PHOTOCATALYTIC INACTIVATION OF BACTERIA IN WATER USING SUSPENDED AND IMMOBILIZED SILVER-TiO$_2$

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ABSTRACT

Incorporation of silver to titanium dioxide is of great interest for photocatalytic disinfection applications since in addition to the enhancement of the electron-hole separation and interfacial charge transfer and the increase in the visible light response, silver compounds present a strong bactericidal effect. Ag/TiO_2 materials used in suspension and immobilized in two different configurations (catalytic wall and fixed-bed reactors) have been prepared, characterized and tested using *Escherichia coli* as model microorganism. Although the incorporation of silver to powdered Degussa P25 TiO_2 increases the activity, the thermal treatment required for the stabilization of the supported metal particles reduces the global efficiency. The comparison with experiments of dye photodegradation indicates that the activity of Ag/TiO_2 is mainly due to the bactericidal role of silver and not to the enhancement of the photocatalytic mechanism. The best tested system has been proved to be the Ag/TiO_2 catalytic wall reactor with a 0.6 wt% of Ag loading, showing a high activity both in relative (per gram of TiO_2) and absolute terms, an optimal use of the radiation source, and a good stability of the film with negligible silver lixiviation, allowing the continuous treatment of water.

KEYWORDS: photocatalysis, disinfection, silver, *E.coli*, immobilized TiO_2

1. Introduction

Oxidation technologies such as chlorination and ozonation have long been used for the disinfection of water. However, several concerns have emerged regarding these treatments, mainly due to the formation of potentially harmful disinfection by-products such as trihalomethanes and haloacetic acids upon reaction with the naturally occurring organic mater and halide ions [1-3].

Advanced oxidation processes (AOP) have been extensively investigated for the treatment of wastewater [4-6]. Among them, TiO_2 photocatalysis has emerged as a promising alternative technology for the disinfection of water with purposes of drinking water supply or reuse of wastewater plants effluents [7-8]. In addition to the high photostability and low cost of the catalyst, the heterogeneous photocatalytic technologies have several advantages over other AOPs such as working under ambient conditions of temperature and pressure, the use of air as oxidant reactant, and the possibility of using solar light to drive the process, all items very interesting from the energy consumption and environmental impact viewpoints.

One of the main drawbacks of TiO_2 photocatalysis is the relatively high band gap energy of the semiconductor (above 3.0 eV for rutile and 3.2 eV for anatase, corresponding to UV-A radiation) what limits the absorption of light to only approximately 3-5% of the solar spectrum [9]. In addition to that, the quantum yield of the process is in the order of 4% [10] what means that only 1 of every 25 electron-hole pairs generated upon radiation absorption are successfully leading to the desired reaction, whereas the remaining recombine releasing heat. For those reasons, important research efforts have been devoted to the improvement of the photocatalytic efficiency by doping or metallization of the catalyst surface [11-12]. Among the metallic species usually incorporated to TiO_2 surface, silver has shown an enhancement of the electron-hole separation and interfacial charge transfer [13-14], increasing the visible light excitation of TiO_2 [15]. In addition to that, the strong bactericidal power of silver compounds makes Ag/TiO_2 materials very attractive to explore the potential in photocatalytic disinfection applications, as confirmed by the enhancement for the photocatalytic inactivation of microorganisms reported by several research groups upon incorporation of silver into the catalysts [16-19]. The mechanism of the silver toxicity is still unclear, being suggested the possible alteration of the membranes properties through the

degradation of lipopolysaccharide molecules and the subsequent increase in the membrane permeability or the damage of the DNA [20].

On the other hand, another important limitation of the photocatalytic technologies using titanium dioxide suspensions is the need of a post-treatment separation stage [21-22]. Consequently, the treatment of water in continuous reactors require the development of immobilised TiO_2 systems to avoid the recovery stage and the losses of catalyst [23], being this aspect particularly important when silver or other expensive metals have been incorporated into the TiO_2 [24]. However, the use of immobilized photocatalysts usually introduces mass transport limitations that reduce the global efficiency of the reaction, a feature that could be particularly significant in disinfection processes due to the high size of microorganisms [25]. Moreover, the adhesion between bacteria and catalyst has been shown to play a crucial role on the efficiency of the process [26-28].

This work is focused on the development of Ag/TiO_2 materials with enhanced photocatalytic efficiency for the disinfection of water. Two different silver-modified titania immobilised systems have been used (catalytic wall and fixed-bed reactors), comparing their activity with that corresponding to powder Ag/TiO_2 in suspension and with bare TiO_2. *Escherichia coli* has been selected as model microorganism, due to its wide use as indicator of faecal contamination.

