

**COMPARISON OF THE PHOTOCATALYTIC DISINFECTION OF *E. COLI*
SUSPENSIONS IN SLURRY, WALL AND FIXED-BED REACTORS**

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ABSTRACT

The performances of different configurations of photoreactors were compared for the photocatalytic disinfection of *E. coli* aqueous suspensions and methylene blue photodegradation. Titania was immobilized in an annular reactor in two different ways: on the inner reactor wall and on the packing of a fixed bed. The influence of the increase in the TiO₂ layer thickness has been studied, and the results have been compared with those obtained with TiO₂ slurries of increasing concentration. Experimental results for methylene blue degradation were in agreement with those expected from the characterization data of the immobilized systems, but they did not fit with the variation of the activity for microorganisms inactivation. The increase in the density of the TiO₂ film caused by the heat treatment carried out after every coating cycle reduce the TiO₂ surface available for the interaction with bacteria, although it remains accessible for the dye molecules. Although immobilized systems show a lower disinfection activity in deionized water than TiO₂ slurries, they show a lower inhibition by the presence of organic matter, leading to comparable irradiation times to reach bacterial concentrations below the detection limit in the treatment of wastewater treatment plant effluents. Moreover, immobilized systems have shown that they are stable and do not present deactivation after several cycles of reuse, being readily applicable for continuous water treatment systems.

KEYWORDS: photocatalysis, disinfection, *E.coli*, immobilized TiO₂, fixed-bed reactor, wall reactor.

1. INTRODUCTION

The formation of potentially harmful chloro-organic disinfection by-products (DBPs) with carcinogenic and mutagenic effects on mammals has derived in an increasing public concern related to the use of chlorination processes for the disinfection of drinking water supplies [1,2]. Other commercial processes such as ozonation and short wavelength UV-C irradiation generally reduce the level of chlorinated by-products, but lead to the formation of other toxicologically important DBPs such as brominated and iodinated compounds by reaction with the naturally-occurring organic matter and halide ions [1,3].

The application of photocatalytic processes as alternative for the inactivation of pathogenic microorganisms has attracted much attention during the last years. Since the early work of Matsunaga et al. [4], many works have reported the successful killing of bacteria, viruses, algae, fungi or protozoa by semiconductor photocatalysis [5]. The main advantages of TiO₂ photocatalysis over other advanced oxidation processes is that it operates under ambient temperature and pressure, but mainly it has the possibility of using solar light as radiation source. Consequently, it is a simple technology that can be applied for the disinfection of water resources in rural areas of developing countries with high levels of solar irradiation [6,7].

The most common type of experimental setup found in the literature to carry out photocatalytic experiments is a discontinuous slurry photoreactor operating with TiO₂ particles in suspension. However, slurry reactors have a number of disadvantages from practical and economical viewpoints, due to the need of catalyst particles removal following the treatment. Moreover, recent studies have raised concerns about the potential toxicity of titanium dioxide nanoparticles [8]. Consequently, many research efforts have been dedicated to the development of immobilized systems following different approaches, synthesis routes and support materials [9-11]. The immobilized photocatalysts usually show lower activities for the oxidation of chemical pollutants when compared with powder TiO₂, mainly due to the decrease in the interphase surface available and the increase in the restrictions to the mass transfer. Moreover, the immobilization procedure must guarantee the long term stability of the TiO₂, avoiding the possible leaching of TiO₂ particles to the solution, and must permit the regeneration of the catalyst in case of deactivation [12]. Several immobilized systems have

been also tested for the photocatalytic inactivation of bacteria [7, 13-16] showing lower efficiencies than the TiO₂ slurries.

The design of immobilized systems for the photocatalytic inactivation of bacteria must take into account the most important difference when compared to the photocatalytic oxidation of chemicals: the size of the target. Microorganisms are several orders of magnitude larger than molecules, being even larger than the TiO₂ photocatalytic particles. For powder TiO₂ suspensions this difference is not so important, because instead of being adsorbed on the titania surface, microorganisms are surrounded by titania particles attached to their external membrane [17]. However, when supported photocatalysts are used, this difference becomes critical because molecules can diffuse inside the porous structure, but the contact between titanium and the microorganisms is restricted to the external TiO₂ surface. This effect has been previously observed when using silica-supported TiO₂ suspensions [18], making not suitable for photocatalytic disinfection processes porous TiO₂/SiO₂ materials that had shown a high activity for the photocatalytic oxidation of chemical pollutants such as cyanides [19], alcohols [20] or dichloroacetic acid [21].

Nevertheless, considering that the main advantage of the immobilized system is that they allow the continuous treatment of the water, not many studies have been focused on the deactivation of the catalysts after several microorganism inactivation cycles. This phenomenon is even more important when considering the strong influence of the chemical composition of water over the inactivation efficiency of TiO₂ slurries [18,22,23]. This point is crucial for the real application of this technology at field scale, as natural waters usually contain significant concentrations of inorganic ions and organic substances.

