Efficiency Evaluation of Different TiO₂ Coatings on the Photocatalytic Inactivation of Airborne Bacterial Spores

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ABSTRACT: The performance of different TiO₂ coatings is compared for the photocatalytic inactivation of dry Bacillus subtilis spores dispersed on TiO₂ films under UV-A radiation. Three different TiO₂ coatings were assayed: Degussa P-25, sol−gel, and composite sol−gel/Degussa P-25. The influence of the increase in the number of TiO₂ layers was also studied. Furthermore, the amount of TiO₂ deposited on the borosilicate glass plates and the fraction of energy effectively absorbed by the catalytic films were determined. Spectral diffuse transmittance and reflectance measurements were performed using a spectroradiometer with an integrating-sphere attachment. The net-radiation method was then applied to evaluate the fraction of energy absorbed by the coatings. To objectively compare the performance of the catalytic films, two types of efficiencies were calculated: the photonic efficiency and the quantum efficiency of inactivation. The highest quantum efficiency was obtained with the TiO₂ Degussa P-25 coating with two layers.

1. INTRODUCTION

Indoor air pollution represents a major risk to human health. Indoor air pollutants include chemical compounds, particulate matter, and biological contaminants present in the form of bioaerosols. The latter consist of bacterial cells and cellular fragments, bacterial and fungal spores, and byproducts of microbial metabolism, which can be present as particulates, liquids, or volatile organic compounds.7

Under unfavorable conditions, vegetative cells of bacilli are able to undergo a differentiation process called sporulation. This process is a survival mechanism in the face of nutrient deprivation. Bacterial spores have no metabolism and can withstand a wide range of environmental assaults, including heat, desiccation, UV light, and the action of deleterious chemicals.7 Also, dormant spores can be found in virtually every type of environment on Earth.³ Despite such extreme dormancy, spores maintain an alert sensory mechanism that enables them to respond to specific nutrients. This leads to germination and outgrowth to form a new vegetative cell.⁴

Heterogeneous photocatalysis, an advanced oxidation technology that uses UV-A radiation (300–400 nm) coupled with a TiO₂ catalyst, is a potential alternative to mitigate the problem of biological contamination in the indoor environment. When TiO₂ is photoexcited by UV-A light, it is well-known that the formation of electron−hole pairs occurs with the generation of oxidative radical species and that these radical species can cause fatal damage against microorganisms in contact with the catalytic surface. The process does not involve any expensive oxidizing chemicals and can be performed under ambient conditions of temperature and pressure.

The pioneering work in the field of gas-phase photocatalytic disinfection was done by Goswami et al.,⁵ who reported the total inactivation of Serratia marcescens in a photocatalytic reactor with recirculation using Degussa P-25 TiO₂. Afterward, several studies on the application of photocatalysis to inactivate bacteria⁶−¹⁰ and spore-forming bacteria¹¹−¹⁷ over TiO₂-coated surfaces were published.

Despite the numerous scientific articles devoted to the mechanisms and modeling of photocatalysis for disinfection purposes, recently compiled in several review papers,¹⁸−²° only a few studies have focused on evaluating the performance of catalytic systems by means of efficiency parameters.²¹−²³ The accurate evaluation of the inactivation activity of different supports is essential for selecting the best photocatalyst and improving the design of disinfection systems. Efficiency parameters relate the inactivation rate of microorganisms to the energy reaching the photocatalyst (photonic efficiency) or absorbed by the photocatalyst (quantum efficiency), thus allowing a comparison of results obtained under different experimental conditions. Using a different approach, Faure et al.²⁴ studied the inactivation of E. coli by different TiO₂ supports and calculated the proportion of photons effectively absorbed by the photocatalyst by means of a Monte Carlo simulation. Then, they plotted the bacterial concentration as a function of the quantity of photons absorbed and compared different supports for an equivalent UV-A dose.