2. Experimental

2.1. Photoreactor

The photocatalytic experiments have been carried out in the experimental setup schematized in Figure 1. The annular photoreactor (15 cm long, 3 cm inner diameter and 5 cm outer diameter) operates in a closed circuit with a reservoir tank, recirculating at 2.5 L min^{-1} of flow rate, being the total working volume of 1 L. A Philips TL6-W black light with an emission maximum at 365 nm was placed in the axis of the annulus to irradiate the reactor with a stationary UV-A incident photon flow of 2.8×10^{-6} Einstein s^{-1} (calculated by ferrioxalate actinometry). In all cases, the lamp was switched on 15 min before the reaction starts to stabilize its emission power and spectrum.
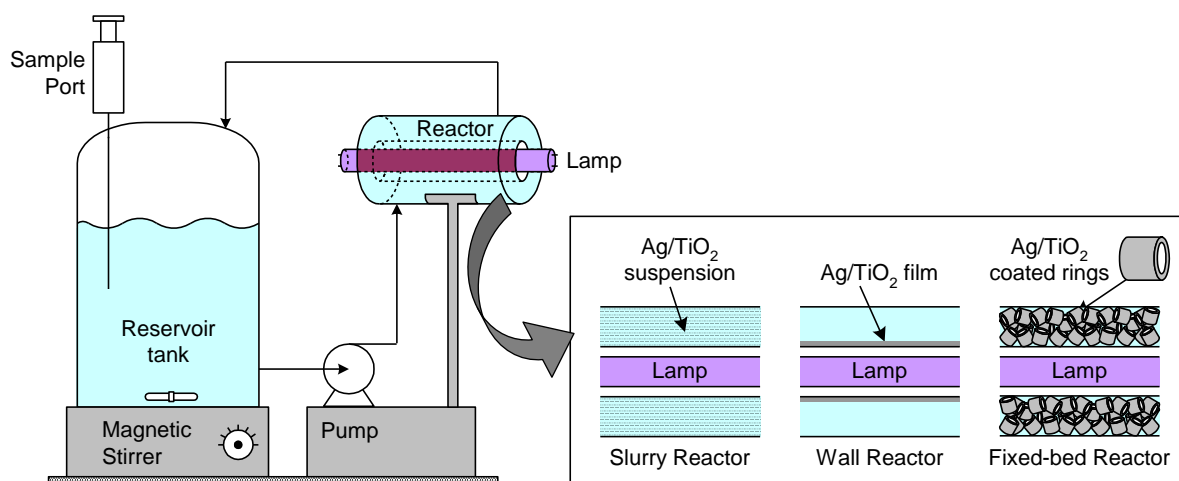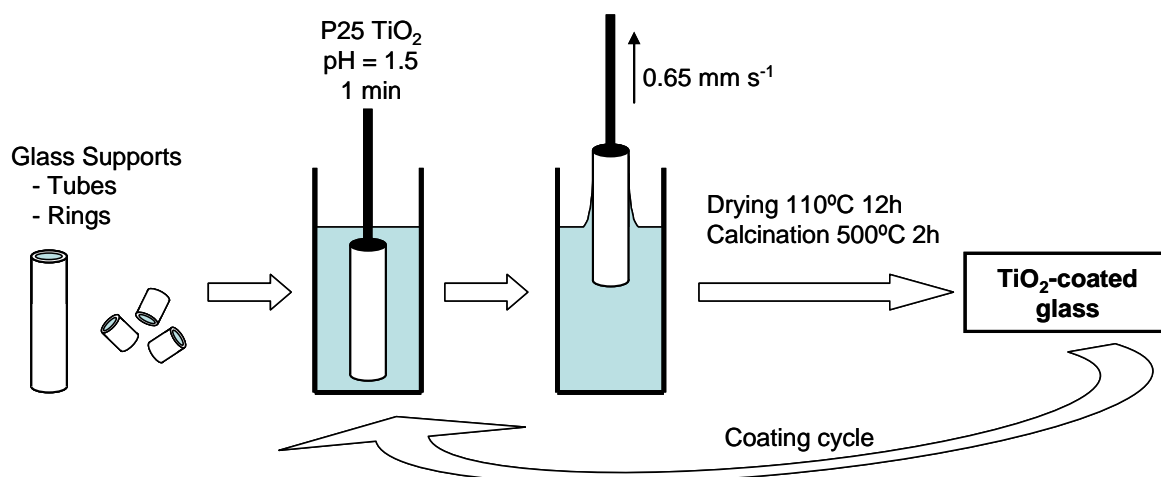
Figure 1. Experimental setup used for the photocalytic reactions (see text for details).

The Ag/TiO$_2$ photocatalysts were tested in three different reactor configurations previously tested using pure TiO$_2$ photocatalysts [23] to investigate the role on the photocatalytic reaction of the silver incorporated into the materials:

i) Slurry reactor, in which the 0.1 g L^{-1} Ag/TiO$_2$ particles are suspended in the whole liquid volume of the recirculation system. This catalysts concentration has been selected as optimum according to previous studies with pure TiO$_2$ suspensions [23].

ii) Wall reactor, in which the Ag/TiO$_2$ photocatalyst is immobilized as a film in the inner-tube wall of the annular photoreactor.

iii) Fixed-bed reactor, in which glass rings coated with the Ag/TiO$_2$ material are placed in the whole annular reactor volume.

2.2. Catalysts preparation and characterization

Degussa P25 titanium dioxide was immobilized onto the glass substrates by a dip-coating procedure schematized in Figure 2. All the materials used in the present work have been prepared following three coating cycles. More details of the method can be found elsewhere [23].

