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Synthesis variables effect on TiO_2/polyester fabrics photoactivity and stability

Efecto de las variables de síntesis de telas de TiO_2/poliéster sobre su fotoactividad y estabilidad

Efeito da síntese variables de tecidos TiO_2/poliéster sobre seu fotoatividade e estabilidade

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Abstract

TiO_2-SiO_2 coatings on fabric samples were obtained by immersion of 9cm^2 of commercial polyester in a TiO_2-SiO_2 suspension. This suspension was prepared by adding TiO_2 P25 to a silica matrix obtained from the hydrolysis of tetraethyl orthosilicate (TEOS). The aim of this work was to study the relationship between the immersion time of the fabric on the photocatalytic activity and stability of the coating against several cycles of use and washing. Obtained samples were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and infrared spectroscopy (FTIR-ATR). Evaluation of modified fabrics was performed by self-disinfection tests under 250W/m^2 of simulated sunlight using *E. coli* as model bacteria. In general, all modified fabrics (except that obtained at 2h immersion time) inactivated bacteria in less than 120min and its regrowth was prevented for at least 24h after the disinfection tests. It was determined that low immersion time (3-4h) lead to active and stable fabrics to 3 cycles of use and washing, whereas higher immersion times (12h) lead to more active but unstable fabrics.

***Keywords:** coated fabric, TiO_2-SiO_2, photocatalysis, E. coli inactivation.*

Resumen

Muestras de tela recubiertas con TiO_2-SiO_2 fueron obtenidas por inmersión de un poliéster comercial de 9cm^2 en una suspensión de TiO_2-SiO_2. Esta suspensión se preparó adicionando TiO_2 P25 a una matriz de sílice sintetizada mediante la hidrólisis de ortosilicato de tetraetilo (TEOS). El objetivo de este trabajo fue estudiar la relación entre el tiempo de inmersión de la tela, y la actividad fotocatalítica y estabilidad del recubrimiento a varios ciclos de uso y lavado. Las muestras obtenidas fueron caracterizadas por microscopía electrónica de barrido (SEM), espectroscopía de energía dispersiva (EDS) y espectroscopía infrarroja (FTIR-ATR). La evaluación de los textiles se llevó a cabo mediante pruebas de autodesinfección bajo 250W/m^2 de luz solar simulada usando *E. coli* como microorganismo modelo. En general, todas las telas modificadas (excepto las obtenidas con 2h de inmersión) inactivaron la bacteria en menos de 120min, previniendo su recrecimiento bacteriano al menos por 24h después de las pruebas de desinfección. Se determinó que los tiempos de inmersión bajos (3-4h) dejan telas activas y estables a 3 ciclos de uso y lavado, mientras que tiempos de inmersión más altos (12h) dejan telas más activas pero inestables.

***Palabras clave:** tela recubierta, TiO_2-SiO_2, fotocatálisis, inactivación de E.coli.*

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Resumo

Amostras de tecido revestidas com TiO_2-SiO_2 foram obtidos por imersão de um poliéster comercial de $9cm^2$ em uma suspensão de TiO_2-SiO_2. Esta suspensão foi preparada por adição de TiO_2 P25 a uma matriz de sílica sintetizado por hidrólise de ortossilicato de tetraetilo (TEOS). O objetivo deste trabalho foi estudar a relação entre o tempo de imersão do tecido, e a atividade fotocatalítica e a estabilidade do revestimento a vários ciclos de utilização e de lavagem. As amostras obtidas foram caracterizadas por microscopia eletrônica de varredura (MEV), espectroscopia por dispersão de energia (EDS) e espectroscopia no infravermelho (FTIR-ATR). A avaliação dos tecidos foi realizada por meio de testes de autodesinfección sob a luz solar simulada a utilização de E. coli como um modelo microrganismo. Em geral, todos os tecidos modificados (exceto aqueles obtidos com 2h de imersão) inativar bactérias dentro de 120min de irradiação, impedindo o seu novo crescimento bacteriano de pelo menos 24h após o teste de desinfecção. Encontrado que com tempos de imersão de baixo (3-4h) são obtidos tecidos ativos e estáveis a 3 ciclos de utilização e de lavagem, enquanto que os tempos de imersão mais elevado (12h) são obtidos tecidos mais ativos mais instáveis.