In a previous work, the inactivation of B. subtilis spores over TiO₂ thin films obtained with a sol−gel technique was studied and modeled, but the time required to inactivate the microorganisms was relatively long.²⁵ In the present study, to improve the photocatalytic inactivation efficiency, three different coatings were assayed: Degussa P-25 TiO₂, sol−gel TiO₂, and sol−gel/Degussa P-25 TiO₂. The amount of TiO₂ coatings...
deposited on the borosilicate glass plates and the fraction of energy effectively absorbed by the catalytic films were also determined. Measurements of the spectral diffuse transmittance and reflectance of bare and TiO₂-coated borosilicate glass plates were obtained with a spectroradiometer equipped with an integrating-sphere reflectance attachment. Afterward, the net-radiation method was used to compute the fraction of energy absorbed by the TiO₂ films as a function of wavelength. Finally, to objectively compare the performance of the three different coatings, the photonic efficiency and the quantum efficiency of inactivation were calculated and compared.

2. MATERIALS AND METHODS

2.1. Experimental Setup. The photocatalytic experiments were carried out in an experimental setup consisting of a UV-radiation emitting system, an irradiation compartment, and a support to hold the coated glass plates with the spore samples during irradiation (Figure 1). A borosilicate glass separated the UV emitting system from the irradiation compartment. The UV-radiation emitting system consisted of a set of seven tubular black-light fluorescent lamps (YLX 8W/BLB) held by a metallic rectangular box above the irradiation compartment in a horizontal parallel arrangement. The emission of the lamps was between 300 and 400 nm, with a maximum at about 350
Conversion from energy content (mW cm\(^{-2}\)) inactivation of Bacillus subtilis (Kit) was employed to measure these variables. Relative spectral emission of the lamps (---) and diffuse transmittance (----) and reflectance (- - -) of the borosilicate glass.

Figure 2. Relative spectral emission of the lamps (---) and diffuse transmittance (----) and reflectance (- - -) of the borosilicate glass.

More details about the experimental setup can be found elsewhere.\(^{25}\)

Inside the irradiation compartment, local measurements of the radiation flux incident at different positions on a plane were made using a radiometer (ILT 1700, International Light Technologies). Only the most illuminated surface, placed at the central zone of the irradiation compartment, was employed for the experiments. The average incident net radiation flux obtained was 1.89 mW cm\(^{-2}\), which is equivalent to 2.01 \(\times\) \(10^{-5}\) Einstein cm\(^{-2}\) h\(^{-1}\) (or 1.21 \(\times\) \(10^{19}\) photon cm\(^{-2}\) h\(^{-1}\)). Conversion from energy content (mW cm\(^{-2}\)) to photon content (Einstein cm\(^{-2}\) h\(^{-1}\)) was made with Planck’s equation, considering the total emission spectrum of the lamps (shown in Figure 2). It should be noted that the measurement of the incident radiation flux was performed by placing the radiometer below the borosilicate glass that separated the lamps from the irradiation compartment; therefore, the value obtained takes into account the absorption of the aforementioned borosilicate glass.

Photocatalytic plates with spore samples were held horizontally in the central zone of the irradiation compartment, where the radiation flux was almost uniform. A saturated solution of ammonium sulfate was included in the irradiation compartment; therefore, the value obtained takes into account the absorption of the aforementioned borosilicate glass.

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The supergel formation was achieved by the dip-coating technique, with a withdrawal speed of 3 cm min\(^{-1}\) at room temperature (25 °C). However, after being applied, the three photocatalysts were treated differently. For the coatings with Degussa P-25 TiO\(_2\), the plates were dried in an oven at 110 °C for 24 h and then heated at 500 °C for 2 h at a heating rate of 5 °C min\(^{-1}\). For the sol–gel TiO\(_2\) coating, the plates were dried in an oven at 80 °C for 1 h and then heated at 200 °C for 6 h. Finally, for the sol–gel/Degussa P-25 TiO\(_2\) coating, the plates were dried at room temperature (25 °C) for 1 h and then heated at 500 °C for 2 h at a heating rate of 11 °C min\(^{-1}\).

When it was necessary to apply two or three layers of photocatalyst to the glass plates, after the drying and heating steps, the next coating layer was applied by repeating the procedure used to deposit the first layer. In particular, it was not possible to apply a third layer with the sol–gel/Degussa P-25 TiO\(_2\) technique because of the poor adhesive properties of the obtained film.

