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Stability of the Photocatalytic Activity of TiO_2 Deposited by Reactive Sputtering

Lucas Caniati Escaliante[a*], ***Kleper de Oliveira Rocha***[b], ***Jose Humberto Dias da Silva***[a]

[a]*Universidade Estadual Paulista (UNESP), Faculdade de Ciências, Programa de Pós-Graduação em Ciência e Tecnologia de Materiais (POSMAT), Bauru, SP, Brasil.*
[b]*Universidade Estadual Paulista (UNESP), Faculdade de Ciências, Departamento de Química, Bauru, SP, Brasil.*

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The photocatalytic activity and stability of TiO_2 thin films deposited by reactive sputtering were evaluated through many cycles of aqueous methylene blue solutions photodegradation. Tests were performed in TiO_2 films deposited onto silica, silicon, and lanthanum aluminate substrates under UV light irradiation. The dye degradation was determined using the optical absorbance spectra at pre-established exposure times. After 16 cycles of reaction, 180 minutes each, no systematic losses in the photocatalytic activity were observed in the samples. The best activity was observed on films deposited onto silica glass. The results indicate that the TiO_2 samples deposited by the sputtering technique are stable concerning the UV degradation of methylene blue.

Keywords: *Photocatalysis, Titanium Dioxide, Sputtering, Stability.*

1. Introduction

Photocatalysis produced by TiO_2 compounds has gained attention since the discovery of such phenomenon, by Fujishima and Honda[1]. Since then, TiO_2 is the most studied compound concerning the photocatalytic degradation of dyes, and a large number of related reports been published in many areas, like environmental remediation[2], self-cleaning surfaces[3], purification and decontamination of water and effluents[4], and hydrogen generation[5].

Being the environmental issues a central theme, the growing population and industrial expansion are closely tied to the depletion of natural resources and the increasing pollution throughout the world. In this context, photocatalysis presents itself as a promising technology as it involves advanced oxidative processes to breakdown pollutants in the environment until mineralization, being able to substitute more conventional techniques that, generally, just modify the phases of these elements, causing secondary pollution, waste generation, and need for later treatments[6].

The advanced oxidative process described as a mechanism with which the photocatalysis can oxidize pollutants is based, mainly, on the irradiation of light with energy higher than the material's bandgap[7-11]. In this process, it is well established that the electrons in the conduction band (e_{CB}^-) of TiO_2, generated by absorbing photons with energies greater than band gap energy (E_{gap}) leave holes (h_{VB}^+) in the valence band. A significant part of these photogenerated electrons can react with adsorbed O_2 on TiO_2 surface or dissolved in the medium, generating superoxide radical anion $O_2^-\bullet$[7-11]. The holes on the TiO_2 surfaces react with OH^- or H_2O oxidizing the hydroxyl radicals $OH\bullet$. The superoxide and hydroxyl radical are responsible for the degradation of the dye[7-11].

Thus, TiO_2, a semiconductor with a relatively wide bandgap is largely explored[12] for its uses in gas sensors[13], solar cells[14], and also for the large utility for photocatalysis[15]. Other advantages are its low cost, being abundant in nature, and non-polluting[16].

TiO_2 thin films can be produced from different techniques, each with its peculiarities and complexities, such as sol-gel[17], chemical vapor deposition[18], electron beam evaporation[19], pulsed laser[20] e sputtering[21]. Among these techniques, sputtering deposition has some advantages[22], such as its simplicity, very low residue production, versatility, scaling possibility, good reproducibility, and relatively low cost when compared to more elaborate techniques, so this method will be the focus of the present study.

Advantages can also be cited with regards to the use of thin films instead of powders in respect to industrial and commercial applications. This is because it is possible to insert and retrieve the photocatalyst in a simple manner, not requiring any type of mechanism to separate and collect the powder from the system. As a counterpart, the powders photocatalyst, generally have larger effective surface areas than thin films.