P25 TiO$_2$
pH = 1.5
1 min

0.65 mm s^{-1}

Glass Supports
- Tubes
- Rings

Drying 110ºC 12h
Calcination 500ºC 2h

TiO$_2$-coated
glass

Coating cycle

Figure 2. Schematic representation of the immobilization of TiO$_2$ onto the glass supports.

The incorporation of silver was carried out by photocatalytic reduction of 1 L of silver nitrate (Scharlab) solutions with the desired concentration, adding 1 mL of 2-propanol (Scharlab) as sacrificial organic acting as hole/hydroxyl radical scavenger. The photodeposition reactions were performed in the same experimental setup described above, using the titania in suspension or immobilized as wall or fixed-bed in the photoreactor. Irradiation with the UV-A lamp lasted for 2h, enough to achieve the total reduction of the silver, as confirmed by the evolution of the silver remaining in solution analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) in a Varian Vista AX equipment. Concentration of silver was quantified using the spectral line at 328.068 nm after calibration with certified standards. If not otherwise specified, the Ag/TiO$_2$ materials were dried at 110ºC and calcined at 400ºC for 6h to assure the fixation of silver to the TiO$_2$ surface [16]. Immobilized Ag/TiO$_2$ photocatalysts were directly used in the photocatalytic tests after calcination, whereas powder Ag/TiO$_2$ was finely ground before being suspended.

The amount of silver incorporated to the materials was also evaluated by ICP-AES after treating the materials with nitric acid, being in all cases in agreement with the nominal silver content estimated from the amount of silver nitrate initially dissolved. Micrographs of the silver nanoparticles incorporated to the TiO$_2$ surface were taken on a Nova NanoSEM-230 ultra-high resolution field emission scanning electron microscope (FESEM) equipped with an energy dispersive X-ray spectroscopy (EDS) microanalysis probe with a superultrathin window (SUTW). Both a Everhart-Thornley secondary electron detector

(ETD) and a low-voltage high-contrast solid state detector (vCD) have been used to obtained textural and compositional information, respectively. The specific surface areas of the powder materials were calculated according to the Brunauer-Emmett-Teller (BET) method from the nitrogen adsorption-desorption isotherms at 77 K recorded in a Micromeritics Tristar 3000 equipment. UV-vis transmission spectra of the immobilized systems were acquired in a Varian Cary 500 Scan UV-vis-NIR spectrophotometer.

2.3. Photocatalytic experiments

Lyophilized *Escherichia coli* K-12 strains provided by the Spanish Type Culture Collection (CECT 4624, corresponding to ATCC 23631) were used as model microorganisms for the disinfection experiments. Fresh bacterial cultures of around 10^9 CFU mL^{-1} of stationary concentration were prepared by inoculation of 20 mL of Luria-Bertani nutrient medium (Miller's LB Broth, Scharlab) and aerobic incubation at 37 ºC under rotary shaking for 24h. 5 mL of this culture were centrifuged and rinsed twice with sterile ultra-pure water (Milli-Q®, 18.2 MΩ cm) before diluting 1 mL of the resultant bacterial suspension to 1 L to prepare the reacting suspension, with an initial concentration of viable bacteria around 10^6 CFU mL^{-1}.

Reactions started just after adding the catalyst to the suspension (for powder Ag/TiO$_2$) and switching on the recirculation pump. No equilibration time has been considered for the system, assuming that the decrease in bacterial concentration due to dark adsorption could be neglected in comparison with the bactericidal properties of silver nanoparticles. The evolution of the reaction has been followed quantifying the concentration of viable bacteria by a standard serial dilution method using LB nutrient agar plates (Miller's LB Agar, Scharlab). Eight replicates of each decimal dilution were incubated at 37 ºC for 24 h before counting the number of bacterial colonies. Lixiviation of silver from the Ag/TiO$_2$ to the solution has been quantified by ICP-AES.

Experiments of photocatalytic degradation of methylene blue (Sigma–Aldrich) 20 µM aqueous solutions were carried out in order to discriminate the bactericidal role of silver from the enhancement of the photocatalytic process. Reactions were followed through the decrease in the absorption of the solution at 664 nm.