2.4. Characterization of Photocatalytic Plates. 2.4.1. Calculation of Absorbed Radiation. The superficial rate of photon absorption by the catalytic films, \(q_{irr}\), averaged over the irradiated area \(A_{irr}\), can be expressed as\(^{33}\)

\[
\langle q_{irr} \rangle_{A_{irr}} = \langle q_{Lin} \rangle_{A_{irr}} - \langle q_{trf} \rangle_{A_{irr}} - \langle q_{ref} \rangle_{A_{irr}} = \langle q_{Lin} \rangle_{A_{irr}} \alpha_I
\]  

(1)

where \(q_{Lin}\) is the local radiative flux that reaches the coated plate, \(q_{trf}\) is the local radiative flux transmitted through the cataytic plate, \(q_{ref}\) is the local radiative flux reflected by the TiO\(_2\) surface, and \(\alpha_I\) is the fraction of energy absorbed by the TiO\(_2\) film. From eq \(1\), \(\alpha_I\) can be calculated as

\[
\alpha_I = \frac{\langle q_{Lin} \rangle_{A_{irr}} - \langle q_{trf} \rangle_{A_{irr}} - \langle q_{ref} \rangle_{A_{irr}}}{\langle q_{Lin} \rangle_{A_{irr}}}
\]  

(2)
To compute $\alpha$, the net-radiation method was employed.\textsuperscript{29} This method considers energy absorption, reflection, and transmission produced by multiple parallel layers. The final mathematical expressions used to calculate the fractions of incident energy transmitted ($T$), reflected ($R$), and absorbed ($\alpha$) are given by

$$T_{fg} = \frac{T_f T_g}{1 - R_f R_g}$$

$$R_{fg} = R_f + \frac{R_f T_g^2}{1 - R_f R_g}$$

$$\alpha_f = 1 - T_f - R_f$$

where $f$, $g$, and $fg$ represent film, glass, and film + glass, respectively. The values of $T_{fg}$ and $R_{fg}$ were obtained by spectrophotometric measurements of diffuse transmittance and reflectance, respectively, of the coated plates. It should be noted that these quantities depend on the wavelength of the incident radiation.

2.4.2. Transmittance and Reflectance Measurements.

Diffuse reflectance and transmittance measurements of the coated plates were made on an Optronic OL series 750 spectroradiometer equipped with an OL 740-70 integrating-sphere reflectance attachment. The device consists of a source attachment (deuterium and tungsten lamps), a monochromator, and an integrating sphere. The integrating sphere is composed of a system of mirrors that routes the beam of light to the necessary position. Also, it has two openings in the wall for reflecting samples, namely, the sample port and the comparison port, and a filter holder compartment for transmittance measurements. The detector is situated in the central part of the integrating sphere (Figure 3).

The methodology employed to record reflectance and transmittance spectra is similar to that described in Satuf et al.\textsuperscript{30} for obtaining the optical properties of TiO$_2$ suspensions. However, in the present work, this methodology was modified to measure uncoated and TiO$_2$-coated borosilicate glass plates. Readings were made in the UV region, with wavelengths ranging from 300 to 400 nm. The integrating-sphere configurations for measurements are schematically shown in Figure 3a–d. For diffuse transmittance measurements, two pressed poly(tetrafluoroethylene) (PTFE) reflectance standards were placed in the comparison and sample ports of the sphere. A transmittance reading of 100% was obtained against

![Integrating-sphere configurations](image-url)
air (Figure 3a). To measure the transmittance of the sample, the glass coated with the photocatalyst was placed in the filter holder compartment (Figure 3b). For diffuse reflectance measurements, a PTFE reflectance standard was used as the reference in the comparison port. A reflectance reading of 100% was obtained by placing another PTFE standard in the sample port (Figure 3c). To measure the reflectance of the sample, the glass with the TiO₂ was placed in the sample port with its back covered by a light trap that absorbed all transmitted radiation, with the PTFE standard still in the comparison port (Figure 3d).