In this context, attention needs to be paid to the stability of the films, besides their efficiency, to guarantee the functionality of products[23-25]. Nevertheless, no reports were found concerning the photocatalytic stability of TiO_2 thin films prepared by reactive magnetron sputtering. So, in this report, films deposited using reactive RF magnetron sputtering are being submitted to testing cycles of photocatalysis to evaluate the activity and stability. Tests were performed in films deposited onto silica, silicon, and lanthanum aluminate substrates, during different exposure times.

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*e-mail: lucas.caniati@unesp.br

2. Materials and Methods

TiO_2 films were deposited by reactive RF magnetron sputtering in a commercial (Kurt J. Lesker, System I) using a metallic titanium target (99.999%) on three different commercial substrates: silica glass (SiO_2), (100) silicon crystals (Si), and (001) lanthanum aluminate crystals (LAO). During depositions, a programmed RF source delivered 120 W constant power to the process. The depositions lasted for 360 minutes. Inside the chamber, a mixture of Ar and O_2 gases, with flow rates of 39.5 and 1.8 sccm respectively, were used under a total pressure of 5×10^{-3} torr. The nominal temperature, established in the substrate heater controller during depositions, was 800°C. Despite that, the real substrate temperature estimated from previous direct measurements was 600 ± 50°C. This reduction is caused by losses in the interface that supports the substrate and by the fact that the chamber walls remain at room temperature and by the low thermal conductivity of the substrates.

All substrates, approximately 0.5x10x15 mm in size, were properly cleaned by ultrasonic baths with deionized water and neutral detergent Merck Extran MA 02 for 10 minutes, followed by acetone for 10 more minutes, isopropyl alcohol for also 10 minutes, and finally dried via hot air jets.

The structural properties of films were analyzed by X-ray diffractometry Rigaku D-Max – 2100/PC was used. The θ-2θ configuration in the 20-70º range with a step size of 0.01º and Cu (Kα = 1.54056 Å) radiation was used.

To verify the surface morphology of deposited samples, a Leica DCM 3D confocal microscope with integrated LED was used. Images were acquired by always observing the center of the samples, to better standardize results.

The thicknesses of the films were obtained from spectral ellipsometry measurements, using a Horiba UVISEL2 Ellipsometer, in the 0.6 to 6.0 eV range. The incident angles were 75º (Si) and 55º (LAO and SiO_2).

The transmittance and absorbance spectra were measured in a Perkin Elmer, model Lambda 1050 UV/Vis/Nir a spectrophotometer, using a data interval of 1.00 nm and scan speed at 141 nm/min. The measurements were performed in the 750 nm - 450 nm wavelength range, which covers the main absorption peak of methylene blue dye. These measurements allow evaluating solution concentration and the dye degradation rate during photocatalysis.

The photocatalysis system was designed and built by the authors to perform the photocatalytic tests of deposited films. The photocatalytic chamber has two germicide mercury lamps OSRAM 11 W, the main wavelength is 254 nm which irradiates 4.7 mW/cm^2 at the reactor position. Four small reactors, having 4 mL internal volume each, stay 8 cm of distance from the UV illumination source. The samples lay 5 mm below the surface reactor, submerged in the solution. Magnetic stirrers are inserted below of the samples, at the bottom of the reactor, and are used to maintain the solution agitated during experiments. A thermocirculator was made to refrigerate the external walls of reactors and maintain solution temperature during measurements at 18 ± 1°C.

In all photocatalytic tests, an aqueous solution of methylene blue dye is used. The dye is an aromatic heterocyclic compound, with the molecular formula $C_{16}H_{18}ClN_3S$ (319.85 g/mol)[26]. To quantify dye concentration in solutions and to be able to relate concentration values with the resulting solution absorbance, a calibration procedure was performed[27]. An aqueous solution of methylene blue was prepared by weighing 0.010 g of the dye and diluting it in 1000 mL of deionized water. After this step, the solution was diluted further to one-fifth of the original concentration to obtain a solution with a concentration of 0.0020 ± 0.0004 g/L, which corresponds to $3.8 \times 10^{18} \pm 0.8$ molecules/L. Starting from this, ten 10 mL test tubes were collected. The first one containing 100% of the original concentration, and the subsequent decreasing 10% in proportions of dye and increasing 10% in proportions of deionized water at each tube, until 10% was reached in the last one. The absorbance was collected for each solution to get the proportion to the concentration values. The pure deionized water was also measured and used as a reference in the calculations.