Palabras-chave: *tecido revestido, TiO_2-SiO_2, fotocatálise, inativação de E. coli.*

Introduction

A self-disinfecting fabric has the ability to inactivate pathogenic microorganisms such as *E. coli* because on its surface a photocatalyst such as TiO_2 is fixed and ready to be activated in the presence of UV light, thus leading to the production of oxidative species that attack the cell wall, and cause lysis and death of the microorganism [1-6].

The development of these fabrics, as a strategy to combat the spread of nosocomial infections [7-11], is still in the primary state due to difficulties to immobilize TiO_2 on the fabric surface, so as to keep it active and stable for several cycles of use and washing [12-14]. Different alternatives have been explored in order to overcome this issue. The use of bonding agents such as silica is one of the most attractive ideas due of its usability and low cost [15-19]. In this case, the linker has two functions: trap TiO_2 particles and strongly adhere them to the fabric, allowing UV light activation of the semiconductor.

In 2008, Li *et al*. [20] studied the interaction between silica and certain fabrics such as cotton, linen, nylon and polyester, and determined that the adhesion of the coatings of SiO_2 in synthetic fabrics is mainly the result of thermodynamic affinities, dipole-dipole interactions and hydrogen bonds, while the adhesion over fabrics based on cellulose is produced by covalent bonds formed between the precursor groups of the silica and hydroxyl groups of the fabric. In 2010, Mejia *et al.* [21] reported that different fabric samples coated by the immersion of polyester in a suspension of TiO_2-SiO_2 were sufficiently active to degrade gaseous methanol. They also found a relationship between the immersion time of the fabric and its photocatalytic activity.

Despite of the progress made by these authors regarding immobilization of TiO_2, it is still necessary to study the behavior of fabrics coated with TiO_2-SiO_2 on self-disinfection processes and their stability during several cycles of use and washing. For this reason, the focus of this paper is to obtain self-disinfecting fabrics by immersion of polyester samples in TiO_2-SiO_2 suspensions and determine the influence of immersion time on the activity and stability during three cycles of use and washing.

Experimental

Preparation of SiO_2-TiO_2 suspension

According to the procedure described by Mejia *et al.* [21], the TiO_2-SiO_2 suspension was prepared in two steps: first, a sol-gel of SiO_2 was prepared by ageing during 24h of isopropyl alcohol (isop-OH, Merck), hydrochloric acid (HCl, Merck), tetraethyl orthosilicate (TEOS, Merck) and distilled water. Second, TiO_2 P-25 (Evonik-Degussa) with surface area of $50m^2/g$ and gap energy of 3.2eV [5,12] was added to sol-gel of SiO_2 under conditions of constant stirring (100rpm). The following molar ratios were used: isop-OH/TEOS=4.86, HCl/TEOS=0.04, TiO_2/Si=0.014 and distilled water/TEOS=1.97.

Modification of PE samples with TiO_2-SiO_2

It was used one type of commercial polyester fabric (PE, polyester:cotton 65:35). Fabric samples of $9cm^2$ were coated with TiO_2-SiO_2 by a single immersion in the TiO_2-SiO_2 suspension during a variable time between 2 to 12h, to adhere different amounts of TiO_2-SiO_2 in the fabric. During immersion, the suspension is kept stirred at 100rpm to keep homogeneity and prevent precipitation of TiO_2. Afterwards, the sample was removed from the suspension and dried in stove at 30±2°C for 15min. Finally, the TiO_2-SiO_2 coated sample was soaked in distilled water and dried in oven at 100°C. The weakly adhered coating particles were detached from the fabric by washing with water under sonication (model LC-ULTRASONICS ELMA 30H) for 15min at 60Hz. The fixed TiO_2-SiO_2 in the fabric was determined by difference in weight of the fabric before and after the coating process.