3. Results and discussion

3.1. Ag/TiO₂ in suspension

Figure 3 shows the results obtained in the photocatalytic inactivation of *E. coli* with 0.1, 0.5 and 1.0 wt% Ag/TiO₂ powders in suspension. The bactericidal efficiency is clearly enhanced for increasing silver loading but in all cases the activity seems to be lower than that observed for the bare TiO₂.
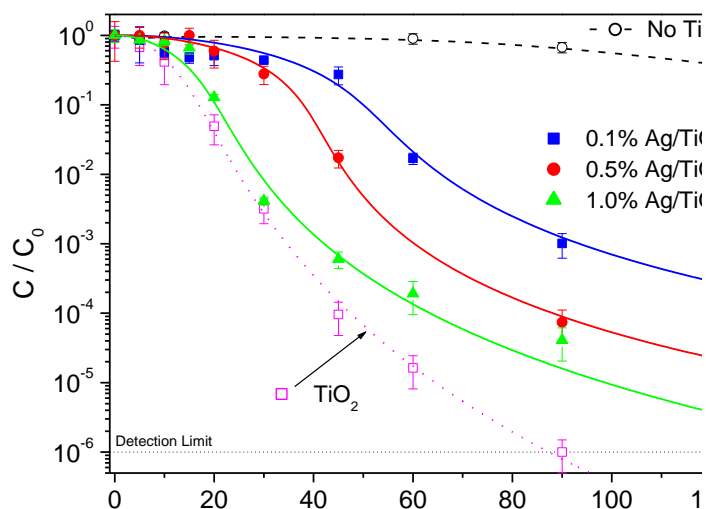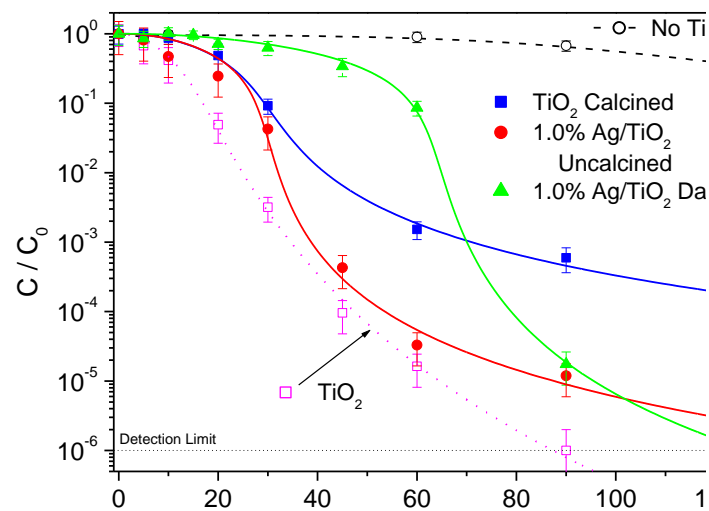

Figure 3. Effect of silver loading on the photocatalytic inactivation of *E. coli* in water using TiO₂ and Ag/TiO₂ in suspension. Fitting lines were calculated using a kinetic model based on a series events disinfection mechanism [25]. Error bars calculated from eight independent bacteria counting measurements.

These results contrast with some of the reports existing in the literature showing an increase in the *E. coli* photocatalytic inactivation efficiency of TiO₂ upon silver incorporation [16-18]. The catalysts used in these papers were: i) commercial anatase TiO₂ (Aldrich) following a thermal treatment to incorporate the silver [16]; ii) Degussa P25 TiO₂ used directly after silver photodeposition without further thermal treatment [17]; and iii) a home-made TiO₂ used in which silver incorporation is produced by either impregnation and thermal

treatment or direct photodeposition [18]. It must be noticed that the combination of base TiO_2 materials and preparation route of the silver-modified photocatalysts is different in each paper and different from that used in the present work. To investigate the influence of the thermal treatment on the activity of the materials, additional experiments of photocatalytic inactivation with calcined TiO_2 (following the same preparation procedure but without silver salt addition) and with uncalcined 1.0% Ag/TiO_2 (following the same preparation procedure but without thermal treatment) were carried out. The results are displayed in Figure 4.

Figure 4. Effect of calcination and dark disinfection on the photocatalytic inactivation of *E. coli* in water using TiO_2 and Ag/TiO_2 in suspension. Fitting lines were calculated using a kinetic model based on a series events disinfection mechanism [25]. Error bars calculated from eight independent bacteria counting measurements.

The activity of the Degussa P25 bare TiO_2 substantially decreases after calcination. Moreover, taking as reference the activity of this calcined TiO_2 material, the incorporation of silver does enhances the photocatalytic efficiency of the material, being more active as the silver content increases from 0.1 % to 1.0 wt%, in agreement with the results in the literature. Consequently, it can be assumed that the decrease in the activity is derived from the thermal treatment and not from the incorporation of silver. A preliminary explanation for this effect could be a decrease in the specific surface area of the catalysts during calcination. Characterization of the samples shows that the BET specific surface area (S_{BET}) of the material decreases from 52 m^2g^{-1} of the commercial P25 TiO_2 to 42 $m^2 g^{-1}$ after calcination.

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In agreement with other reports [18], incorporation of silver does not seem to affect the textural properties of the material, having all the calcined Ag/TiO_2 samples comparable specific surface areas (42.2 ± 1.0 m^2 g^{-1}) whereas uncalcined 1.0% Ag/TiO_2 maintains 51 m^2 g^{-1} of S_{BET}. In any case, this reduction of the textural properties of TiO_2 does not seem to be enough to justify the decrease in the activity of the catalysts upon calcination, being also caused by the dehydroxylation of the titania surface, as proposed by Fernandes Machado and Santana [29].

