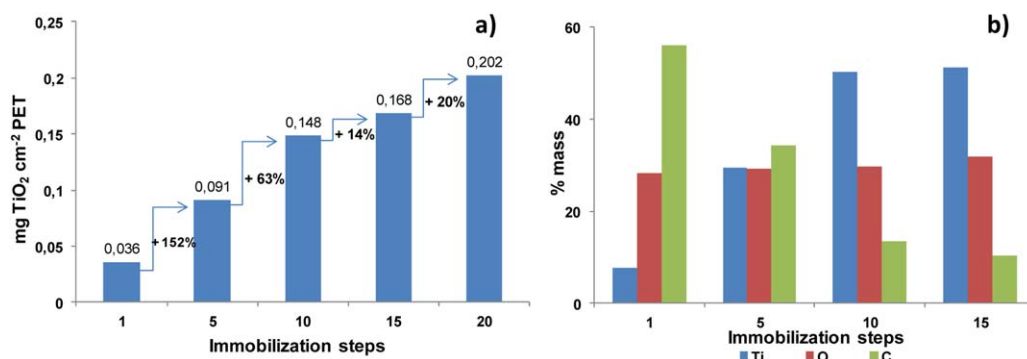


Figure 3. Mass of TiO₂ immobilized per area of PET (a) and semiquantitative (mass-normalized) EDX analysis of PET/TiO₂ films (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

until a total number of 10 immobilization steps, remaining nearly the same when 10 or 15 immobilization steps are performed. Even though the *mass* of TiO₂ immobilized [Figure 3(a)] keeps growing until 20 immobilizations, after 10 immobilizations the *relative* (mass-normalized) amounts of titanium detected by EDX analysis are only slightly increased, the opposite happening to the values for carbon. This is possibly due to a gradually more dense covering of the PET support by the increasing amounts of photocatalyst. Since the only carbon source was the PET support, the detection of carbon atoms from the polymer became more difficult as more TiO₂ was deposited. Finally, the relative amounts of oxygen remained nearly constant, probably due to the fact that this element is present in both PET and TiO₂ compositions.

These results are indicative that dense covering of the PET support had probably been achieved when 5–10 immobilizations were performed, so that relative changes in the composition of the film are no longer observed by EDX analysis.

The thickness of the film “10×” was measured according to the previously described procedure. Average thicknesses of 270 and 282 μm were found for clean PET surfaces and 10× PET/TiO₂ films, respectively. Since the films have TiO₂ equally deposited on *both sides* of the PET support, the 12-μm difference between the medium values was divided by 2, resulting in an estimated average thickness of 6 μm for each 10× TiO₂ layer.

SEM Analyses. Figure 4 displays the SEM images of the PET support and the PET/TiO₂ films. The SEM images evidence the improvement on the TiO₂ coating provided by the increase in the number of immobilization steps, especially when comparing the samples PET, 1×, and 5×. The surface of the PET sample looks quite smooth, with just some minor scratches on it. As expected, no relevant particles are observed on the polymer surface. However, after the first immobilization procedure (film “1×”), many TiO₂ particles are observed on the PET surface, but not in enough quantity to provide complete covering. As a result, some regions of the surface appear to be much more densely covered than others.

More dense covering of the PET by TiO₂ particles was observed in the film 5×, but some regions of the film still remain poorly covered. The photocatalyst particles formed spherical agglomer-

ates of greater diameter than those observed in the film 1×. In the films 10× and 15×, the number of immobilization steps seem to have been enough to provide complete covering of the PET support. Although the diameter of some spherical agglomerates observed was increased when compared to film 5×, the surfaces of both films were quite similar.

As described above, the TiO₂ dispersion was acidified to prevent the photocatalyst particles to form aggregates. The acidification is expected to have this effect since it brings pH to a value much lower than the point of zero charge (PZC) of TiO₂. Several PZC values are mentioned for TiO₂ in literature. For Degussa P-25, medium values range from 6 to 6.5.²⁵ Thus, the acidification to pH 2.5 results in a favorable condition in which the particles become positively charged and their agglomeration is inhibited due to electric repulsion, resulting in greater stability of the dispersion.²⁶

In addition, ultrasound bath was used to provide a microscopic separation of the particles, as a complement to the macroscopic homogenization resulting from mechanical stirring. In spite of such precautions, the formation of some aggregates was still observed.

Effect of the Number of Immobilization Steps on the Photocatalytic Efficiency

The films characterized by SEM and EDX were used in bench-scale experiments to study the effect of the number of immobilizations on the photocatalytic degradation of 2 mg L⁻¹ paracetamol.

