

**ANALOGIES AND DIFFERENCES BETWEEN PHOTOCATALYTIC OXIDATION
OF CHEMICALS AND PHOTOCATALYTIC INACTIVATION OF
MICROORGANISMS**

Javier Marugán, Rafael van Grieken*, Cristina Pablos, Carlos Sordo

Department of Chemical and Environmental Technology, ESCET, Universidad Rey Juan
Carlos, C/ Tulipán s/n, 28933 Móstoles, Madrid, Spain

* Phone: +34 91 488 7007 Fax: +34 91 488 70 68 E-Mail: rafael.vangrieken@urjc.es

Published on

Water Research, 44: 789-796 (2010).

[doi:10.1016/j.watres.2009.10.022](https://doi.org/10.1016/j.watres.2009.10.022)

Abstract

This study reports the analogies and differences found when comparing TiO₂ photocatalytic treatment for chemical oxidation and microorganisms inactivation, using methylene blue and *Escherichia coli* as references, respectively. In both processes the activation is based on the same physicochemical phenomena and consequently a good correlation between them is observed when analyzing the effect of operational variables such as catalyst concentration or incident radiation flux, both factors influencing common stages such radiation absorption and generation of reactive oxygen species. However, different microbiological aspects (osmotic stress, repairing mechanism, regrowth, bacterial adhesion to the titania surface, etc) makes disinfection kinetics significantly more complex than the first-order profiles usually observed for the oxidation of chemical pollutants. Moreover, bacterial inactivation reactions are found to be extremely sensitive to the composition of water and modifications of the catalysts in comparison with the decolorization of the dye solutions, showing opposite behaviors to the presence of chlorides, incorporation of silver to the catalysts or the use of different types of immobilized TiO₂ systems. Therefore, the activity observed for the photocatalytic oxidation of organics can not be always extrapolated to photocatalytic disinfection processes.

Keywords: Photocatalysis, disinfection, *E. coli*, methylene blue, water composition, immobilized TiO₂.

1. Introduction

Recently public awareness about the importance of adequate disinfection processes to supply drinking water has been increasing since the traditional disinfection methods such as chlorine-based technologies lead to the formation of chloro-organic disinfection by-products (DBPs) with carcinogenic and mutagenic effects on mammals (Richardson, 2003). For that reason, new disinfection technologies are currently in development to fulfill the WHO Guidelines for drinking-water quality (World Health Organization, 2008). Among them, the application of TiO₂ heterogeneous photocatalysis has attracted much attention during the last years (McCullagh et al., 2007; Malato et al., 2009). The application of this technology for the oxidation of many organic chemical pollutants in water has been long studied due to their advantages over other advanced oxidation processes (AOPs), such as operation conditions (ambient temperature and pressure, natural pH) without the need of additional chemicals apart from air.

As an AOP, heterogeneous photocatalysis is based on the generation of the highly reactive hydroxyl radicals, in this case upon irradiation with UV light of the TiO₂ semiconductor particles. This is the common feature of several photocatalytic applications such as the oxidation of chemicals or the inactivation of microorganisms. Cho et al. (2004) reported the existence of a linear correlation between the inactivation of *E. coli* and the concentration of OH radicals, and in a very recent work, Chen et al. (2009) have established the possibility of evaluating the antimicrobial effect of the photocatalytic treatment from the extrapolation of the activity for the oxidation of organic compounds, much easier to measure quantitatively. In contrast, the reports of other research groups studying in depth different aspects, such as the use of solar radiation (Rincon and Pulgarín, 2004a; Sichel et al., 2007; Malato et al., 2009), the influence of the water composition (Rincon and Pulgarín, 2004a; Rincon and Pulgarín, 2007a; Cushnie et al., 2009) and the kinetic description of the reactions (Marugán et al., 2008), point out to the existence of certain differences between the photocatalytic oxidation of organics and the inactivation of microorganisms. Some of them can be easily explained considering that microorganisms are several orders of magnitude larger than molecules (Blanco-Gálvez et al., 2007; Benabbou et al., 2007; Guillard et al., 2008), whereas other differences require more complex explanations.