Results of bacterial inactivation with uncalcined 1.0% Ag/TiO_2 (Figure 4) do not apparently confirm the decrease in the activity produced by the thermal treatment in the case of silver-modified titanium dioxide materials, showing similar activity to the corresponding calcined 1.0% Ag/TiO_2 catalyst, and lower than that of bare P25 TiO_2. This suggests that the incorporation of silver induce a decrease in the activity not only derived of the calcination. Figure 4 also displays the results of bacterial inactivation with calcined Ag/TiO_2 in the dark. Surprisingly, after a longer initial delay the activity is comparable to that observed under irradiation and higher than that shown by the calcined TiO_2 material. The explanation of these unexpected results was found on the high concentration of silver lixiviated to the solution measured by ICP-AES (above 50% of the silver loading at the end of the reaction). Similar silver lixiviation values were measured in the experiment with uncalcined Ag/TiO_2, whereas only 15% of the silver was lixiviated when using the calcined Ag/TiO_2 material. As a consequence, only the calcined Ag/TiO_2 material could be considered as partially reusable. Moreover, such high values of silver in solution suggest that the disinfection profiles could not be linked exclusively to pure photocatalytic process but from the well-known bactericidal properties of silver [20]. Summarizing, despite the decrease in the global activity observed after silver incorporation, it seems that calcination stabilizes the silver deposits and increase the pure photocatalytic activity of the material in comparison with the uncalcined Ag/TiO_2 material, whose lower activity is probably counteracted by its higher silver lixiviation.

To discriminate between the bactericidal role of silver and the enhancement of the photocatalytic process, additional experiments of photocatalytic degradation of methylene blue solutions were carried out (Figure 5). In this case, the decrease in the activity of the bare TiO_2 after calcination is even more pronounced than that shown in the disinfection experiments. Moreover, incorporation of silver further reduced the activity, probably due to detrimental effects derived from excessive silver loading, as will be discussed later. In any

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case, these results confirm that the observed bacterial inactivation should be substantially attributed to the bactericidal role of silver.
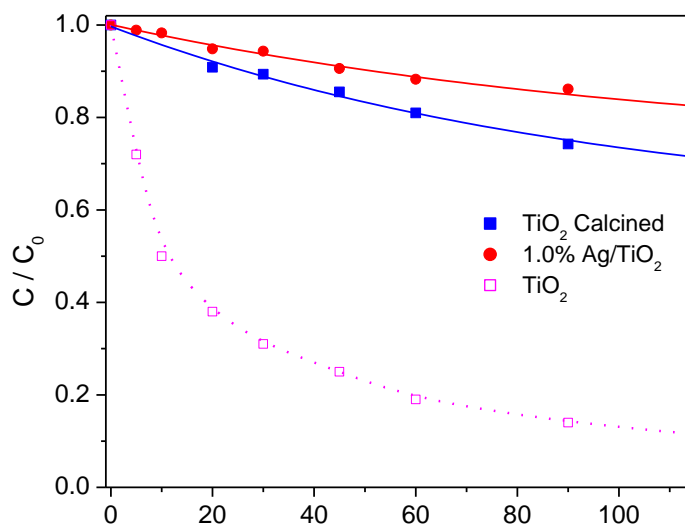
Figure 5. Photocatalytic degradation of methylene blue solutions using TiO_2 and Ag/TiO_2 in suspension.

3.2. Immobilized Ag/TiO$_2$ catalytic systems: wall and fixed-bed reactor

Immobilized Ag/TiO_2 systems with increasing silver loadings have been prepared by photoreduction of $AgNO_3$ solutions, quantifying the amount of deposited silver by ICP-AES. Figure 6 displays the photographs of the reactor inner wall coated with TiO_2 and Ag/TiO_2. It can be seen that incorporation of high amounts of silver darkens the tube. In fact, UV-vis transmission spectra (not shown) confirm that this highly loaded Ag/TiO_2 tube present negligible transmittance in the whole studied wavelength range from 300 nm to 800 nm, whereas TiO_2 tubes only absorb in the UV-A range. This visible light response of Ag/TiO_2 can be attributed to the characteristic silver surface plasmon band, indicative of the formation of nanometer sized silver metal [15].

Figure 6. Photographs of the TiO$_2$ and Ag/TiO$_2$ photocatalytic wall systems.