Characterization of fabric samples

Samples were analyzed by scanning electron microscopy (SEM) by using a FEI Quanta FEG TM model 650 provided with a BS-SE-detector and an energy dispersive spectrometer (EDS), under high vacuum ($6x10^{-4}$Pa) and vacuum (10-130Pa) conditions, resolution of 6 to 100000x, voltage of 200V to 30kV and peak current continuously adjustable ≤200nA. Infrared spectroscopy (ATR-FTIR) was done using an Attenuated Total Reflectance cell (ATR) equipped with a ZnSe crystal to avoid damage of the polyester. The equipment used to perform spectroscopy was a Bruker Tensor 27 FTIR model supplemented with Bruker ATR Platinum.

Evaluation of photocatalytic activity of TiO_2-SiO_2 coated samples Bacterial suspension. The bacterial strain used as model microorganism was *E. Coli* ATCC 11229 (*E. coli*) provided by Microbiologics® Inc. This microorganism was preserved in cryobanks at -70°C. Two bacterial colonies from cryobank were inoculated into 5mL of nutrient medium Luria Bertani (LB) and incubated for 8h at 35°C with constant aerobic agitation of 100rpm. Then, the incubated culture broth was added to 25mL of fresh LB and remained in growth for 15h at the same temperature and stirring conditions until reaching the stationary growth phase. Subsequently, 1mL of the resulting culture was centrifuged at 3000rpm for 15min, as a result a biomass pellet was obtained to be twice washed with sterile saline solution (0.85g NaCl diluted in 100mL of distilled water). Finally, the washed biomass pellet was suspended in 1mL of sterile water, reaching a concentration of approximately 10^7 colony forming units (CFU)/mL.

Fabrics Self-disinfection tests. Duplicate modified PE samples, were contaminated with 100mL of bacterial suspension with a concentration of 10^7CFU/mL (C_0). Then, samples were irradiated at 250W/m² in a solar simulation chamber (SUNTEST CPS+, with temperature control, radiation between 300-800nm with 7% of photons emitted in the UV-A to B ranges and no photons emitted in UV-C range). Samples were withdrawn from the chamber at different times up to 120min to track their photodisinfection efficiency. Quantification of microorganisms in each sample (C) was conducted by the technique of serial dilutions, sowing on plate count agar (Merck) and plate count by microdroplet [22].

Additionally, the following control tests were performed: first, disinfection test without irradiation, second, disinfection test with the polyester fabric unmodified, third, disinfection test with the polyester fabric coated with SiO_2.

Stability of modified PE samples. The self-disinfection test of each sample was performed 3 times in a row (reuses) in order to determine the stability of the coating. Before each reuse, the coated fabric was washed with distilled water to remove residual organic material from the preceding disinfection.

Moreover, the percentage of detachment TiO_2-SiO_2 from modified PE samples (% Detachment) during the first use was determined. The following formula was used: $\%Detachment = ((W_b - W_a) / W_b) * 100$, where W_b and W_a mean weight before and after first use, respectively.

Effective disinfection time (EDT_{24}). After each self-disinfection test it was determined the EDT_{24} for all the modified PE samples. In this case, the samples that were subjected to disinfection tests are stored in dark for 24h. After this time regrowth microorganisms on the sample is quantified. EDT_{24} determination was used as an indication of any microorganism regrowth after 24h of no light irradiation after the photocatalytic treatment [5,6].