The pseudo-first-order kinetic model [eq. (1)] was tested to determine the kinetic constant in each case. The sum of the squares of the errors (ERRSQ) [eq. (2)] was considered for every experimental data set and the kinetic constants were calculated for the lowest error values, by adjusting and optimizing the function with the *solver* add-in for Microsoft ExcelTM.

$$C = C_0 \times 10^{(-kt)} \quad (1)$$

$$\sum_{i=1}^P (C_{\text{est}} - C_{\text{exp}})_i^2 \quad (2)$$

where C is concentration (experimental or estimated) at any given time, C_0 is its initial concentration, k is the kinetic

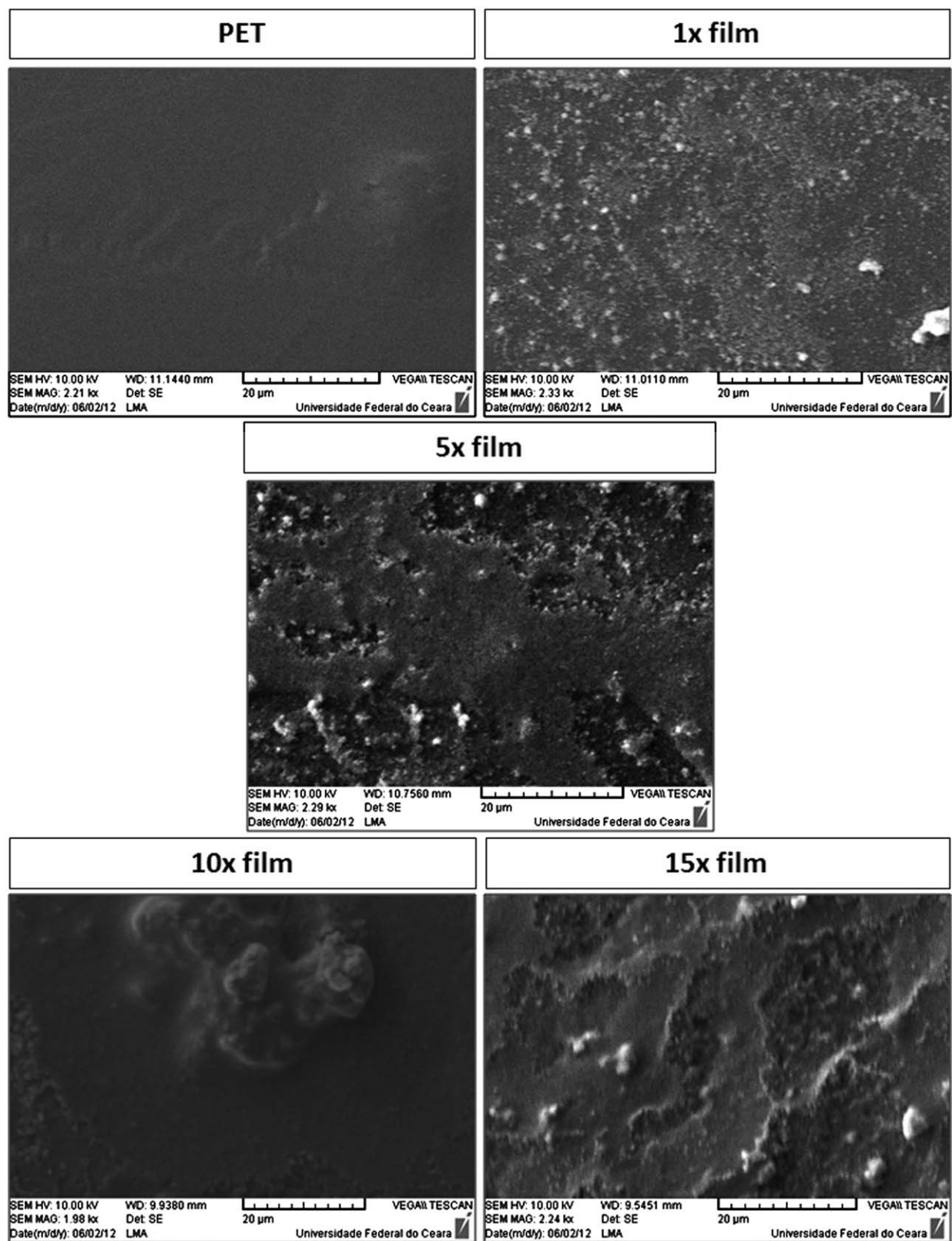


Figure 4. SEM images of PET and PET/TiO₂ films. The scale below each image corresponds to 20 μm.

constant (min^{-1}), and t is the time (min); P is the total number of points in each data set, C_{exp} is the experimental concentration, and C_{est} is the respective value estimated by the model.