This work reports the development of TiO₂-based photocatalysts immobilized on the wall or on the surface of glass rings used in packed fixed-bed reactors and the comparison of their efficiency for the photocatalytic inactivation of bacterial suspensions with slurry TiO₂ systems. As model microorganism, *Escherichia coli* has been chosen, the most widely accepted microorganism indicative of the existence of faecal contamination in water. Both immobilized systems have been evaluated in the treatment of non-ideal waters with complex chemical composition, analyzing the evolution of the activity after several cycles of reuse.

2. EXPERIMENTAL

2.1. Photoreactor and catalysts.

The experimental setup for the photocatalytic reactions, represented in Figure 1, consists of an annular reactor 15 cm long, 3 cm inner diameter and 5 cm external diameter operating in a closed recirculating circuit driven by a centrifugal pump, with a stirred reservoir tank of 2 L volume equipped with a device for withdrawal of samples. Experiments have carried out using a total working volume of 1 L and a recirculation flow rate of $2.5 \text{ L}\cdot\text{min}^{-1}$, what leads to a residence time in the irradiated photoreactor of 4.5 s. Illumination was carried out using a Philips TL 6W black light lamp placed in the axis of the reactor. The lamp provides a nominal UV-A radiation power of 0.7 W with a maximum emission peak centred at 365 nm. The UV-A incident photon flow, determined by ferrioxalate actinometry, was $1.2 \times 10^{-5} \text{ Einstein s}^{-1}$. Considering an average radiation wavelength of 365 nm ($328 \text{ kJ Einstein}^{-1}$), this value is equivalent to $3.93 \times 10^{-3} \text{ kJ s}^{-1}$. Consequently, although all the results would be expressed as a function of the irradiation time, they can be easily converted to accumulated energy using a conversion factor of 0.24 kJ/min.

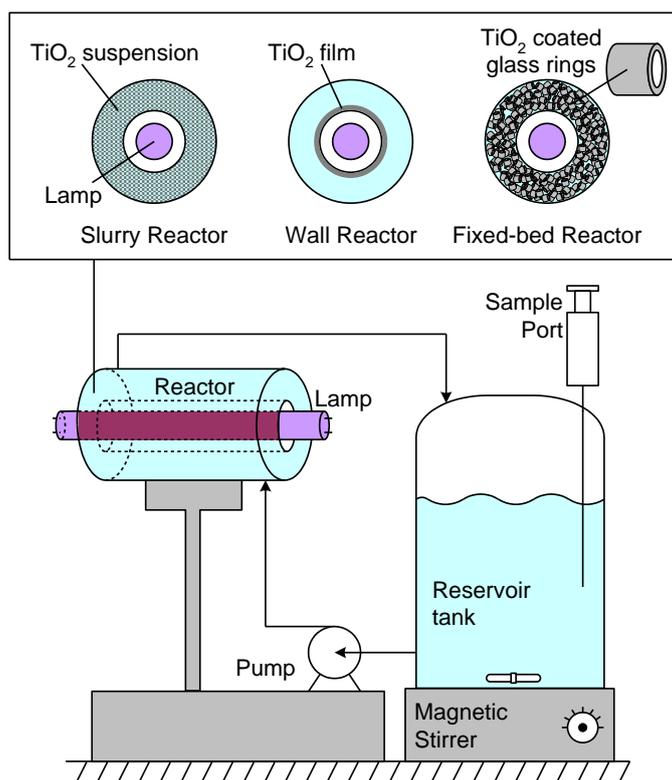


Figure 1. Schematic representation of the experimental setup (see text for details).

Three different types of reaction systems have been tested (Figure 1):

- i) A slurry reactor, using suspensions of Degussa P25 TiO₂.
- ii) A wall reactor, immobilizing Degussa P25 TiO₂ onto the 15 cm long glass tube that constitutes the inner wall of the reactor.
- iii) A fixed-bed reactor, immobilizing Degussa P25 TiO₂ onto 6x6 mm glass Raschig rings and placing them into the annular reactor volume.

Immobilization of TiO₂ has been carried out by a dip-coating procedure. The glass material was first cleaned-up with soap and water and then immersed in a KOH-isopropanol bath (200 g L⁻¹) for 24 h. The coating suspension consists of 150 g L⁻¹ of Degussa P25 TiO₂ in deionized water at a pH value of 1.5 (adjusted with HNO₃). The process was assisted by a Bungard Elektronik RDC-15 equipment working at a controlled withdrawal speed of 0.65 mm s⁻¹. After every coating cycle, the glass pieces were dried at 110 °C for 24 h and calcined at 500 °C for 2 h with a heating rate of 5 °C min⁻¹. Prior to be tested in reaction, the coated

systems were mounted on the photoreactor and cleaned with water for 30 minutes to remove all the semiconductor particles poorly adhered to the glass.

Scanning electron microscopy (SEM) micrographs of the coated glass wall of the reactor were taken on a JEOL JSM-6400 working at an acceleration voltage of 15-30 kV. UV-vis absorption spectra in the 300-500 nm range were recorded with a Varian Cary 500 Scan UV-VIS-NIR spectrophotometer operating in the transmission mode.