Before starting each test, 3.8 mL of the methylene blue aqueous solution, the magnetic stirrers, and TiO_2 film samples were inserted into the reactors and kept in the dark for 120 minutes, at 18 ± 1°C the temperature of thermocirculator, to stabilize the adsorption[28]. After stabilization time, 2 ml of the methylene blue solution were collected from each reactor and poured onto 10 mm thick glass cuvettes, which were used to measure the absorbance. These collections were called the "initial rate" and were returned to the respective reactors. After the adsorption step, the light was turned on, the photodegradation reaction started. Then, with the lamps turned off, solution samples were collected at 90 minutes and 180 minutes, and uses in absorbance measurements. After each measurement, the sample was returned to reactor and the lamp turned on again.

Initially, 12 photocatalytic tests were performed in illumination cycles whose duration was fixed at 180 minutes. In the 13th and 14th cycles, besides the regular initial 180 min measurements, tests lasting a total of 1800 minutes were also performed. The 15th cycle was done with a standard duration of 180 minutes. To complete the sequence of measurements, the 16th cycle was performed only for TiO_2 deposited on silica (TiO_2/SiO_2), using the same procedure, but now with total duration was 540 minutes, completing 108 hours of irradiation exposure.

TiO_2 grown on silica substrate had a surface area of 1.70 cm^2, while in silicon the value was 2.07 cm^2 and in lanthanum aluminate, the area was 1.48 cm^2. To standardization of the results obtained from the degradation of the dye by photocatalysis, the degradation rates were divided by the respective values of the areas to show the stability of the material concerning the 16 cycles of 180 minutes.

3. Results and Discussions

The thickness of the TiO_2 film onto Si was measured by spectral ellipsometry. This sample was used because it presented better spectra. The measured thickness was 150 nm. Due to the fact that the samples were grown simultaneously in the same deposition process, we can infer that all samples have similar thicknesses.

The surface root mean square roughness of the TiO_2/SiO_2, TiO_2/Si and TiO_2/LAO samples were 0.21 μm, 0.22 μm, and 0.26 μm. It is observed that there are no important variations in the roughness among the samples.

XRD measurements on the films presented small counts. The few small peaks observed correspond to the rutile phase only. Analyzing these results, it is important to consider the widely reported fact that the TiO_2 samples prepared by sputtering have strong texture effects, thus the orientation of crystallites may not be favorable to detection by XRD in certain measurement geometries[29,30]. Besides, the thicknesses of the films are small (150 nm) difficulting experiments in other geometries. These facts leave the results inconclusive concerning the presence of other phases, and, more importantly, about the surface distribution of these phases on the films.

Concerning the photocatalytic activity of the samples, the absorbance measurements of the methylene blue solution for different irradiation times are presented in Figure 1a. The measurements were performed at pre-defined times; 0, 90, 180 minutes in all the regular tests. The measurements correspond to the 13th cycle, the tests lasted 1800 minutes. In order to check the significance of the results, the measurements of the control solution for the same conditions as the photocatalytic sample were shown in Figure 1b.

The results of the 13th test are plotted in Figure 1, for the sample deposited onto silica glass. By comparison of Figures 1a and 1b, it is clear that the rate of degradation in the first 180 min is much higher in the reactor containing TiO_2/SiO_2 sample than in the reactor containing the control solution. Nevertheless, for the 1800 min measurements, variations of 0.418 and 0.396 are observed in the TiO_2/SiO_2 and control solution respectively. These results show that, for long periods of exposure, the photodegradation effect of the methylene blue dye is substantial, and approaches the total degradation observed in the sample reactor. In this way, the photodegradative effect of the methylene blue dye when exposed for long periods can be linked to water photolysis. The energy required for the occurrence of water splitting is approximately 2.76 eV. As the lamp has a main peak at 254 nm, such an effect is possible because there is enough energy for it to occur. During photolysis, water molecules that are irradiated by UV lamps undergo the breaking process, for example, in hydroxyl radicals that are highly oxidative and can react with methylene blue molecules, degrading them[31-33].