Results and Discussion

Figure 1 shows SEM micrographs of: a) unmodified PE sample and b) to d) modified PE sample with 4h immersion time in different approaches. By comparing the a) and b) micrographs it is observed that the modification of PE sample produces a thick and cracked coating of TiO_2-SiO_2. The c) and d) micrographs shows that TiO_2-SiO_2 coating is also amorphous and porous. It was determined in the SEM-EDS analysis that this coating is composed by a TiO_2/Si mass ratio of 2.26 which is similar to that used in the synthesis of the coating.

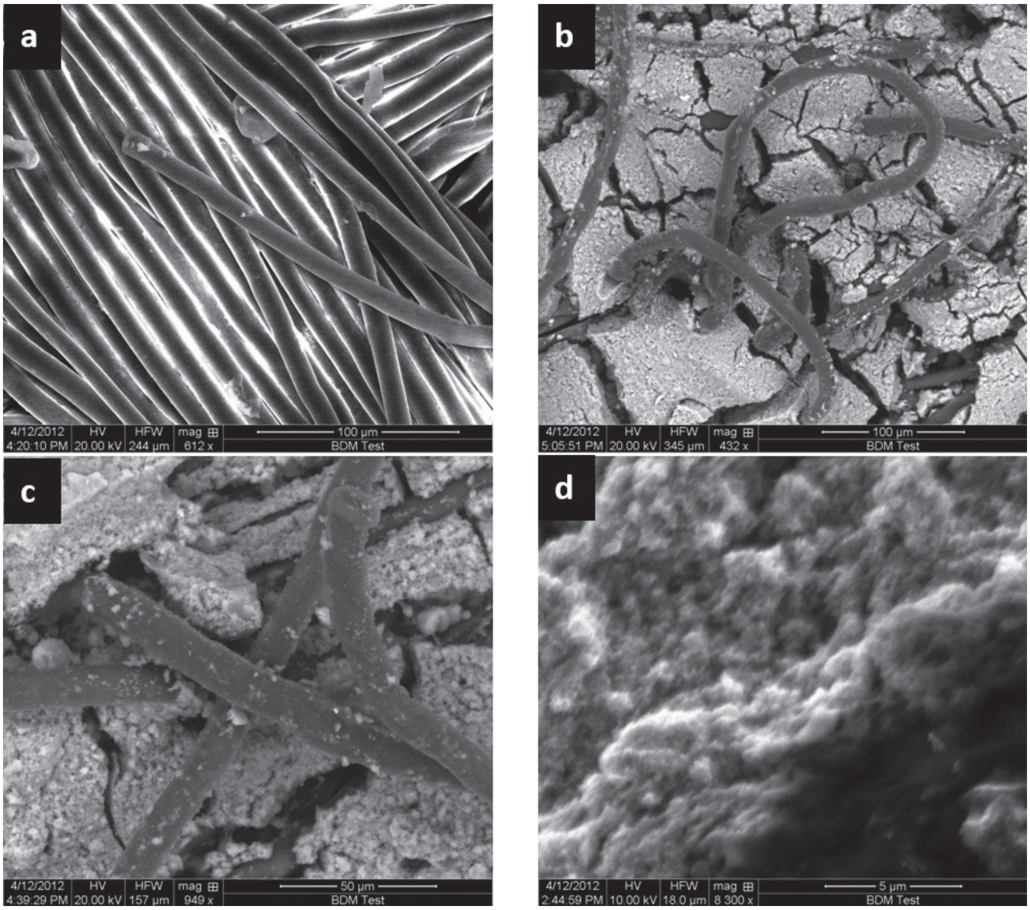

Figure 1. SEM images of the unmodified PE sample (a) and modified PE with 4h immersion at different magnifications (b)-(d).

Figure 2 presents FTIR-ATR spectra of modified PE samples with TiO_2-SiO_2 to different immersion times. All spectra have the same peaks with different intensities. In general the bands shown in IR spectra are attributed to both fabric functional groups and coating species.