2.2. Photocatalytic experiments.

Bacterial suspensions were prepared from lyophilized *Escherichia coli* K12 strains provided by the Colección Española de Cultivos Tipo (CECT 4624, corresponding to ATCC 23631). Fresh liquid cultures with a stationary concentration around 10^9 CFU mL⁻¹ were prepared by inoculation in a Luria-Bertani nutrient medium (Miller's LB Broth, Scharlab) and incubation at 37°C for 24h under constant stirring on a rotary shaker.

The reacting suspensions were prepared by centrifuging 5 mL of the liquid culture at 3000 rpm for 15 minutes, rinsing twice the bacteria with 5 mL of sterile deionized water (Milli-Q®, 18.2 MΩ cm) and finally diluting 1 mL of the aqueous *E. coli* suspension to 1 L (corresponding to initial concentration of bacteria around 10^6 CFU mL⁻¹) with the water sample to be tested. Three different kinds of water have been used: i) deionized water; ii) real wastewater from the secondary treatment effluent of the Rey Juan Carlos University wastewater treatment plant (Móstoles, Spain); and, iii) synthetic municipal wastewater [24] diluted to a total organic carbon value of 15 mg L⁻¹, corresponding to the average value of the real wastewater effluents.

The bacterial suspension was charged in the reservoir tank and the pump was switched on to drive the recirculation flow. For the slurry experiments, the catalyst was added to the reservoir tank. In all cases, the system was equilibrated for 15 minutes, and in the meantime, the lamp was switched on outside the reactor to stabilize its emission power and spectrum before the reaction starts.

The bacterial inactivation was followed by analyzing the concentration of viable bacteria in the samples taken along the reaction. The quantification was carried out following a standard

serial dilution procedure, spotting 10 μL of each decimal dilution 8 times on LB nutrient agar plates (Miller's LB Agar, Scharlab) and incubating them at 37°C for 24h before counting. For high irradiation times (low bacterial concentrations) higher volumes of 100 μL and 1mL of the undiluted suspension were also plated to reduce the limit of detection to 1 CFU mL^{-1} . Key experiments were repeated three times to test the reproducibility of the disinfection results.

With the aim of establishing a suitable comparison between disinfection and oxidation activities of the different catalytic systems, experiments of photocatalytic degradation of methylene blue (Sigma-Aldrich) 20 μM aqueous solutions were carried out. The reason for using this chemical compound is that it has been proposed as a standard method to determine the activity of photocatalytic coatings [25]. The evolution of the reactions was followed colorimetrically through the decrease in the absorption of the solution at 664 nm, after filtering the samples through 0.22 μm nylon membranes to remove the catalyst in the case of TiO_2 slurries.

3. RESULTS AND DISCUSSION

3.1. Characterization of the immobilized photocatalysts.

Figure 2a displays the SEM micrograph of the glass wall after three TiO_2 coating cycles. From these analysis, it has been determined that the average thickness of the TiO_2 layer increases from $0.75 \pm 0.1 \mu\text{m}$ for 1 coating to $1.1 \pm 0.2 \mu\text{m}$ for 2 coatings and $1.5 \pm 0.2 \mu\text{m}$ for 3 coatings. Moreover, as the number of coatings increases, the surface of the TiO_2 film becomes less rough and heterogeneous, being for 3 coatings a continuous and smooth particulate layer of almost homogeneous thickness (see Figure).

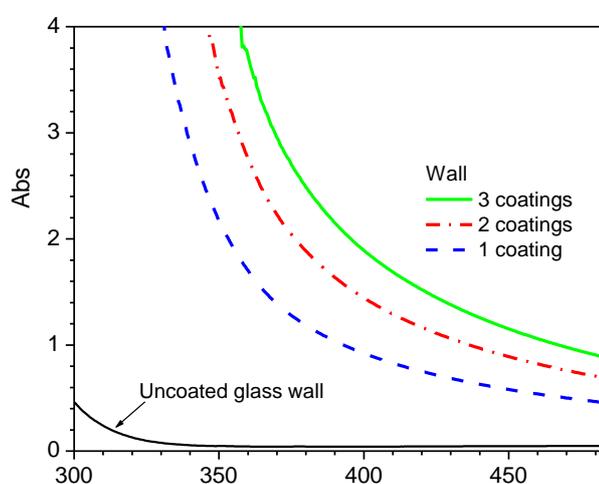
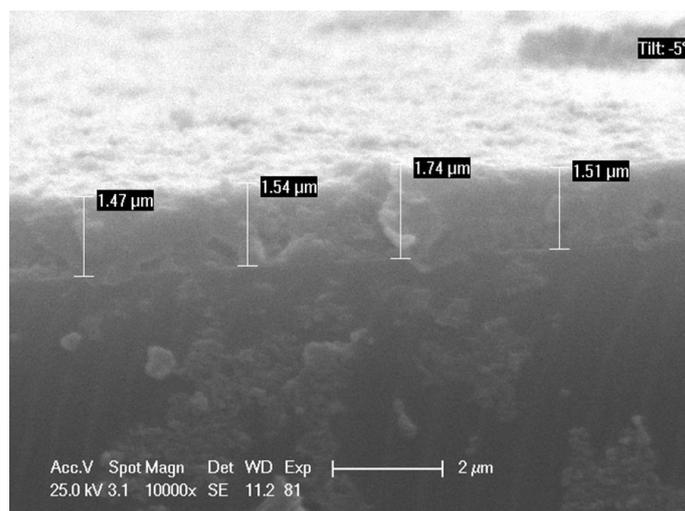