Electron micrographs of the immobilized Ag/TiO$_2$ surface are displayed in Figure 7. First micrograph, taken with the ETD detector, shows the particulate nature of the TiO$_2$ film, being this roughness favourable for the adhesion of bacteria. Second micrograph, taken with the vCD detector, emphasizes the differences in the atomic composition of the film, being attributed the brighter dots to the heavier atoms of silver. Finally, the third micrograph is a magnified view of the compositional image, in which the nanometric size of the bright clusters is clearly shown, being confirmed their silver composition by the EDS microanalysis.
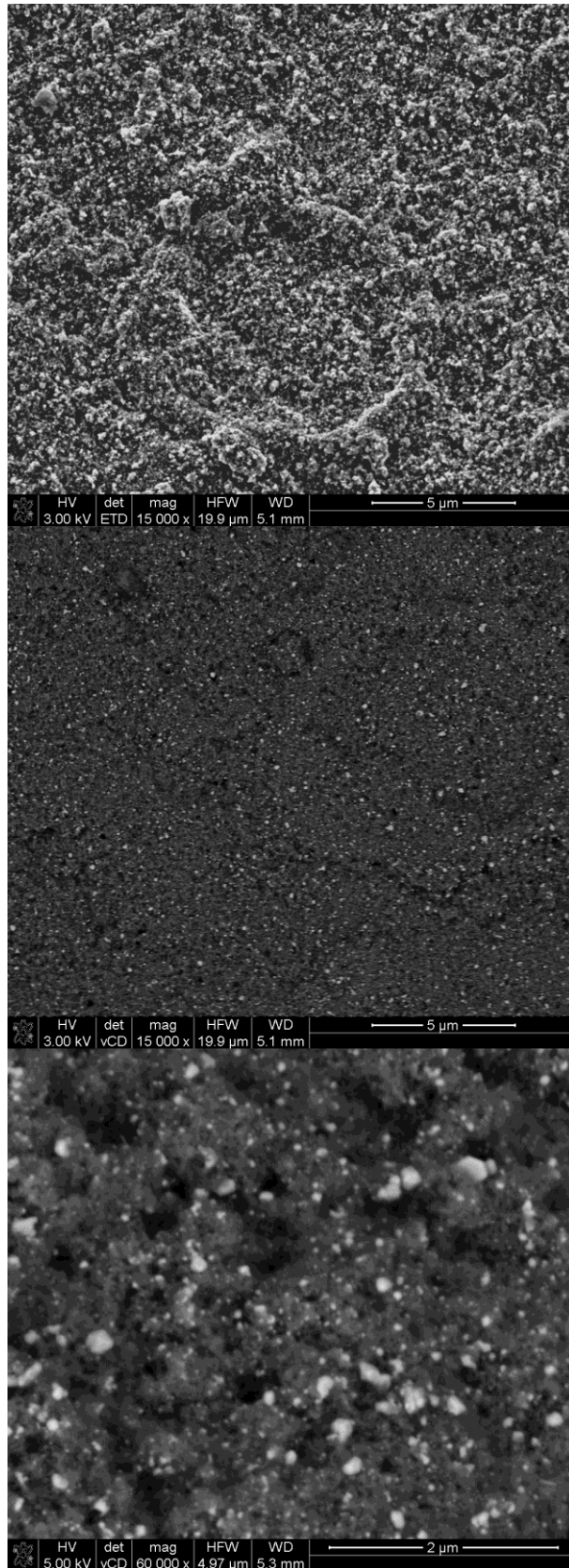
Figure 7. FESEM micrographs of the surface of the Ag/TiO$_2$ fixed-bed glass rings

Bacterial inactivation profiles achieved with immobilized Ag/TiO$_2$ wall reactors are shown in Figure 8. In all cases the inactivation is more effective than that obtained with the bare TiO$_2$ tube, apparently being an optimum with a maximum efficiency for 0.6% wt% of silver loading.
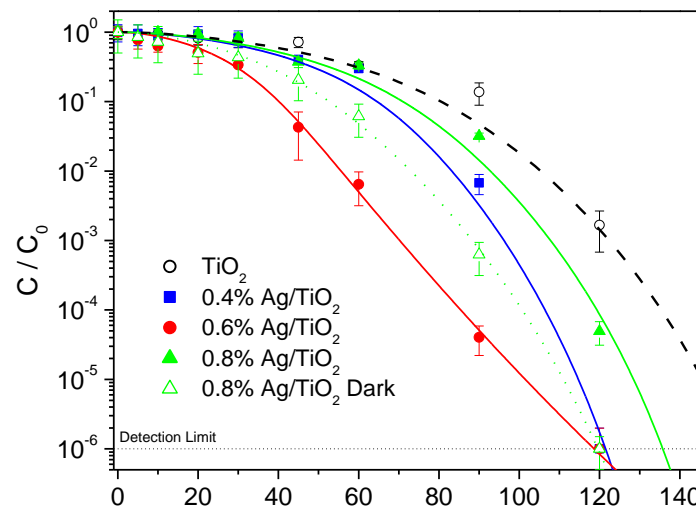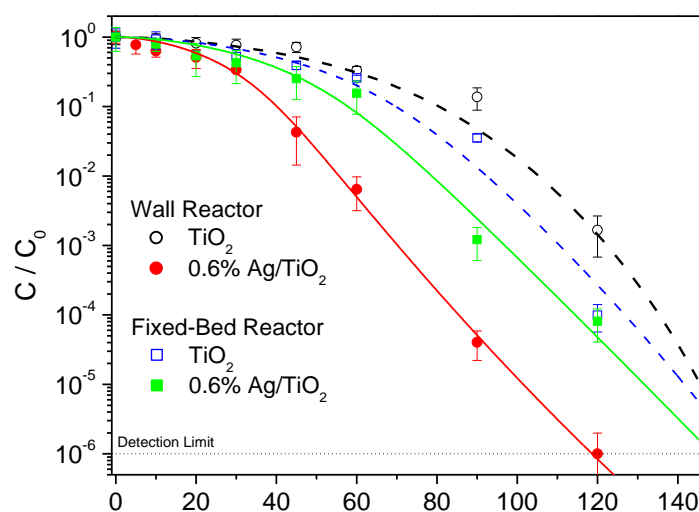

Figure 8. Photocatalytic inactivation of *E. coli* in water using TiO$_2$ and Ag/TiO$_2$ wall reactors. Fitting lines were calculated using a kinetic model based on a series events disinfection mechanism [25]. Error bars calculated from eight independent bacteria counting measurements.