First, the bands at 1713cm^{-1}, and 1300-1600cm^{-1} are associated to vibrations of saturated esters due to carbonyl groups ($-C=O$), and $-C-H$ bonds associated to the benzene ring [2], respectively. Second, there are bands at 810 and 1095cm^{-1} ascribed to symmetric vibration of $Si–O–Si$ and to asymmetric stretching of $Si–O–Si$, respectively [23-25]. The band at 1254cm^{-1} is associated with disorder modes of SiO_2 amorphous layers [25]. The band at 720cm^{-1} is attributed to TiO_2 [4,24]. Additional bands are observed in the ranges 3000-3800, 1610-1650, 850-990cm^{-1}. The band located in the first range corresponds to fundamental stretching vibration of the hydroxyl groups.

These hydroxyl groups derived from adsorbed water (3400-3500cm^{-1}), silanols linked to molecular water through hydrogen bonds (3540cm^{-1}), and Si and OH pairs mutually linked by hydrogen bonds and internal silanol (3660cm^{-1}) [26]. The second range is assigned to the deformation of molecular water. There is a contribution near to 1650cm^{-1} which may be due to residual ethanol. The third range is associated with silanol bonds vibration (Si-OH) [25,26]. The Peak in the 2800-2980cm^{-1} region is associated to C-H stretching vibrations of CH_3 and CH_2 attributed to the PE sample structure or contamination [17].

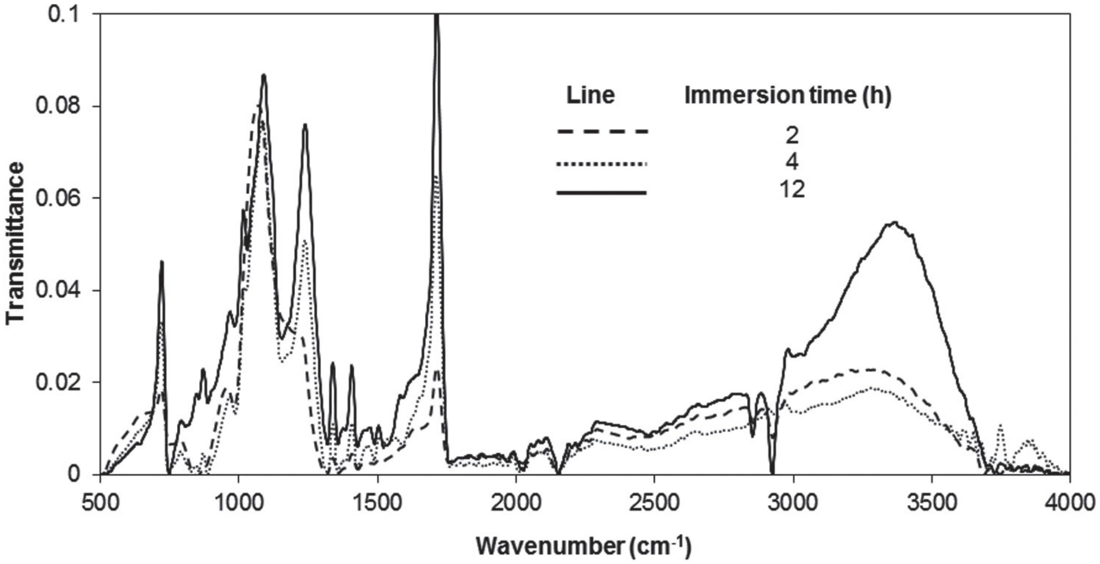

Figure 2.ATR-FTIR spectra for modified PE samples with immersion time of 2, 4 and 12h.

The presence of *Si-O-Si* and *Si-OH* in the samples analyzed by FTIR-ATR confirms that during the preparation of the sol-gel of SiO_2, hydrolysis and polycondensation reactions occurred as shown in Equations 1 to 3 [24,25].