2.4.3. Determination of the Amount of Photocatalyst Immobilized over Glass Plates. The amount of TiO₂ deposited on the borosilicate glass plates was measured by a spectrophotometric procedure adapted from Jackson et al. involving the digestion of the photocatalyst followed by a colorimetric detection. The solution used to dissolved the TiO₂ (solution A) was prepared by mixing 10 g of (NH₄)₂SO₄ into 25 mL of concentrated H₂SO₄. Each coated glass was placed in a receptacle containing 4 mL of solution A. The mixture of TiO₂-coated glass in solution A was boiled until the TiO₂ was completely dissolved (about 1 h) and cooled, then 6 mL of ultrapure water were added. All of the liquid was quantitatively transferred to a 25-mL volumetric flask. The flask was filled to exactly 25 mL with a 5/95 volume percent solution of concentrated H₂SO₄/H₂O. Three drops of H₂O₂ were added to 10 mL of the solution and then stirred. Finally, the absorbance of the colored solution was measured at 410 nm (Perkin-Elmer Lambda 35 UV/vis spectrophotometer). A calibration curve was constructed by adding different weighed amounts of Degussa P-25 TiO₂ to solution A and then following the same procedure as described for the plates.

2.5. Spore Formation and Collection. The model microorganism used in this work was Bacillus subtilis (ATCC 6633 strain). Following the technique proposed by Shehata and Collins, suspensions of spores in distilled water were prepared. To do this, a Roux bottle containing a sporulation medium, consisting of nutritive agar (Merck Chemicals) with 0.05% MnSO₄ and 0.05% MgSO₄ was inoculated and incubated at 30 °C for a 7–10-day period. Then, the spores and vegetative cells obtained were recovered by washing the surface of the sporulation medium with sterile buffer phosphate (pH 6.8). After this step, the spores recovered were centrifuged three times for 15 min each at 3500 rpm with the same buffer. The suspension was kept at 30 °C for 48–72 h to induce vegetative cell lysis. Then, the vegetative cells and the spores were washed again according to the instructions outlined above. This procedure was repeated three times to wash the cells. The spores were finally suspended in sterile distilled water and conserved at 4 °C.

2.6. Irradiation of Spore Samples and Measurement of Spore Viability. To ensure the absence of vegetative cells before carrying out the irradiation experiments, the spore suspension was held for 10 min at 80 °C. Next, 10 μL of this suspension was uniformly spread over the surface of each coated glass plate (2.25 cm²) and dried at 50 °C for 30 min. Afterward, these plates were placed in the irradiation compartment and exposed to UV-A radiation for different time periods (2, 4, 6, or 8 h). The remaining viable spores were counted according to the technique detailed elsewhere. The tests were repeated twice for each experimental condition studied, and the counting of the viable spores of each repetition was made in duplicate.

The decay of viable spores as a function of the irradiation time was fitted with the exponential equation

\[ N = N_0 e^{-kt} \]  

where \( N \) (CFU cm⁻²) is the bacterial concentration, \( N_0 \) (CFU cm⁻²) is the initial bacterial concentration, \( k \) (h⁻¹) is the kinetic constant, and \( t \) (h) is the time.

2.7. Photocatalytic Efficiency Calculation. Two types of photocatalytic inactivation efficiencies were evaluated: the photonic efficiency \( \eta_{app} \), also known as the apparent quantum efficiency, and the quantum efficiency of inactivation \( \eta_{abs} \).

\[ \eta_{app} = \frac{-(dN/dt)|_{t=0}}{(q_{abs})_\lambda} \]  

where \( (q_{abs})_\lambda \) is the area-average radiative flux that reaches the coated plate. The value of \( (q_{abs})_\lambda \) experimentally obtained using a radiometer (section 2.1), was \( 1.21 \times 10^{19} \) photon cm⁻² h⁻¹.