The concentrations of molecules in the reactor for the 13th cycle for different irradiation times are displayed in Table 1 and Figure 2a. These results are based on the calibration curve obtained for the methylene blue solutions and procedure described in the Methods section.

It was also possible to calculate, the percentage of degradation related to absorbance over time, using Formula 1 below.

$$Degradation(\%) = \frac{A_i - A_t}{A_i} x100 \qquad (1)$$

A_i = Initial absorbance
A_t = Absorbance at t time

The results are shown in Table 2.

It is possible to note that the degradation of the methylene blue solution is faster in the TiO_2 samples than in the control solution (Table 2), however, because the methylene blue solution also presents photodegradative characteristics probably mediated by photolysis[31-33], after

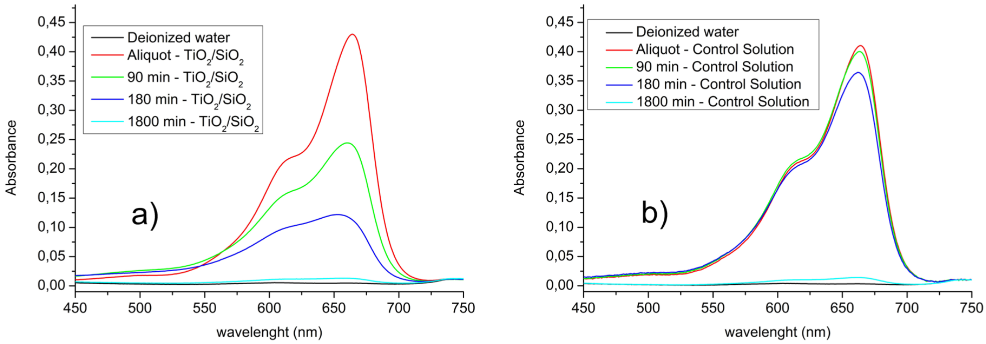

Figure 1. Absorbances as a function of the wavelength of methylene blue solutions taken at 0, 90, 180, and 1800 minutes, corresponding to the 13th cycle of the irradiation stability tests. (a) Corresponding to the solution in the reactor containing the TiO_2/SiO_2 film. (b) Corresponding to the control solution in the reactor without photocatalyst.

Table 1. Comparison of the concentration in molecules/L on methylene blue solution for the reactor without photocatalyst and for reactors containing TiO_2/SiO_2, TiO_2/Si, and TiO_2/LAO as photocatalysts in the 13th cycle of the material stability test. The results correspond to UV irradiation of a mercury lamp, delivering 4.7 mW/cm^2 at the reactor position.

Samples	Concentration (molecules/L)			
	Initial	90 min	180 min	1800 min
Control Solution	4.76×10^{18}	4.63×10^{18}	4.23×10^{18}	1.63×10^{17}
TiO_2/SiO_2	4.97×10^{18}	2.83×10^{18}	1.40×10^{18}	1.16×10^{17}
TiO_2/Si	5.01×10^{18}	3.31×10^{18}	1.92×10^{18}	1.63×10^{17}
TiO_2/LAO	5.37×10^{18}	4.12×10^{18}	2.89×10^{18}	1.05×10^{17}

Table 2. Comparison of the degradation rate of the methylene blue solution in % and %/cm^2 for the reactor without photocatalyst (control solution) and for reactors containing TiO_2/SiO_2 (1.70cm^2), TiO_2/Si (2.07 cm^2), and TiO_2/LAO (1.48 cm^2) as photocatalysts in the 13th cycle of the material stability test. The results correspond to UV irradiation of a mercury lamp, delivering 4.7 mW/cm^2 at the reactor position. The area of the cross-section of the reactor is 3.80 cm^2 and was used to calculate the degradation in %/cm^2 of the control solution.