According to Mejia *et al.* [21], these reactions lead to the formation of a three-dimensional network of $\equiv Si–O–Si \equiv$. The principal function of this network is to trap the TiO_2 and keep it stationary on the fabric such as it is observed in SEM analysis.

$$Si(OC_2H_5)_4 + H_2O \rightarrow Si(OC_2H_5)_3OH + C_2H_5OH \quad (1)$$

$$\equiv Si - O - H + H - O - Si \equiv \rightarrow \equiv Si - O - Si \equiv + H_2O \quad (2)$$

$$\equiv Si - O - C_2C_5 + H - O - Si \equiv \rightarrow \equiv Si - O - Si \equiv + C_2H_5OH \quad (3)$$

On the other hand, Figure 2 shows that the intensity of both TiO_2 and *Si-O-Si* symmetric vibration peaks increases with immersion time but the intensity of *Si-O-Si* asymmetric stretching peak is similar for all analyzed samples. These results indicate that the increase of immersion time causes an increment in the disorder modes of the SiO_2 network that it is associated to increase in the TiO_2 peak.

Photocatalytic activity and coating loss of modified PE samples: effect of immersion time

Figure 3 shows the amount of adhered TiO_2-SiO_2 to each PE sample as a function of the immersion time. An increase in the amount of adhered coating on fabric is observed when increasing immersion time. There was a raise in adhesion between 4 and 5.5h in relation to others immersion times. In contrast, the adhesion of the coating tends to stabilize for immersion time nearby to 12h. This stabilization indicates that adhesion limit of TiO_2-SiO_2 in PE samples is nearby to $25 mgcm^{-2}$.

Figure 4 shows the relationship between immersion time and photocatalytic activity of modified PE samples. It is observed that after 3h of immersion time the modified PE samples can inactivate *E. coli* (10^7CFU/mL) and achieve effective disinfection in times less than 120min under $250 W/m^2$ of simulated sunlight irradiation.

Furthermore, the photocatalytic activity increases with the amount of adhered coating and this one increases with time of immersion as previously observed, although this tendency is not notable between samples with 4 and 5.5h immersion time which have a similar photocatalytic activity. In all cases the EDT_{24} was equal to the inactivation time shown in Figure 4 indicating that the inactivation of *E. coli* was complete.

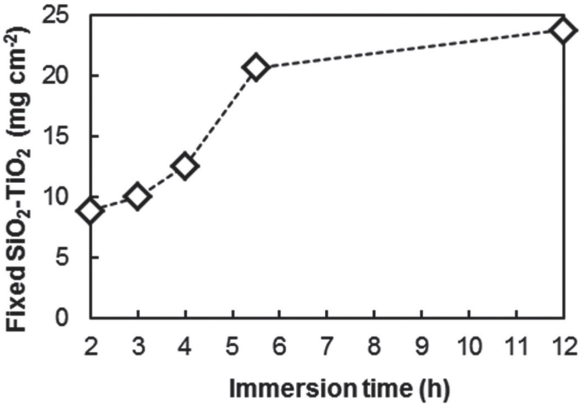

Figure 3. Adhered TiO_2-SiO_2 to modified PE samples with different immersion times.