On the other hand, \( \eta_{abs} \) can be defined as the ratio of the initial photocatalytic inactivation rate to the rate of the absorbed radiation energy within the useful wavelength range

\[ \eta_{abs} = \frac{-(dN/dt)|_{t=0}}{(q_{abs})_\lambda \sum \alpha_{\lambda} \phi_{\lambda}} \]  

where \( \phi_{\lambda} \) is a normalized distribution function of the wavelengths that reach the coated plates. \( \phi_{\lambda} \) takes into account the spectral emission of the lamps and the slight modification of the lamp spectrum produced by the absorption of the borosilicate glass that separates the lamps from the irradiation compartment, mainly at wavelengths lower than 340 nm (Figure 2).

3. RESULTS

3.1. Characterization of the Photocatalytic Plates. 3.1.1. Spectrophotometric Determination of the Photocatalyst Quantity over the Plates. The quantity of TiO₂ deposited on the borosilicate glass plates, measured by the spectrophotometric determination adapted from Jackson et al., is reported in Table 1, where each determination was done in triplicate. As expected, a gradual increase in the TiO₂ content (mg cm⁻²) with the number of coating layers was observed.

<table>
<thead>
<tr>
<th>Table 1. Amount of TiO₂ (mg cm⁻²) Deposited on the Glass Plates</th>
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<tbody>
<tr>
<td>coating</td>
</tr>
<tr>
<td>Degussa P-25 TiO₂</td>
</tr>
<tr>
<td>sol–gel TiO₂</td>
</tr>
<tr>
<td>sol–gel/Degussa TiO₂</td>
</tr>
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</table>

3.1.2. Optical Characterization. Figure 4 presents the diffuse transmittance and reflectance spectra of the borosilicate glass coated with Degussa P-25 TiO₂, sol–gel TiO₂, and sol–gel/Degussa TiO₂, for the corresponding number of layers assayed. For each coating technique, different optical behaviors were observed, in direct relation to the amount of TiO₂ deposited on each sample. The Degussa and Degussa/sol–gel
coatings presented significantly greater absorptions than the sol–gel samples, especially at wavelengths lower than 375 nm. Nevertheless, a gradual increase in the absorption of radiation with the number of layers was noticed for the three types of coatings. These experimental results, along with other characteristics of the films, are analyzed in section 4.

Using eqs 3 and 4 and the experimental values of transmittance and reflectance presented in Figures 2 and 4, we evaluated \( T_f \) and \( R_f \) and then calculate \( \alpha_f \) (eq 5) between 300 and 400 nm. Table 2 shows an example of the results obtained at the most important wavelength (350 nm). The absorbed fraction (\( \alpha_f \)) was relatively high for the coatings made with Degussa P-25 TiO\(_2\) and sol–gel/Degussa TiO\(_2\), whereas for the sol–gel TiO\(_2\) coating, this fraction was considerably lower.

To complete the characterization of the plates, SEM images of coating surfaces were obtained. Figure 5 shows the images corresponding to the three coatings assayed with two layers. The coating obtained with the sol–gel method (Figure 5a) presents the most uniform surface. The Degussa P-25 image (Figure 5b) reveals a more irregular surface, where dark regions of uncoated glass are observed. The roughest surface was obtained with the composite technique (Figure 5c,d), with considerable irregularities throughout the plate. This unevenness is better observed in Figure 5d, at lower magnification. It should be noted that the adherence of the composite coating to the glass was also poor.

Additionally, the film thickness for the coating with the highest quantum efficiency of all tested samples, the Degussa P-25 coating with two layers, was estimated from SEM images of the cross section of the TiO\(_2\) plates (images not shown). The approximate value measured was 14 \( \mu \)m.

### 3.2. Spore Inactivation Results

Figure 6 shows the experimental results and the curve fittings using eq 6 obtained in the photocatalytic inactivation of Bacillus subtilis spores over the plates coated with Degussa, sol–gel, and sol–gel/Degussa TiO\(_2\). Error bars represent the 99% confidence intervals. It is worth noting that no detectable changes in the survival of

![Figure 4](image-url)

**Figure 4.** Experimental transmittance (\( T_f \)) and reflectance (\( R_f \)) values.

![Figure 5](image-url)

**Figure 5.** SEM images of the TiO\(_2\) coating surfaces with two layers: (a) sol–gel, (b) Degussa P-25, (c,d) sol–gel/Degussa. The white bar represents (a–c) 1 and (d) 10 \( \mu \)m.