Figure 2. Characterization of the wall TiO_2 coatings: a) SEM micrograph of the glass wall after 3 TiO_2 coating cycles; and, b) UV-Vis absorption spectra of the wall with increasing number of coatings.

The weight of TiO_2 incorporated to the wall tube in each coating is about 0.01 g, leading to an apparent density of the film (estimating the volume from the average thickness of the layer) that increases from 0.94 g cm^{-3} for 1 coating to 1.2 g cm^{-3} for 2 coatings and 1.4 g cm^{-3} for 3 coatings. Considering that the density of the anatase crystalline phase is 3.9 g cm^{-3} , that means that the TiO_2 layer presents some porosity and that the thermal treatment carried out between every coating cycle leads to an increase in the density of the film, reducing the pore volume.

Concerning the optical properties of the materials, Figure 2b shows the UV-vis absorption spectra of the glass wall of the reactor after increasing number of TiO₂ coatings. First of all, it is important to notice that the glass wall is almost totally transparent in the wavelength range of interest, being the TiO₂ layer the only responsible of the decrease in the radiation transmission. As the number of coatings increases, and consequently the thickness of the TiO₂ layer, the absorbance of the wall increases, with only a 1% of transmission below 390 nm for the material with 3 coatings (absorbance around 2). The increase in the number of coatings above 3, does not modified substantially the absorption of the materials on the UV- A wavelength range of interest, leading to lower transmission values due to the increase in the scattering produced by the particulate layer. Consequently, from a pure characterization viewpoint, 3 TiO₂ coating cycles are sufficient to maximize the absorption of the catalysts, being useless a further increase of the amount of titania in the film. Finally, it is worth noting that the determination of the UV-vis absorption spectra constituted a very simple, quick and non-destructive quality control for the test of every newly synthesized catalyst, showing that the coating procedure leads to very reproducible materials.

3.2. Photocatalytic activity in deionized water.

Figure 3a shows the results of the photocatalytic inactivation of *E. coli* using increasing concentrations of TiO₂ slurries. Maximum activities were observed for catalyst concentrations above 0.1 g L⁻¹, being selected this value as a good compromise between maximizing the absorption of the inlet radiation and minimizing the catalyst loading. Experimental results have been fitted (see solid lines in Figure 3a) using a kinetic model recently developed [18]:

$$\frac{dC_{undam}}{dt} = -k \frac{KC_{undam}^n}{1 + KC_{undam}^n + KC_{dam}^n} \quad (1)$$

$$\frac{dC_{dam}}{dt} = k \frac{KC_{undam}^n - KC_{dam}^n}{1 + KC_{undam}^n + KC_{dam}^n} \quad (2)$$

This model is based on a serial events disinfection mechanism, where C_{undam} represents the undamaged population of bacteria and C_{dam} is a lump of the bacteria in all the intermediate levels of damage. It presents three independent parameters with defined physical meaning: kinetic constant (k), pseudo-adsorption constant (K) and inhibition coefficient (n), whose values can be estimated from the fitting of experimental data.