Other research groups have reported the existence of an optimal silver loading [14,18, 30], although it has been stated that the correlation between photocatalytic activity and silver loading strongly depends on the preparation method [18] and the tested organic pollutant [31-33]. The activity enhancement has been attributed not only to the electron sink role of the silver clusters but also to an improvement of the pollutant adsorption over the modified titania surface [34]. The dependence of the results with the specific tested pollutant has been justified through the different degradation mechanisms including hole trapping intermediates or the possibility of reductive degradation pathways [32-33]. Kubacka et al. [18] found evidences of the local-type modification of hydroxyl radicals formed upon light absorption in the neighbourhood of silver entities, being this property strongly related to the photokilling activity, more than changes in the adhesion of bacteria or the electron trapping role. On the other hand, high silver loadings show a detrimental effect on the activity. As reviewed by

Tran et al. [31], a decrease in the activity of Ag/TiO_2 materials for the mineralisation of organics in comparison with bare TiO_2 has been observed by other researchers, justifying the detrimental effects by: i) a reduction in the access of radiation to the TiO_2 surface due to excessive surface coverage by the silver deposits; ii) blockage of the TiO_2 active sites by the metal deposits which are necessary for the photocatalytic process; iii) an increase in charge carrier recombination rates at high silver loadings; and iv) a inhibition in the role of oxygen due to the preferential electron transfer from the TiO_2 surface to the silver deposits. Additionally, Kubacka et al. [18] suggest that silver can change the surface characteristics of titania, leading to measurable variations in the point of zero charge (PZC), modifying the adhesion between bacteria and catalyst, a critical point for the efficiency of the process [26-28]. However, despite the large number of papers related to silver modification of titanium dioxide, only few research groups have studied the lixiviation of silver to check the stability of the silver deposits [18]. In all the experiments using irradiation, the analysis of silver in solution along the reaction shows a negligible lixiviation and a high stability of the surface silver deposits. In contrast, the results of the dark experiment with the 0.8% Ag/TiO_2 tube show a substantial lixiviation of silver to the medium, justifying the increase in activity shown in Figure 8 by the higher bactericidal effect of soluble silver compounds. From dark experiments, both with the catalysts in suspension and the wall reactor, it can be concluded that radiation is an important factor to assure the stability of the Ag deposits, supplying the necessary electrons to maintain the silver in metallic state, whereas an important reoxidation takes place in dark.

Figure 9 shows the comparison of the photocatalytic inactivation of bacteria with both wall and fixed-bed reactors, using bare TiO_2 and 0.6% Ag/TiO_2. In both cases the incorporation of silver enhances the photokilling activity, being the effect much more pronounced in the immobilized wall reactor. In fact, whereas the time required to achieve the bacterial detection limit is quite similar for both bare TiO_2 configurations and the 0.6% Ag/TiO_2 fixed-bed, it is substantially decreased by the use the 0.6% Ag/TiO_2 wall reactor.

Figure 9. Comparison of the photocatalytic inactivation of *E. coli* in water using both wall and fixed-bed TiO_2 and Ag/TiO_2 immobilized systems. Fitting lines were calculated using a kinetic model based on a series events disinfection mechanism [25]. Error bars calculated from eight independent bacteria counting measurements.

Analyzing the bacterial inactivation profiles showed in Figure 8 and 9, an important feature of these disinfection curves is that they do not show the characteristic ending tail that presents the disinfection experiments with catalyst in suspension represented in Figure 3 and 4, reaching the bacterial detection limit during the log-linear region that appears after the initial delay of the curve. This fact has been previously observed for bare TiO_2 immobilized materials and attributed to a reduced competition of the organic residuals released to the medium upon the bacterial lysis for the photogenerated oxidant species [23]. Although the initial activity is clearly lower than those obtained with TiO_2 slurries, the irradiation time required to reach the detection limit in the wall reactor at the optimal silver loading is not far from that required with bare TiO_2 slurry and comparable to Ag/TiO_2 slurries. Consequently, in addition to the advantage related to the separation of the catalysts after the reaction, the immobilized systems seem to show a higher resistance to the inhibition by organic matter, a clear benefit for the disinfection of natural waters and effluents from wastewater treatment plants for reuse purposes.

From all the tested catalytic systems, it can be concluded that the 0.6% Ag/TiO_2 wall reactor configuration is the most effective immobilized system for the bacterial inactivation.