### Table 2. Calculated Values of \( T_f \), \( R_f \), and \( \alpha_f \) for a Wavelength of 350 nm

<table>
<thead>
<tr>
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<tbody>
<tr>
<td></td>
<td>one layer</td>
<td>two layers</td>
<td>three layers</td>
</tr>
<tr>
<td>( T_f )</td>
<td>0.002</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>( R_f )</td>
<td>0.091</td>
<td>0.093</td>
<td>0.094</td>
</tr>
<tr>
<td>( \alpha_f )</td>
<td>0.907</td>
<td>0.907</td>
<td>0.906</td>
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</tbody>
</table>
spores were observed when the samples were kept in the dark or in the absence of photocatalyst.

It can be noticed that, when B. subtilis spores were irradiated over TiO₂ surfaces, their viability decreased significantly, and the extent of inactivation increased with the irradiation time. Values of the parameters in eq 6, namely, N₀ and k, for each coating and each number of layers are reported in Table 3.

3.3. Evaluation of Photocatalytic Efficiencies. To compute the photonic and quantum efficiencies, the initial photocatalytic inactivation rates are needed (numerators of eqs 7 and 8). These values were calculated from the slope of the inactivation curves (Figure 6) and are listed in Table 4. Also, the values of the energy absorbed by the coated plates (denominator of eq 8) are presented in the table. The denominator of eq 7 (incident radiation flux) was always 1.21 × 10¹⁹ photon cm⁻² h⁻¹.

The final results for both photocatalytic efficiencies are summarized in Table 5 for each photocatalyst studied and for the different layers tested. It should be noted that ηₐₑ more closely represents the efficiency of the photocatalytic inactivation of the bacterial spores because it considers not only the radiation reaching the plate but the rate of energy effectively absorbed by the catalytic film.

4. DISCUSSION

For the Degussa coating, a high percentage of the incident radiation was absorbed by the three samples tested, as evidenced by the values of α in Table 2 and (εₑ)ₐₑ in Table 4. Moreover, an appreciable increment in the amount of immobilized TiO₂ was found as the number of layers increased. It is noted that the highest inactivation rate was obtained with two layers. Because the amount of absorbed energy was similar for the three samples, the quantum efficiency was also higher for the plate with two layers of TiO₂. In fact, the highest quantum efficiency of all tested samples was obtained with the Degussa coating with two layers: ηₑₑ = 2.27 × 10⁻¹⁴ (Table 5). Between one and two layers, an appreciable increment in the amount of immobilized TiO₂ was found (Table 1). Therefore, it was expected that a greater inactivation of spores would be obtained because of the increase in the amount of photocatalyst available to interact with the microorganisms. With three layers, although the amount of photocatalyst was higher than that with two layers, the inactivation rate was lower and similar to that found with one layer. A possible explanation can be found in the surface roughness of the obtained film with three layers. Bacterial spores could lie in the irregularities of the coating where radiation could not impinge. In high TiO₂ concentrations, as is the case for three layers, the reactions represented by eqs 9 and 10 could contribute to the diminution of bacterial inactivation. In eq 9, OH dimerizes to form H₂O₂, which, in turn, produces HO₂⁻ (eq 10). The hydroperoxyl radical is less reactive than the hydroxyl radical and does not contribute significantly to the oxidative process.

\[ \text{HO} + \text{HO} \rightarrow \text{H}_2\text{O}_2 \]  

(9)