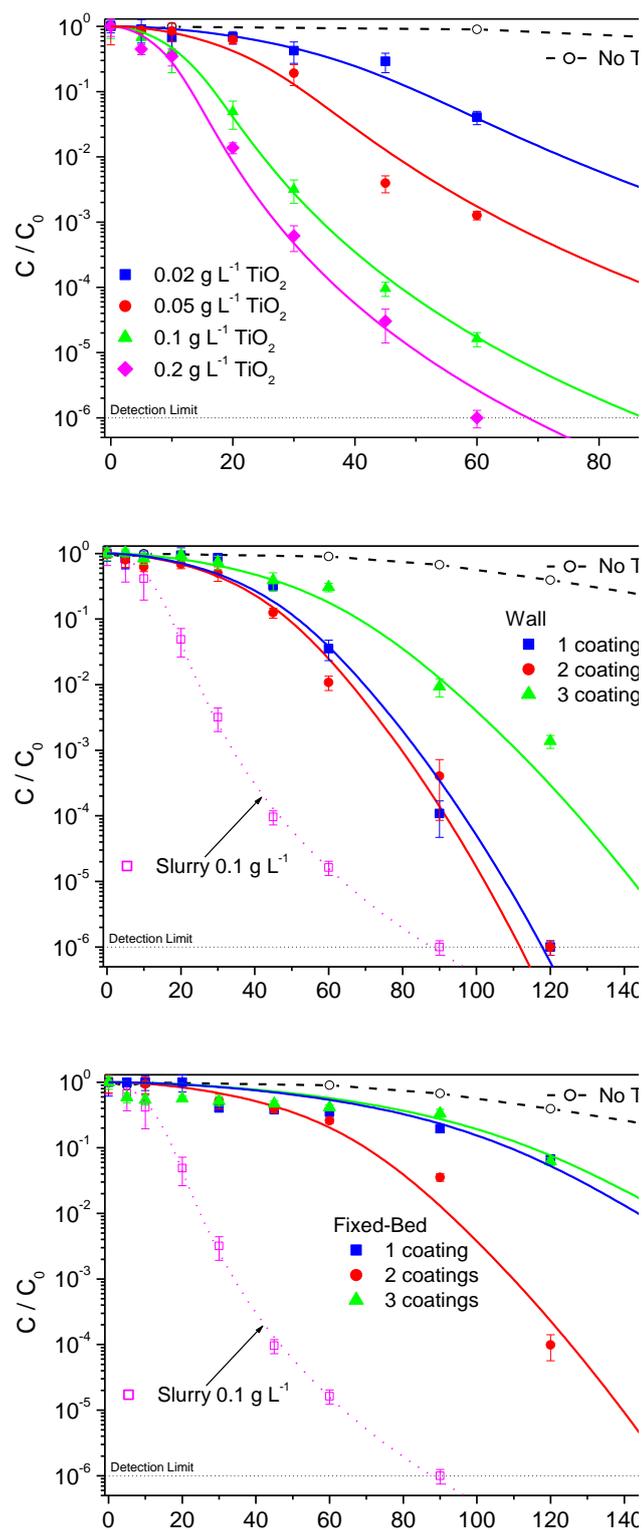


Figure 3. Experimental results (dots) and kinetic model fitting (lines) of the photocatalytic disinfection of *E. coli* suspensions using different catalytic systems: a) slurry; b) wall reactor; and c) fixed-bed reactor. Error bars calculated from eight independent bacteria counting measurements.

In a previous work [18], we have shown that the value of the inhibition coefficient, n , does not depend on the catalyst concentration, and that the value of the pseudo-adsorption constant, K , is also constant except for the lower range of catalysts loadings. Consequently, we have assumed that both values can be considered equal for the four experiments with increasing catalyst concentration, whereas the value of the kinetic constant, k , will be different. Simultaneous multiparameter fitting using a Levenberg-Marquardt non-linear regression algorithm coupled with a fifth-order Runge-Kutta numerical integration procedure leads to the values of the kinetic parameters shown in Table 1. A very good reproduction of the experimental data is achieved, as shown the kinetic curves in Figure 3a. As it was expected, the values of the kinetic constants increase with the TiO₂ loading. In contrast, the value of the inhibition coefficient ($n = 1.14$) is quite different from that previously reported for a discontinuous photoreactor ($n = 1.31$) [18], being dependent of the experimental setup.

Table 1. Values of the disinfection kinetic parameters determined by fitting the experimental data.

Disinfection Experiment	Water	$k \times 10^{-4}$ (CFU mL ⁻¹ min ⁻¹)	$K \times 10^6$ (mL ⁿ CFU ⁻ⁿ)	n (dimensionless)
TiO ₂ slurry, 0.02 g L ⁻¹	Deionized	6.6		
TiO ₂ slurry, 0.05 g L ⁻¹	Deionized	10.5		
TiO ₂ slurry, 0.1 g L ⁻¹	Deionized	19.7	0.47	1.14
TiO ₂ slurry, 0.2 g L ⁻¹	Deionized	25.2		
TiO ₂ wall, 1 coating	Deionized	7.4		
TiO ₂ wall, 2 coatings	Deionized	7.8	3.27	0.96
TiO ₂ wall, 3 coatings	Deionized	5.6		
TiO ₂ fixed-bed, 1 coating	Deionized	3.1		
TiO ₂ fixed-bed, 2 coatings	Deionized	4.9	3.66	0.97
TiO ₂ fixed-bed, 3 coatings	Deionized	3.0		
TiO ₂ slurry, 0.1 g L ⁻¹	Wastewater 2 nd Aug 2007	5.6	0.47	1.14
TiO ₂ slurry, 0.1 g L ⁻¹	Wastewater 26 th Sept 2007	16.6	0.47	1.14
TiO ₂ wall, 3 coatings	Wastewater 29 th Nov 2007	4.8	3.27	0.96
TiO ₂ wall, 3 coatings	Wastewater 18 th Dic 2007	2.4	3.27	0.96
TiO ₂ slurry, 0.1 g L ⁻¹	Synthetic Wastewater	5.7	0.47	1.21
TiO ₂ wall, 3 coatings	Synthetic Wastewater, 1 st use	2.0	10.0	0.96
TiO ₂ wall, 3 coatings	Synthetic Wastewater, 2 nd use	1.9	10.0	0.96
TiO ₂ wall, 3 coatings	Synthetic Wastewater, 3 rd use	2.0	10.0	0.96