Samples	Degradation (%)				Degradation (%/cm^2)	
	Initial	90 minutes	180 minutes	1800 minutes	90 minutes	180 minutes
Control Solution	0	2.7	11.2	96.6	0.7	2.9
TiO_2/SiO_2	0	42.9	71.7	97.2	25.2	42.2
TiO_2/Si	0	34.0	61.8	96.8	16.4	29.9
TiO_2/LAO	0	23.3	46.2	98.1	15.7	31.2

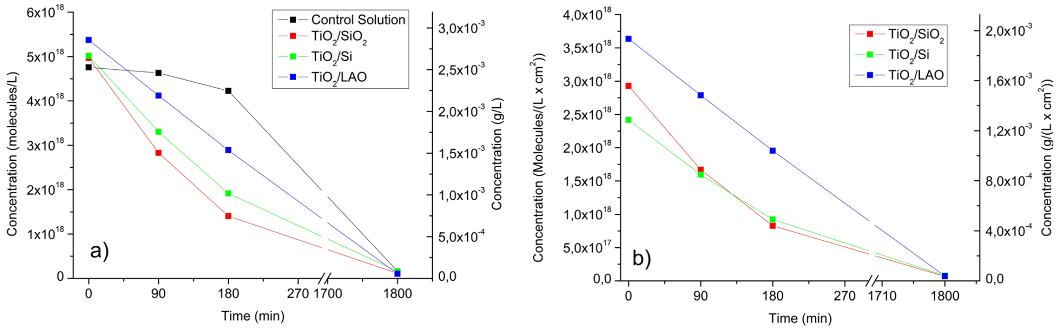

Figure 2. (a) Concentration in molecules/L and g/L up to 1800 minutes in the 13th cycle of the photocatalytic test comparing three different substrates and the result of photodegradation of methylene blue without a photocatalyst in the same interval of time. (b) Concentration in molecules/(L x cm^2) and g/(L x cm^2) up to 1800 minutes in the 13th cycle of the photocatalytic test comparing three different substrates. The areas of the films were 1.70 cm^2 in the silica substrate, while in silicon the value was 2.07 cm^2 and in lanthanum aluminate, the area was 1.48 cm^2. The results correspond to UV irradiation of a mercury lamp, delivering 4.7 mW/cm^2 at the reactor position.

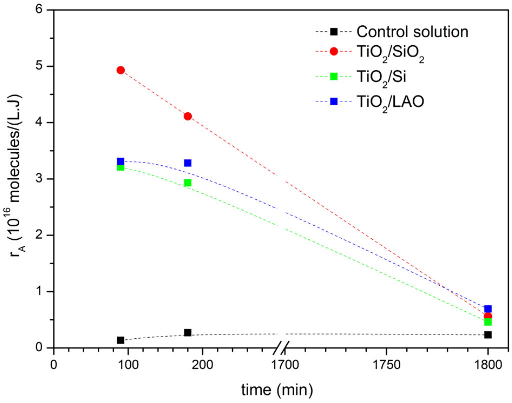

Figure 3. Rate of the reactor in 10^{16} molecules/(L.J) up to 1800 minutes in the 13th cycle of the photocatalytic test comparing three different substrates. The dot lines are just a guide to the eyes.

a long time of exposure to irradiation, they tend to present similar final results, as shown in Figure 2a. Figure 2b displays the degradation and concentration of methylene blue of the three samples deposited on different substrates, standardized to the percentage of degradation at 1 cm^2 of the sample area.

The reaction rate for all samples and control solution is presented in Figure 3. The determination of the reaction rates was made by Formula 2.

$$r_a = \frac{C_0 - C(t)}{t.A.P} \tag{2}$$

Where C_0 is the initial concentration of the solution (molecules/L), C(t) is the concentration in time t, t is the irradiation time t (s), A (cm^2) is the geometric surface area of the samples or the reactor in the case of control solution, and P is the irradiated power (W/cm^2).

It is possible to observe that, although the photodegradation of methylene blue occurs through water photolysis (control solution), in the presence of films the rate of reaction is higher for all samples, been the TiO_2/SiO_2, the sample with a higher rate reaction.