Table 3. Estimated Parameters of Eq 6

<table>
<thead>
<tr>
<th>coating</th>
<th>N₀ (CFU cm⁻²)</th>
<th>k (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>one layer</td>
<td>two layers</td>
</tr>
<tr>
<td>Degussa P-25 TiO₂</td>
<td>2.13 × 10⁶</td>
<td>3.20 × 10⁶</td>
</tr>
<tr>
<td>sol–gel TiO₂</td>
<td>2.87 × 10⁶</td>
<td>2.31 × 10⁶</td>
</tr>
<tr>
<td>sol–gel/Degussa TiO₂</td>
<td>1.06 × 10⁶</td>
<td>1.85 × 10⁶</td>
</tr>
</tbody>
</table>
increase in the TiO₂ content with the number of layers was also obtained. The maximum absorption of all coatings, and a clear decrease in the inactivation rate was performed by the same procedure as used in the present work. The maximum activity was found with two layers of coating, and a clear decrease in the inactivation rate was obtained when the reactors were coated with three layers of Degussa coating with three layers. A decrease in the inactivation rate, and photonic efficiency values higher than those obtained in this work, on the order of 10⁻¹¹ CFU photon⁻¹. In this case, the model microorganism was a vegetative bacterium, which is much less complex than a bacterial spore.

5. CONCLUSIONS

The highest efficiency of all tested samples was obtained with the Degussa P-25 TiO₂ coating with two layers. This result can be attributed to the characteristics of the film, which (i) contained a high amount of TiO₂, rendering high absorption of the incident radiation, and (ii) presented a regular surface, which enhanced the contact between the spores and the photocatalytic particles.

The calculation of efficiency parameters represents a valuable tool for comparing different catalytic systems. The photonic efficiency η₆₆₅ and the quantum efficiency of inactivation η₆₈₃ can be used to evaluate the performance of coatings. Nevertheless, η₆₈₃ provides more useful information because it shows how efficiently the absorbed radiation is employed to inactivate microorganisms, providing an indirect insight into the photocatalytic mechanism. Also, it can guide the design of better coatings, as the results can provide evidence for deficient contact between bacteria and photocatalyst or poor absorption of radiation.

Table 5. Photocatalytic Inactivation Efficiencies (CFU photon⁻¹)

- H₂O₂ + *OH → H₂O + HO₂*

Also, an increase in the recombination rate of electrons and holes produced by the excess of catalytic particles could contribute to the decrease of the inactivation rate. Our results are in accordance with those obtained by van Grieken et al. in wall and fixed-bed reactors employed for the inactivation of E. coli aqueous suspensions. Immobilization of TiO₂ was performed by the same procedure as used in the present work, the maximum activity was found with two layers of coating, and a clear decrease in the inactivation rate was obtained when the reactors were coated with three layers of photocatalyst.

For the coatings obtained by the sol–gel technique, a gradual increase in the TiO₂ content with the number of layers was found, resulting in increases in the absorption of radiation, inactivation rate, and photonic efficiency. However, regarding η₆₈₃, the sample with two layers was the most efficient; in this case, it can be noted from Table 4 that the increase of the energy absorbed by the coating with three layers (denominator of eq 8) was higher than the slight increase of the initial inactivation rate (numerator of eq 8). It is worth highlighting that the amount of photocatalyst and the percentage of radiation absorbed were significantly lower than those obtained with the Degussa coating, although the values of the quantum efficiency of inactivation were similar.

Finally, a significant increment in the amount of immobilized TiO₂ was found with the sol–gel/Degussa coating between one and two layers. Increases in the radiation absorption, inactivation rate, and efficiency parameters with the number of layers were also obtained. The maximum absorption of all tested samples was achieved with two layers of the composite catalyst (92%). Regarding the transmittance and reflectance spectra, we can affirm that the remaining 8% of radiation was lost by reflection (the transmittance of this sample was almost null). Although the coatings obtained with the sol–gel/Degussa technique contained high amounts of TiO₂ and absorbed high percentages of the incident radiation, the inactivation rates were similar to those obtained with the sol–gel samples, and the values of η₆₈₃ were the lowest among the three coating techniques. This behavior can be ascribed to the undesired increase in the recombination of electron/hole pairs and hydroxyl radicals, as discussed previously in the case of the Degussa coating with three layers. A deficiency in the contact of the spores with the surface of the composite coatings can also explain the relatively low inactivation rate values. This possibility is supported by the SEM images, which revealed significant irregularities in the composite coating surface (Figure 5c,d).