Figures 3b and 3c show the results of the *E. coli* inactivation using both the wall and fixed-bed immobilized catalytic systems with increasing TiO₂ layer thickness. In both cases the activity observed is lower than that obtained for the 0.1 g L⁻¹ TiO₂ slurry, considered as the optimum concentration of TiO₂ in suspension because higher values only lead to slightly better activities. It must be noticed that the specific activity per gram of TiO₂ is much higher for the immobilized systems, as the amount of catalyst in the wall reactor is from three to ten times lower, but the inactivation rate can not be improved with higher TiO₂ loadings because is limited by the optimal TiO₂ layer thickness that absorb all the incident radiation. The idea behind the use of the fixed-bed reactor was to increase the inactivation rate by increasing the TiO₂ surface and by placing the catalyst in the whole photoreactor volume. However, the expected improvement in the activity of the fixed-bed over the wall reactor was not experimentally verified. Moreover, in both cases unexpected results were obtained when increasing the number of TiO₂ coatings, showing a maximum activity for 2 coatings and a clear decrease in the activity when further increasing the TiO₂ layer thickness.

For comparison purposes, experiments of methylene blue degradation were carried out with all the tested photocatalytic systems. As shown in Figure 4, the results of these reactions were in agreement with the expected increase in the activity for thicker TiO₂ layers. In both immobilized systems, the activity of the 3-coatings materials was slightly higher than that of the 2-coatings samples, as it was predicted by the UV-vis absorption spectra of the walls. Additionally, much higher activities were obtained for the fixed-bed reactor systems in comparison with the wall systems, as expected from the higher TiO₂ surface. In fact, the fixed-beds with 2 and 3 coatings reach the activity of the slurry system after sufficient irradiation time.

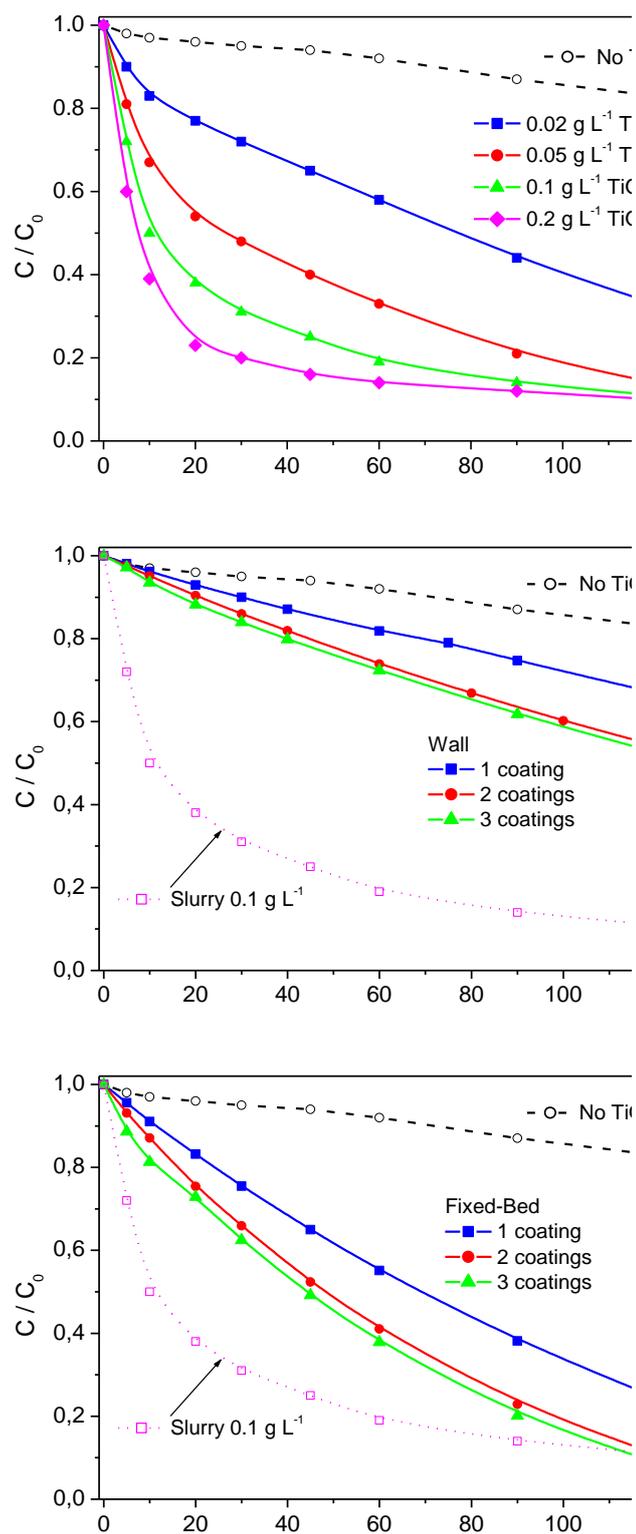


Figure 4. Experimental results of the photocatalytic degradation of methylene blue solutions using different catalytic systems: a) slurry; b) wall reactor; and c) fixed-bed reactor.