To check whether the degradation of methylene blue is directly affected by the substrates, the test shown in Figure 4 was performed. Only substrates were used in these tests and the result was compared to the control solution, obtained previously and shown in Table 2. It was possible to notice that, despite the differences, the behavior of the degradation of the bare substrates qualitatively follows the control solution. Thus, a direct influence of the substrate surface in the photocatalytic process is not expected in the photocatalytic experiments with the samples.

The results of the last test (16th cycle), which had a duration of 540 min are shown in Figure 5. The samples were collected every 90 minutes, up to 540 minutes. These results were used to calculate the chemical kinetics[34] from order 0 to order 4 and the results are presented in Table 3.

Table 3. Coefficient of determination in zero, first, second, and third-order observing the 16th cycle of the stability test, in the control solution and the TiO_2/SiO_2 reactors, for 360 and 540 minutes.

Order	Control Solution in 360 min (R^2)	TiO_2/SiO_2 in 360 min (R^2)	Control Solution in 540 min (R^2)	TiO_2/SiO_2 in 540 min (R^2)
Zero	0.960	0.780	0.899	0.680
1st	0.972	0.871	0.993	0.936
2nd	0.999	0.997	0.996	0.980
3th	0.988	0.993	0.996	0.994
4th	0.963	0.957	0.982	0.985

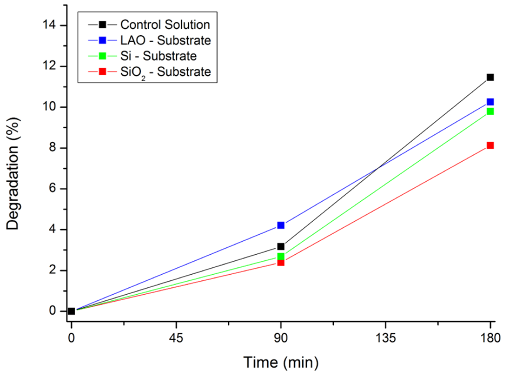

Figure 4. Degradation of methylene blue by the bare substrates only. The reactors containing LAO, Si, and SiO_2 substrates were irradiated by UV lamps for 0, 90, and 180 minutes test for control solution, The square dots represent the results of the measurements. The thin solid lines are just a guide to the eyes.

The results indicate that the 2nd and 3rd order reactions are the ones that best fit the experimental data. Figures 5a and 5b show the graphs related to second and third-order kinetics, respectively.

In early irradiation times, as shown in Figure 5, a kinetics that is probably linked to the degradation of the dye is observed. In longer times, we notice a change in slope that may be associated with the start of competitive reactions for the degradation of the intermediates. Thus, part of the hydroxyl radicals produced by the photoinduced hydrolysis in the TiO_2 surface may now be used to degrade the by-products[35]. In order to have more knowledge about this degradation, more in-depth tests are needed, considering different initial concentrations in short test times and other characterizations of the products and intermediates of the reactions like High-Performance Liquid Chromatography associated with Mass Spectrometry (HPLC-MS).

Considering the first 360 min of irradiation, Table 4 displays the results of the velocity rate constant at second and third orders kinetics for TiO_2/SiO_2 and control solution.

Clearly, in either in 2nd or 3rd order, the velocity rate constant for TiO_2/SiO_2 is significantly higher than the control solution indicating, even though the photolysis occurs, the presence of the film accelerates the reaction 2.6 and 3.9 times for 2nd or 3rd order, respectively.

As said earlier, the focus of the present work is to analyze the photocatalytic stability of thin TiO_2 films grown by sputtering. In this way, Figure 6 describes the photocatalytic behavior in all 16 cycles of photocatalysis performed for the TiO_2/SiO_2 sample analyzed and totaling 108 hours of activity.