The kinetic constants calculated for each data set are presented in Table II, with the respective ERRSQ and determination coefficient values.

Table II. Pseudo-First-Order Constants Observed for Different TiO₂ Coverings

Film	PET	1×	5×	10×	15×
k' (min ⁻¹)	0 ^a	0.0148	0.0266	0.0271	0.0273
ERRSQ	-	0.0022	0.0001	0.0069	0.0001
R ²	-	0.9925	0.9998	0.9857	0.9986

^aNo degradation observed.

The ERRSQ and R² values presented in Table II demonstrate that the experimental data fit well the pseudo-first-order kinetic model. Besides other assumptions, it means that within certain limits the substrate concentration determines the degradation rate, with other experimental conditions being held. Also, the surface covered by the substrate plays an important role in the degradation kinetics.²⁴

According to the experimental data presented in Table II, the surface available for the substrate to react seems to have been significantly improved by increasing the deposition of TiO₂ up to five immobilization steps, when the kinetic constant reached its highest value. When greater amounts of TiO₂ were deposited the kinetic constant remained approximately the same, probably because the PET surface was completely covered after five immobilization steps. The time course of the concentration throughout the degradation experiments with the different films is displayed in Figure 5. For better visualization, experimental data regarding films 1× and 10×, as well as the respective curves predicted by the pseudo-first order model, are provided as Supporting Information.

The difference between the degradation rates observed for film 1× and the others is very clear, with film 1× showing intermediate activity when compared to PET without TiO₂ (no degradation observed) and the films 5×, 10×, and 15×. The films 5×, 10×, and 15× showed similar photocatalytic activities, so that the respective data sets appear superposed in Figure 5. Figure 6 depicts the relation between the amount of TiO₂ deposited per area of PET (mg TiO₂/cm² PET) and the pseudo-first-order kinetic constants calculated.

The data displayed in Figure 6 show that no degradation was observed in the essays performed with the PET surfaces without

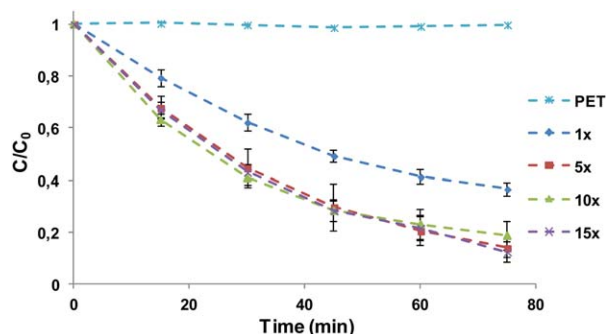


Figure 5. Time course of concentration (200-nm absorbance) during photocatalytic degradation of paracetamol (2 mg L⁻¹) in bench-scale reactor, with PET/TiO₂ films obtained with 0 (PET only), 1×, 5×, 10×, and 15× immobilization steps. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TiO₂. That means that the UV radiation power used was not enough to promote the direct photolysis of the molecules.^{27,28} This result also demonstrates that the photocatalytic activity of TiO₂ was preserved after the immobilization, since its presence was found to be an imperative condition for the degradation to occur in the reactor used. The results for each film are further discussed below.

The use of the 1× film resulted in the lowest kinetic constant, which can be explained by the partial covering of the PET support in this film, as observed in MEV analyses (“Visual aspect of the films” section), resulting in lower TiO₂ surface area and consequently reduced photocatalytic activity.²⁹

It can be seen in Table II and Figures 5 and 6 that to the increase in the mass of immobilized TiO₂ corresponds an increase in the value of the kinetic constant, notably until five immobilization steps. From 5 to 15 depositions, <3.0% variation is observed in the values of the kinetic constant, even though the amount of deposited TiO₂ still increased until 20 depositions (“Film thickness, mass, and composition” section). These results are in accordance with the fact that the photocatalyst surface area plays a key role in the degradation performance of UV/TiO₂ based processes. This is expected, since several surface phenomena take place in such systems, e.g., the adsorption of reagents, oxidation–reduction reactions and desorption of products.³⁰

The photocatalytic activity of TiO₂ films can be considerably affected by some parameters such as porous volume, surface area and thickness of the film.^{29,31} Regarding the influence of such parameters in the results obtained, in this work the TiO₂ films were prepared according to the same procedure, so there seems to