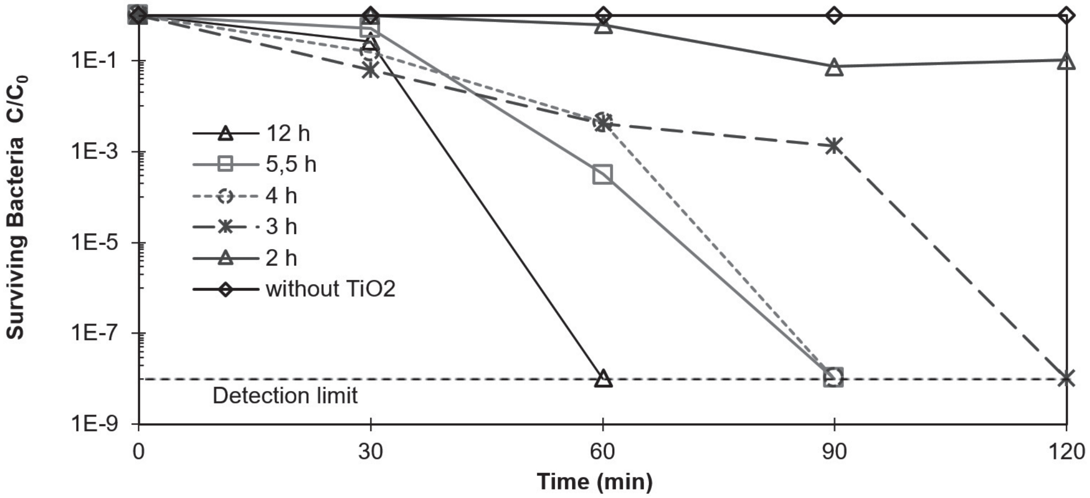

Figure 4. *E. coli* inactivation by effect of photocatalytic activity of the modified PE samples at different immersion times.

Inactivation of *E. coli* and effective disinfection of samples was due to TiO_2 presence in the samples, which was observed by SEM-EDS. Since the nature of TiO_2 P25 was not modified as shown in IR analysis, it is expected that when irradiated with UV light below λ<385nm (UV-A to B range) in the presence of water or air this semiconductor generates oxidizing radical species (OH*, O_2^{*-}) able to degrade the cell wall of microorganisms [5,12,27]. These processes of radicals formation occurs only in the surface of coating because the TiO_2 particles located inside the SiO_2 matrix of TiO_2-SiO_2 coating do not have access to the incident light. In this case the TiO_2 particles are not photoactivated [28]. Therefore, due to different morphologies, as observed in Figure 1, it is expected that semiconductor coverage do not allow the photocatalytic activation of the entire coating on the fabrics.

An unexpected behavior is observed in modified PE samples with 5.5 and 12h immersion time since it was found a low difference in TiO_2-SiO_2 adhesion (Figure 3) but a significant difference in photocatalytic activity compared to other samples. This behavior evidences that the photocatalytic activity of modified PE samples may depend on the TiO_2/SiO_2 ratio in the coating surface. Mejia *et al.* [21] showed that samples with immersion times up to 11h increase in %TiO_2 loading compared with lower immersion times. Here, a different result was observed for samples with 4 and 5.5h immersion time that show a higher difference in TiO_2-SiO_2 adhesion (Figure 4) but a negligible difference in photocatalytic activity as compared to higher immersion times. These samples have different amounts of TiO_2-SiO_2 as shown in Figure 3, but have a similar amount of TiO_2 in the coating surface. This indicates that increasing the immersion time cause a variation in the adhesion of the TiO_2-SiO_2 and a variation in the TiO_2/SiO_2 ratio of the coating surface, as well as it was observed by Selishchev *et al*. [29].

Another determining factor on the sample photoactivity is the adsorbed water on the coating because, as it explain above, the water is necessary for the production of oxidants species (Equation 2) that cause bacterial inactivation. FTIR-ATR analysis showed that the adsorbed water increases with the immersion time. Therefore, the increase of the photoactivity with immersion time can also be associated to the increment in the adsorbed water amount.

Table 1 shows the percentage of detached coating from the modified PE samples during the first use. The samples with 2, 3 and 4h had negligible losses but samples with 5.5 and 12h immersion times have considerable losses. This indicates that increasing the immersion time causes a decrease in the adhesion strength of the aggregates located on the coating surface, possibly because it reaches the adhesion limit of TiO_2-SiO_2 in PE samples, as previously discussed. Such a decrease in the resistance of the coating may be associated with the increased vibrations related with disordered modes of amorphous SiO_2 observed by FTIR-ATR analysis.

Table 1. TiO_2-SiO_2 detachment during the first use of the modified PE samples with different immersion time.