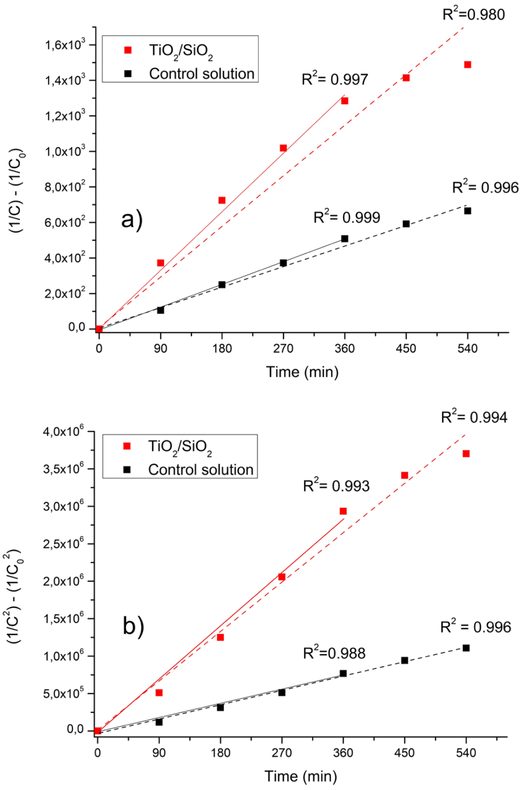

Figure 5. Linearization of 2nd (a) and 3rd (b) order kinetics from the concentration (g/L), obtained from the photocatalysis with the TiO_2/SiO_2 sample and from the photodegradation of methylene blue in a control solution in the 16th test cycle of the material stability. The solid lines correspond to the fits up to 360 min, while the dashed lines correspond to all data points.

Figure 6 shows the degradation (%/cm²) of the solution after 90 minutes, 180 minutes, and 1800 minutes (for tests 13 and 14), concerning each cycle of photocatalysis.

Over the 16 cycles of TiO_2/SiO_2 photocatalysis, the average photodegradation was 37% with a standard deviation of 4% for 180 minutes of reaction. This standard deviation of the mean value is in agreement with experimental error or variation in the experimental activity. No significant loss

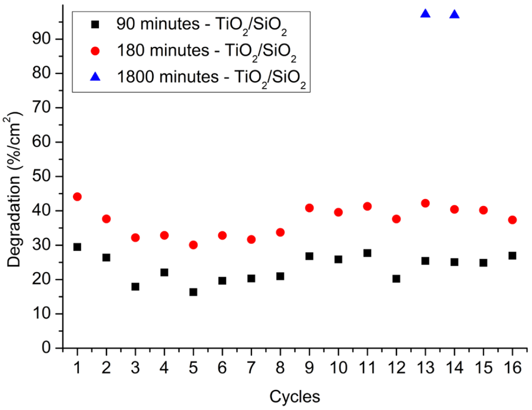

Figure 6. Results of 16 cycles of photocatalysis tests, comparing the degradation rates (%/cm^2) at 90 (black squares), 180 (red circles), and 1800 minutes (blue triangles) of exposure to UV light irradiation, made to evaluate the photocatalytic stability of the TiO_2 film deposited by sputtering on a silica glass substrate.