Moreover, considering that the amount of titanium dioxide incorporated to the tube is around 0.03 g [23] in comparison with 0.35 g loaded in the fixed-bed and the 0.1 g L^{-1} used in suspension, it is derived that the specific activity of the wall reactor is even higher than that of titanium dioxide in suspension. A possible explanation for this higher efficiency of the wall reactor is the differences existing in the titanium dioxide illumination pattern. Figure 10 schematizes how the absorption of photons of silver modified titanium dioxide in suspension takes place through the same surface in which silver has been deposited (the same is valid for the fixed-bed reactor configuration). In contrast, in the wall reactor the TiO_2 film is irradiated from the surface adhered to the inner reactor glass tube wall, whereas silver has been deposited onto the external surface of the TiO_2 film, in contact with the solution. Consequently, silver deposits are not reducing the radiation flux reaching the titania surface, leading to an optimal configuration in which the radiation absorption is maximized whereas the electron trapping, the improvement of the bacterial adhesion and the direct bactericidal attack of silver is simultaneously achieved. Additionally, the wall reactor configuration avoids the existence of dark Ag/TiO_2 regions in the most external volume of the reactor, reducing the lixiviation of silver to the solution by reoxidation.
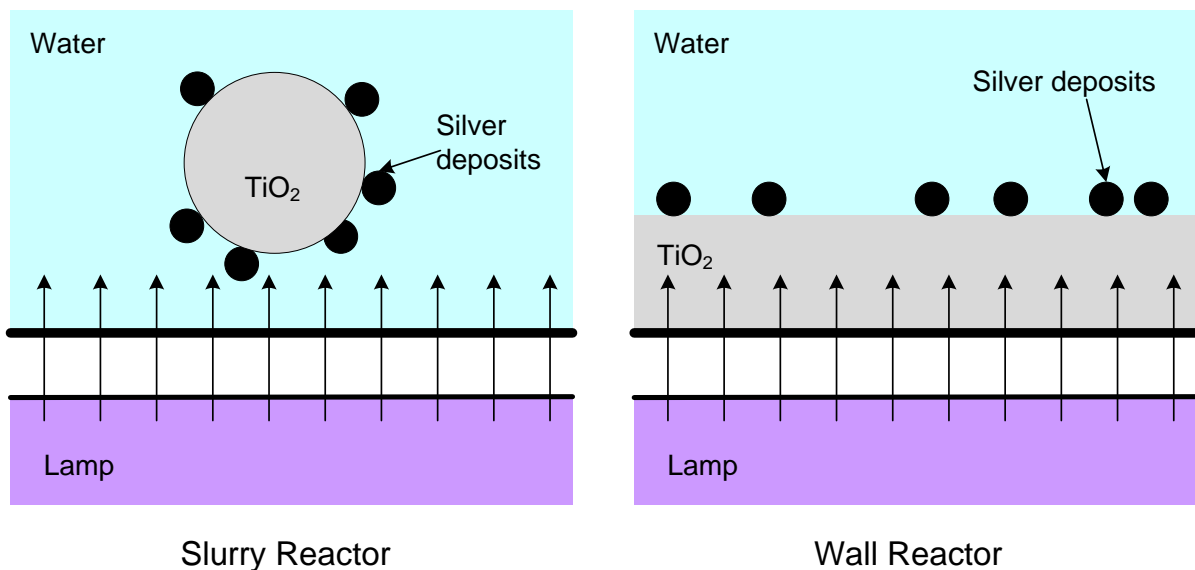
Figure 10. Schematic representation of the irradiation patterns in slurry and wall reactors (glass tube width has been omitted for clarity purposes).

4. Conclusions

The potential effect of silver incorporation in the photocatalytic behaviour of titania slurries is overcome by the bactericidal effect of Ag leached to the solution by reoxidation of the metal particles in the darker regions of the reaction system. A thermal treatment is required to stabilize the silver deposits and reduce the lixiviation of silver to the solution, whose extent is really high for uncalcined materials and for experiments in the dark, suggesting that irradiation is required to stabilize the photoreduced silver clusters in the metallic state.

Experiments of dye photodegradation show a decrease in the activity upon incorporation of silver, what could be produced by a decrease in the absorption of radiation produced by the silver deposits or by a reduction in the adsorption of the dye due to the modification of the TiO_2 surface. So, the enhancement in the activity for *E. coli* inactivation could be due to the improvement in the bacterial adhesion to the titania surface or more likely to the direct bactericidal role of silver, and not exclusively to a better electron-hole separation and interfacial charge transfer.

Immobilized Ag/TiO_2 systems in wall reactor configuration has been demonstrated to be optimal from several points of view: i) Silver incorporation increase the activity of the bare TiO_2 systems, as result of reduction of the charge carriers recombination, an improvement of the bacterial adhesion and specially of a parallel non-photocatalytic disinfection mechanism based on the toxicity of the silver; ii) the time required to reach the bacterial detection limit is comparable to that of Ag/TiO_2 suspensions; iii) their specific activity per gram of TiO_2 is higher than that of slurries or fixed-bed systems; iv) the reactor configuration, with irradiation from the opposite side to the silver modified surface in contact with the solution, maximizes the radiation absorption, reducing simultaneously the lixiviation of silver produced in the darker regions of fixed-bed and slurry systems; and v) the Ag/TiO_2 film is stable, shows no deactivation or lixiviation, and present no inhibition by the organic residuals released after bacterial lysis, allowing the continuous treatment of water.

Acknowledgements

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