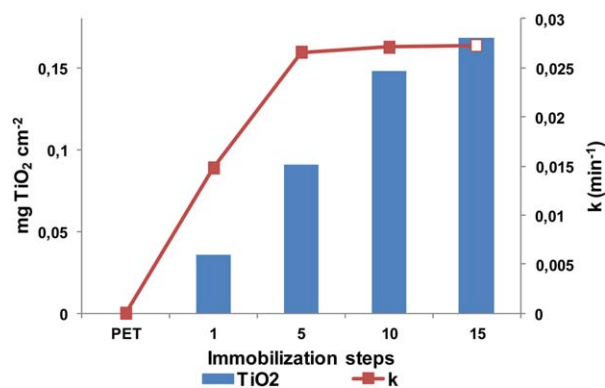


Figure 6. Mass of TiO₂ deposited in different PET/TiO₂ films and the respective pseudo-first-order kinetic constants obtained in the photocatalytic degradation of paracetamol (2 mg L⁻¹) in bench-scale reactor (15 mL). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

be no need to take variations in porous volume into account. On the other hand, surface area played a key role in the results obtained, being demonstrated that the increase in the covering of the PET support resulted in higher photocatalytic activity, up to the maximum kinetic constant observed for the films 5 \times , 10 \times , and 15 \times . Finally, after complete covering of the PET support—achieved with five immobilization steps—additional amounts of deposited TiO₂ are expected to have increased the thickness of the films⁶ beyond the 6 μm found to film 10 \times , possibly making a greater number of pores and surface area available. Such effect, if happened, could explain the slight changes observed in the kinetic constants for films 5 \times , 10 \times , and 15 \times .

Characterization of the TiO₂ Films After Use in a UV/TiO₂/O₃ System

A typical time course of paracetamol concentration during an essay in the pilot scale reactor is provided as Supporting Information, as well as the conditions used in HPLC analyses. Samples of the films were analyzed by SEM and EDX after being used for 10 and 30 h in the pilot scale system. SEM images are presented in Figure 7(a–c). According to Figure 7, PET surfaces remained covered by TiO₂ even after 30 h of use, exposed to the liquid flow, UV radiation and ozone.

On the other hand, reduction in the number and size of TiO₂ spherical agglomerates is observed in the samples, possibly due to

a progressive removal of the bigger TiO₂ grains by the liquid flow. It must be mentioned that such removal of photocatalyst particles was detected neither visually nor by UV–vis spectroscopy, a technique quite sensitive to the presence of small amounts of TiO₂ particles in water. These results indicate that some detachment of photocatalyst takes place on the surface of the TiO₂ layer, but too slowly to be detected in the analyses of treated solutions or to cause major changes in the opacity of the film.

The decrease in the mass percent of Ti observed in EDX analysis [Figure 7(d)] seemed to confirm the gradual loss of TiO₂, as indicated by SEM. However, after 10 h of use, the mass-normalized amount of Ti *detected* is similar to that on “1 \times ” film, becoming even lower after 30 h of use. If these were absolute values, these films would be expected to be more transparent than the “1 \times ” films, prepared with only one immobilization step, which has been proved not to be true.

Since after 30 h of use the opacity of the “10 \times ” film still looks similar to that of a new “10 \times ” sample [Figure 7(e,f)], it can be deduced that such decrease in the *relative* amount of Ti may not be *exclusively* due to the detachment of TiO₂ from the films. In fact, gravimetric analysis of “10 \times ” films after 30 h of use revealed 0.2087 ± 0.0253 mg of deposited material per cm² PET, an amount of TiO₂ similar to that deposited on “20 \times ” new films. Such *increase* in the mass of material deposited on the PET