Consequently, it is clear that the activity results obtained in the evaluation of immobilized systems for the photocatalytic degradation of chemical pollutants are in agreement with those expected from the characterization data, but can not be extrapolated to the activity for microorganisms inactivation. The much bigger size of the *E. coli* cells in comparison with the methylene blue molecules is the responsible of the observed discrepancies. As the number of coatings increases the thickness of the layer increases but also its density, due to the constriction of the porosity of the layer. This effect is not so important for the degradation of chemicals, as they still can diffuse through the porosity of the layer, reaching a larger extension of surface area of the TiO₂ film. However, as the interparticle macroporosity of the titanium dioxide layer decrease, the titanium surface area really available for the interaction with the microorganism decreases, being active only the most external surface of the film.

Coming back to the bacterial inactivation profiles showed in Figure 3, both immobilized system present an important feature from the kinetic point of view: the inhibition coefficient obtained from the fitting of the data to the kinetic model represented by eq. (1) and (2) is very close to 1.0 (see Table 1). In contrast to inactivation experiments with TiO₂ slurries, the bacterial survival profiles observed for all the immobilized systems do not show the typical tail at long irradiation times, reaching the bacterial detection limit during the log-linear region that appears after the initial delay of the curve. Consequently, although the values of the kinetic constants of the immobilized systems are much lower than those of the TiO₂ slurries, the increase in the irradiation time required to reach the detection limit is not so high. According to the physical meaning of the inhibition coefficient and the presence of the tail in the curve, this indicates that competition for the photogenerated oxidant species between bacterial inactivation and oxidation of organic residuals reactions is much more important when TiO₂ is in suspension. Similarly to the results shown for the bacterial inactivation profiles, the curves of methylene blue photodegradation with the immobilized systems (Figures 4c y 4d) do not show a substantial decrease in the activity at high dye conversion, in contrast with the TiO₂ slurries in which an important decrease in the reaction rate is observed, probably due to the competition produced by the intermediate compounds of the dye degradation pathway. Consequently, in addition to the advantage related to the separation of the catalysts after the reaction, the immobilized systems seems 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.

3.3. Photocatalytic activity in wastewaters.

Photocatalytic disinfection has been applied as tertiary treatment to the inactivation of *E. coli* in the effluents of a wastewater plant. Figure 5 shows the results obtained with a 0.1 g L^{-1} TiO_2 slurry and the 3-coatings wall reactor system, corresponding the material with the thicker TiO_2 layer. In both cases very different activities were achieved for different reactions, due to the acute fluctuation of the effluents characteristics depending on the date of sampling. In any case, it can be stated that the photocatalytic disinfection of the effluent can be achieved, although the required time would depend on the specific water to be treated.

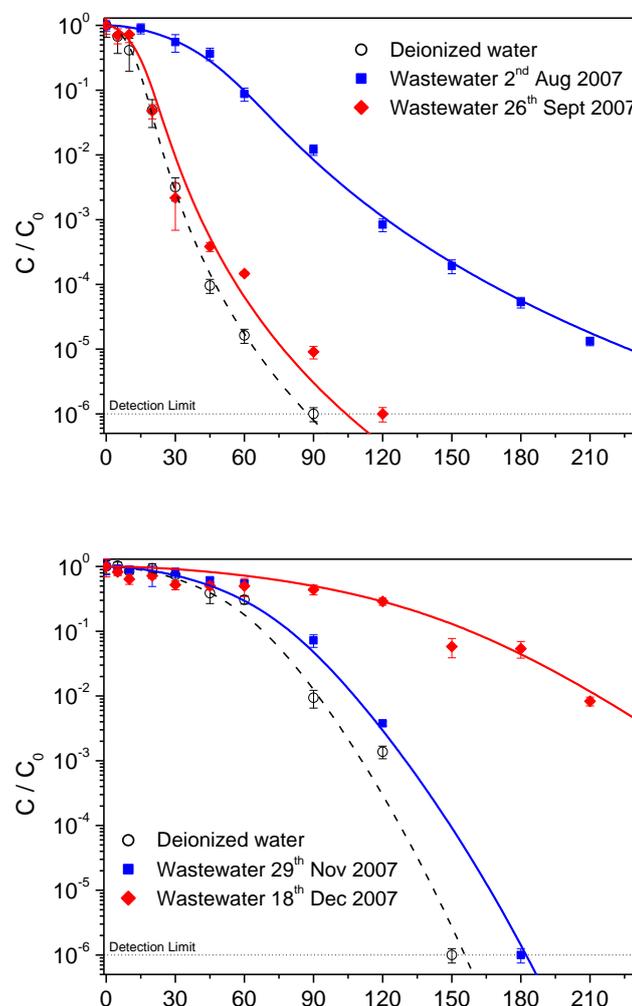


Figure 5. Experimental results (dots) and kinetic model fitting (lines) of the photocatalytic disinfection of *E. coli* suspensions in wastewater effluents from different dates using different catalytic systems: a) 0.1 g L^{-1} TiO_2 slurry; and b) 3-coatings wall reactor. Error bars calculated from eight independent bacteria counting measurements.