The efficiency values obtained in this work can be compared with those recently reported by Briggler Marcó et al. They studied the photocatalytic inactivation efficiency of 10 bacteriophages dispersed on TiO₂-coated plates exposed to UV-A radiation for different periods of time and found the highest inactivation efficiency for the bacteriophage J-1 (2.273 × 10⁻¹² PFU photon⁻¹). This efficiency value is 2 orders of magnitude higher than that found in our work for Degussa P-25 TiO₂ coating with two layers (Table 5). This variation might be due to the structural differences between the J-1 bacteriophage and the B. subtilis spore. In general, virus structures are much simpler than those corresponding to bacterial spores.

Also, Marugán et al. studied the photocatalytic disinfection of E. coli in aqueous suspensions. They also found photonic efficiency values higher than those obtained in this work, on the order of 10⁻¹¹ CFU photon⁻¹. In this case, the model microorganism was a vegetative bacterium, which is much less complex than a bacterial spore.

Table 4. Initial Inactivation Rates and Energy Absorbed by Each Coating

<table>
<thead>
<tr>
<th>coating</th>
<th>one layer</th>
<th>two layers</th>
<th>three layers</th>
<th>one layer</th>
<th>two layers</th>
<th>three layers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degussa P-25 TiO₂</td>
<td>1.40 × 10⁵</td>
<td>2.45 × 10⁵</td>
<td>1.42 × 10⁵</td>
<td>1.07 × 10⁴</td>
<td>1.08 × 10⁴</td>
<td>1.08 × 10⁴</td>
</tr>
<tr>
<td>sol–gel TiO₂</td>
<td>3.99 × 10⁴</td>
<td>4.67 × 10⁴</td>
<td>4.91 × 10⁴</td>
<td>3.36 × 10⁴</td>
<td>3.39 × 10⁴</td>
<td>4.01 × 10⁴</td>
</tr>
<tr>
<td>sol–gel/Degussa TiO₂</td>
<td>2.34 × 10⁴</td>
<td>6.94 × 10⁴</td>
<td>–</td>
<td>1.00 × 10⁴</td>
<td>1.11 × 10⁴</td>
<td>–</td>
</tr>
</tbody>
</table>

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**NOMENCLATURE**

\( A_{ir} \) = irradiated area (cm\(^2\))

\( q^\alpha \) = superficial rate of photon absorption by the TiO\(_2\) catalytic films (photon cm\(^{-2}\) h\(^{-1}\))

\( k \) = kinetic constant (h\(^{-1}\))

\( N \) = viable spore concentration (CFU cm\(^{-2}\))

\( N_0 \) = initial viable spore concentration (CFU cm\(^{-2}\))

\( q_{\alpha,i} \) = local radiative flux that reaches the TiO\(_2\) catalytic films (photons cm\(^{-2}\) h\(^{-1}\))

\( q_{\alpha,f} \) = local radiative flux reflected by the TiO\(_2\) catalytic films (photons cm\(^{-2}\) h\(^{-1}\))

\( q_{\alpha,l} \) = local radiative flux transmitted through the TiO\(_2\) catalytic films (photons cm\(^{-2}\) h\(^{-1}\))

\( R \) = reflectance

\( t \) = time (h)

\( T \) = transmittance

**Acronyms**

ATCC = American Type Culture Collection

CFU = colony forming units

PTFE = poly(tetrafluoroethylene)

**Greek Letters**

\( \alpha \) = fraction of energy absorbed by the TiO\(_2\) films

\( \eta \) = photocatalytic inactivation efficiency (CFU photon\(^{-1}\))

\( f \) = distribution function of the wavelengths that reach the TiO\(_2\) catalytic films

\( g \) = relative to a property of the TiO\(_2\) film + glass

\( \lambda \) = relative to specific wavelength

**Subscripts**

abs = denotes the quantum efficiency of inactivation

app = denotes the photonic efficiency (or apparent quantum efficiency)

f = relative to a property of the TiO\(_2\) film

fg = relative to a property of the TiO\(_2\) film + glass

\( \langle \rangle \) = average

**REFERENCES**