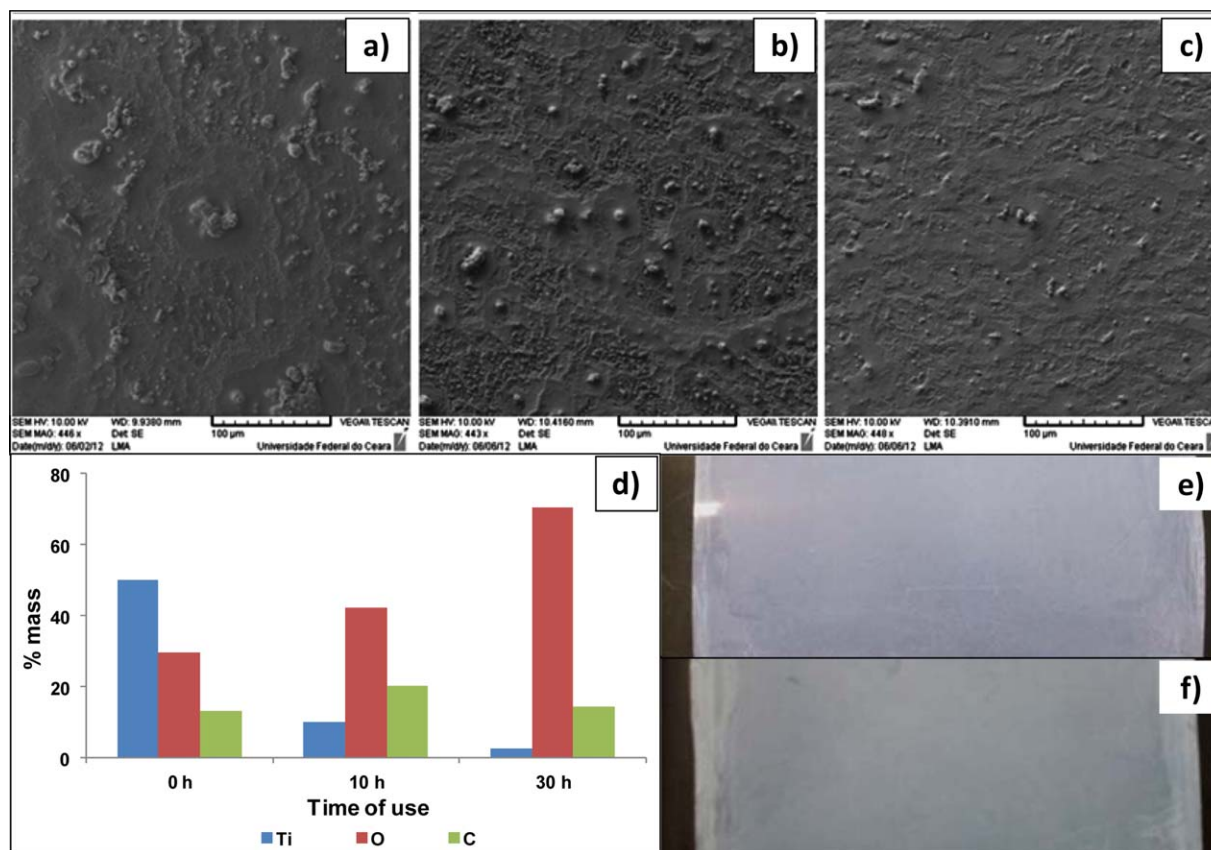


Figure 7. “10 \times ” film used in a pilot scale UV/TiO₂/O₃ reactor: SEM images after 0 (a), 10 (b), and 30 h (c) of use (the scale below each image corresponds to 100 μm); EDX analysis (d); visual aspect of the film with 0 h (e) and 30 h (f) of use. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

support can possibly be due to the adsorption of organic compounds present in the solution throughout the experiments. It cannot be caused by the deposition of new TiO₂ since the photocatalyst is not even present in the solution under treatment. The contamination of the films by degradation products may also explain the lower relative quantities of Ti detected. These contaminants seem to be—at least partially—continuously removed from and adsorbed onto the films during the treatment, since the photoactivity is preserved after repeated cycles of use.

CONCLUSIONS

Satisfactory immobilization of different amounts of TiO₂ on PET surfaces was achieved with a simple, low-cost procedure proposed. Photocatalytic activity of the films was demonstrated by the degradation of paracetamol, which only occurred in the presence of TiO₂. The pseudo-first-order kinetic constants were increased as a result of increasing in the covering of PET surfaces by the immobilized TiO₂. Maximum kinetic constants were observed when at least 0.091 mg TiO₂ was deposited per cm² PET.

SEM and EDX analyses showed that the immobilization of 0.148 mg TiO₂ or more per cm² PET resulted in more dense covering of the PET support. Considering the respective kinetic constants, after complete covering of the PET support the amount of deposited TiO₂ seems not to have affected considerably the photocatalytic activity of the films.

The integrity of the films was preserved after 30 h of use in a UV/TiO₂/O₃ system operated in pilot scale, with no signs of detachment of the TiO₂ by the liquid under recirculation. Degradation of the PET supports was not evidenced and the photoactivity of the films was preserved after repeated cycles of use. An increase in the mass of used films is probably related to the adsorption of compounds throughout the experiments.

Regarding the use of PET as a support material for TiO₂ in different AOPs and reactors, the immobilization procedure proposed can possibly result in economical and environmental advantages related to the reduced consumption of energy and chemicals, the reuse of PET, and almost no residue generation.

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