To evaluate the possible deactivation of the immobilized catalyst after several cycles of reuse, a diluted synthetic wastewater has been used, avoiding the effect of the real wastewater variability. Figure 6 shows the results obtained in three consecutive experiments performed with the same wall catalyst mounted on the reactor. The presence of organics and inorganics in the water reduces the efficiency of the photocatalytic disinfection with immobilized TiO_2 when compared with the results for deionized water. However, the decrease in the inactivation rate when treating real effluents instead of deionized water is even higher when using TiO_2 slurries, leading to irradiation times required to reach a concentration of viable bacteria below the detection limit comparable to those of the immobilized systems. A possible explanation of these results is that the effect of the presence of organic matter (naturally occurring humic acids or intracellular components released after the lysis of the bacterial cells) in the inactivation of bacteria is not only a competition for the adsorption on the TiO_2 surface but also a competition for the absorption of photons. In the wall reactor configuration, all the inlet radiation is absorbed in the inner tube without reaching the suspension. In contrast, in slurry systems the absorption of the photons is distributed in the whole photoreactor volume, allowing the competition of compounds in the aqueous phase for the absorption of photons.

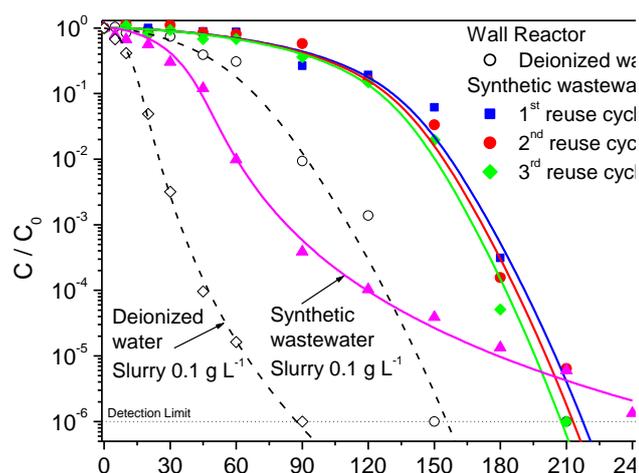


Figure 6. Experimental results (dots) and kinetic model fitting (lines) of the photocatalytic disinfection of *E. coli* suspensions in synthetic wastewater effluents using a 0.1 g L^{-1} TiO_2 slurry and the 3-coatings TiO_2 wall reactor. Error bars have been omitted for clarity purposes.

The results shown in Figure 6 confirm that the immobilized TiO₂ is more resistant to the inhibition produced by the presence of organic matter in the water. Moreover, no decrease in the activity is observed in the subsequent reaction cycles, showing very reproducible results. Additionally, the UV-vis absorption spectra of the coated wall recorded after the reactions remain essentially unchanged, indicating that the TiO₂ film is stable under the reaction conditions, allowing their application in continuous processes for water treatment.

4. CONCLUSIONS

Wall and fixed-bed immobilized TiO₂ catalytic systems constituted by continuous titania layers of homogeneous thickness supported on borosilicate glass have been developed. The thickness and density of the film increase with the number of coating cycles being a compromise between maximizing the absorption of the inlet radiation and minimizing the catalyst loading for three coatings.

Although both the wall and fixed-bed reactors show a lower activity than TiO₂ slurries, the increase in the irradiation time required to reach a concentration of viable bacteria below the detection limit is relative low, as they show a lower inhibition by the presence of organic matter. This fact is confirmed by the absence of a tail in the inactivation curves at long irradiation times and by values very close to 1.0 of the inhibition coefficients obtained in the kinetic modelling.

The influence of the TiO₂ layer thickness on the activity of both immobilized systems is rather complex. The results of activity for the degradation of methylene blue were in agreement with those expected from the characterization data, but they do not correlate the activity for microorganisms inactivation. The reason is that the much bigger size of the *E. coli* cells makes its inactivation very sensitive to the decrease in the TiO₂ surface available for the interaction with bacteria produced by the decrease in the interparticle macroporosity during the densification of the film produced by the heat treatments carried out after every coating cycle.

In any case, immobilized systems have shown that they are active for the inactivation of bacteria in effluents from a wastewater treatment plant, requiring comparable irradiation

times than TiO₂ slurries to reach the bacterial detection limit. Moreover, they are stable and show no deactivation after several reaction cycles, being readily applicable for continuous water treatment systems for water reuse purposes.

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