Immersion time (h)	% Detachment
2	0.2
3	0.3
4	0.3
5.5	5
12	10

Photocatalytic stability of modified PE sample

Figure 5 shows the results of first, second and third use of the modified PE samples with 4h immersion time. Control test indicate that both the unmodified PE sample under irradiation and the modified PE sample in obscurity have no photoactivity, therefore, the photocatalytic activity of the modified PE samples with 4h immersion time in the three uses was caused by TiO_2 presence. An important difference is observed between the result of first and second use which could be associated to a low detachment of TiO_2 as shown in Table 1. A different result is observed between second and third use where it is not shown variation on photoactivity indicating that the TiO_2-SiO_2 coating did not suffer significant changes during the evaluation and washing procedures. The similarity in the results presented in Figure 5 indicates that the fabrics are stable at least until the third use.

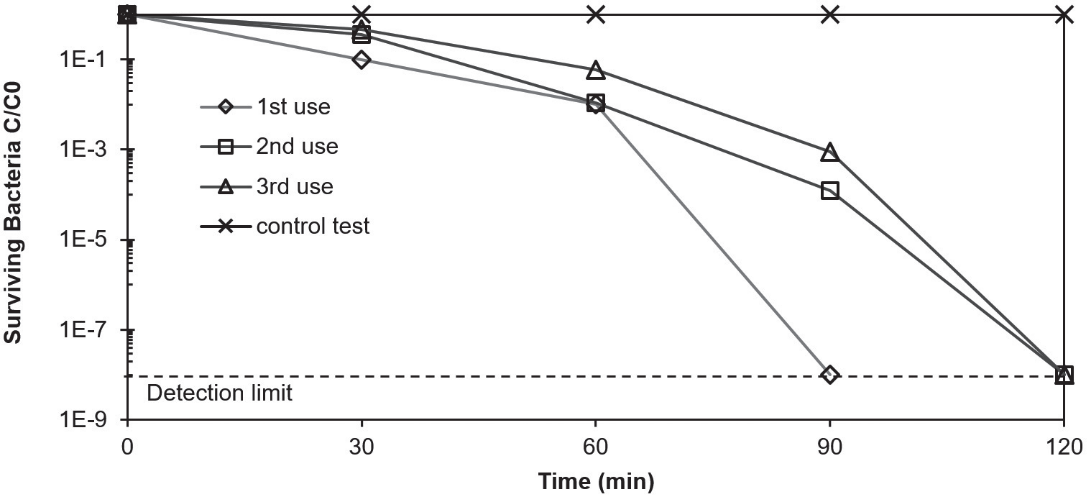

Figure 5. Photocatalytic activity of the modified PE sample with 4h immersion time in first, second and third use.

This stability is related with *–Si–O–Si–* groups from SiO_2 present in the coating as observed in IR analyses, these groups have the function of trapping the TiO_2 and keep it immobile over the fabric surface. Several authors have mentioned that the modified fabric without SiO_2 shows TiO_2 detachment and indeed a total loss of photoactivity caused by reuse of modified sample [19]. Accordingly, the detached coating from modified PE sample between the first and second use could be TiO_2 deposited in the coating surface that wasn't trapped by SiO_2 matrix

Conclusion

The use of a SiO_2 matrix obtained by the hydrolysis of TEOS, as a binder between the commercial polyester and TiO_2 allows the modified fabric to remain active and stable during self-disinfection tests. TiO_2-SiO_2/PE samples inactivate an *E. coli* inoculum (10^7CFU/mL) in times of 120min under constant irradiation of 250W/m^2. The immersion time of the fabric in the TiO_2-SiO_2 suspension is directly related to the self-disinfecting activity of the TiO_2-SiO_2/PE. High immersion times (12h) lead to highly active but unstable samples, whereas smaller immersion times (2-4h) lead to less active but stable fabrics during three cycles of use and washing.

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