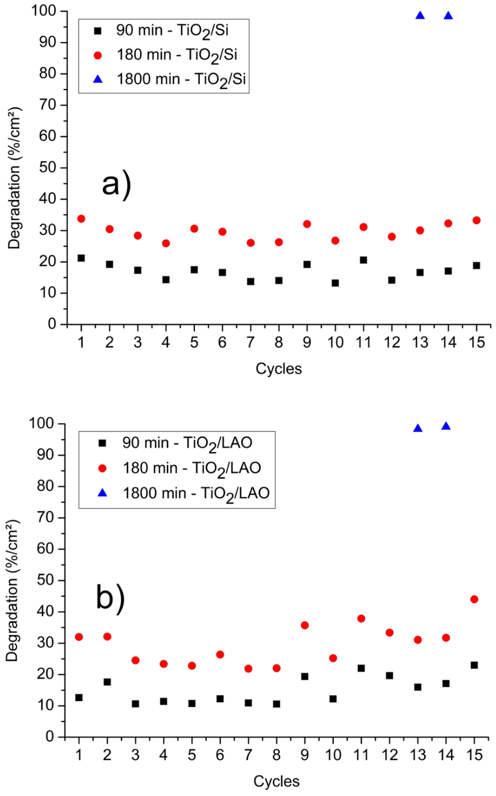

Figure 7. 15 cycles of photocatalysis tests, comparing the degradation rates (%/cm^2) at 90, 180, and 1800 minutes of exposure to UV light irradiation, made to evaluate the photocatalytic stability of the TiO_2 film deposited by Sputtering. (a) TiO_2 film deposited on a silicon substrate. (b) TiO_2 film deposited on a lanthanum aluminate substrate.

Table 4. Velocity rate constant (k), for TiO_2/SiO_2 and control solution for the first 360 minutes of reaction.

	k for 2nd order	k for 3rd order
	(mg^{-1}.L.min^{-1})	(mg^{-2}.L^2.min^{-1})
TiO_2/SiO_2	0.0037	0.0077
Control solution	0.0013	0.0019

in the activity is observed over the 16 cycles, evidencing the stability of the thin film prepared by RF magnetron sputtering.

In the same way that the dye degradation was demonstrated for the TiO_2/SiO_2 sample, there were 15 cycles of photocatalysis also performed for the TiO_2/Si and TiO_2/LAO samples as shown in Figure 7.

From Figure 7a and b it is possible to observe the same variation in the rate of dye degradation for TiO_2/Si and TiO_2/LAO with the mean value and standard deviation of 27% ± 3% and 27% ± 7%, respectively, indicating there is no significant loss in photocatalytic activity.

Although TiO_2/SiO_2 has the smallest surface area, it showed superior photocatalytic activity than the other samples in 14 of the 15 tests that can be compared. In 8 of the 15 tests, there was a pattern of photocatalytic activity concerning the substrates used in the tests, with TiO_2/SiO_2 having a higher photocatalytic response, followed by TiO_2/Si and TiO_2/LAO. Following this line of reasoning, even though TiO_2/LAO has a larger surface area, there is a tendency to present poorer photocatalytic results than those observed in the other two samples.

The results obtained were performed in a bench-scale reactor of 4 mL and evidenced the potential of utilization of a thin film prepared by reactive sputtering as an efficient and stable photocatalyst to promote water splitting and organic molecule degradation. However, regarding potential applications using larger reactors, the scaling up may involve import technological problems[35], so the application of the present benchtop results to large-scale processes is not straightforward. One of the bigger challenges is probably the reactor design to ensure homogenization and diffusion of light in the reactor[35]. On the other hand, the reactive sputtering deposition processes are suitable for large area deposition[36,37], so enhancing the size of the photocatalyst surface shall not be a limitation for the scaling-up process when using this technique[36,37].

4. Conclusions

The TiO_2 films produced by reactive sputtering displayed photocatalytic activity when deposited on different substrates. Concerning the reaction kinetics, the results indicated are more compatible with the reaction being of second or third order but further characterizations of the intermediate reactions are needed to generate more in-depth conclusions about this point.

Stability tests, performed on TiO_2/SiO_2 samples during 16 cycles of UV degradation reactions (total of 108 h of exposure), as well as after the 15 cycles performed for the TiO_2/Si and TiO_2/LAO samples (total 99 h of exposure), showed no evidence of degradation activity of the samples, on the contrary, samples maintained their photocatalytic properties over time and proved to be chemically stable under these conditions

Considering the kind of substrate on which the TiO_2 films are deposited, a certain pattern in the efficiency of the photocatalytic activity is observed. In most results presented in the different cycles, the photocatalytic activity is shown to be higher in the TiO_2 film on SiO_2 substrate, followed by the activity of the film on the Si substrate and finally on the films deposited onto LAO substrate, which showed weaker photocatalytic activity. Also, the samples deposited on different substrates with (slightly) higher roughness display weaker photocatalytic activity, indicating that the structure of the films formed on different substrates plays an important role in the efficiency of the photocatalytic activity.

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