In spite of the common initial stages of both photocatalytic processes, the microbiological aspects involved in disinfection treatment make it particularly difficult to be modelled. The complex structure of living cells, the existence of several mechanisms for cell regeneration, and the possibility of post-irradiation regrowth could be considered as

drawbacks when microorganism inactivation is compared to the oxidation of chemical pollutants. However, the supplementary stress provided by some species present in water (Coleman et al., 2005; Rincón y Pulgarín, 2007b), temperature (Rincón y Pulgarín, 2003), mechanical stress (Sichel et al., 2007) and direct germicidal effect coming from UV light (Benabbou et al., 2007; Rincón y Pulgarín, 2007b; Rincón y Pulgarín, 2003) could also help to a faster inactivation.

The present work is focused on the evaluation of analogies and differences between the photocatalytic inactivation of microorganisms and the photocatalytic oxidation of chemical compounds, trying to highlight the physicochemical and microbiological aspects that condition the efficiency of both processes. Operational parameters such as catalyst concentration and intensity of radiation, modification of the catalyst by incorporation of silver and the effect of the chemical composition of water have been analyzed, comparing their influence on both types of photocatalytic applications.

2. Materials and methods

2.1. Photoreactor.

The experimental setup is basically an annular photoreactor operating in recirculation with a stirred reservoir tank. The reactor allows the possibility of being used with just the catalyst suspension, with the catalyst fixed on the inner wall of the annular section of the reactor (catalytic wall) or fixed on Raschig rings dispersed in the reactor volume (fixed-bed). A detailed description can be found elsewhere (van Grieken et al., 2009). Illumination was provided by a Philips TL 6W black light lamp placed in the axis of the annular reactor. The maximum UVA incident photon flow, determined by ferrioxalate actinometry, was 2.8×10^{-6} Einstein s^{-1} . Lower values of the irradiation intensity were achieved by placing neutral filters in the light path. Neutral filters consist of a polymeric substrate in which a controlled black coverage level is achieved by high quality laser printing. The reproducibility and stability of the filters after several hours of irradiation has been positively verified by checking the intensity and spectrum of the filtered UV radiation with a Gigahertz-Optik X97 irradiance meter and a Varian Cary 500 Scan UV–vis–NIR spectrophotometer, respectively.

2.2. Catalysts.

Degussa P25 titanium dioxide powder was used as photocatalyst. If not otherwise stated, a concentration of 0.1 g L^{-1} in suspension was used, considered as the optimum

concentration of TiO₂ in suspension for this experimental setup according to previous studies (van Grieken et al., 2009). Experiments with Ag/TiO₂ were carried out by incorporation of silver to the titanium dioxide surface through the photoreduction of AgNO₃ solutions in the presence of isopropanol as sacrificial organic compound and further calcination at 400°C.

2.3. Photocatalytic experiments.

Escherichia coli was selected as model microorganism due to its wide use as faecal contamination indicator. *E. coli* K12 strain was provided by the Colección Española de Cultivos Tipo (CECT 4624, corresponding to ATCC 23631). The reactions were followed by analyzing the concentration of viable bacteria along the reaction through a standard serial dilution procedure. Details of the procedure followed to prepare the cultures, the initial reaction suspension and the bacterial quantification can be found elsewhere (van Grieken et al., 2009).

Experiments of photocatalytic oxidation of organic pollutants were carried out using methylene blue solutions, chemical proposed to standardize the determination of the photocatalytic activity of coatings (Tschirch et al., 2008). The evolution of the reactions was followed colorimetrically through the decrease in the absorption of the solution at 664 nm after removal of the catalyst particles in suspension.

Three different kinds of water have been used: i) deionized water; ii) model water with defined concentration of inorganic ions and humic acids; iii) synthetic municipal wastewater (Kositzki et al., 2004) diluted to a total organic carbon value of 15 mg L⁻¹ to simulate a wastewater plant effluent.

3. Results and Discussion

3.1. Mechanism and Kinetics.

Figure 1 shows the experimental results of *E. coli* inactivation and methylene blue oxidation obtained under the same experimental conditions. Photodegradation experiments are usually fitted by Langmuir-Hinshelwood or pseudo-first order kinetic equations, being considered a 90% of conversion as acceptable. In contrast, disinfection efficiency is usually quantified by the number of “logs” decrease (e.g. 5-logs decrease) in the concentration of colony forming units (CFU). The concentration of bacteria is very low in terms of molar concentration (if applicable). For instance, the initial concentration of bacteria used in this work, 10⁶ CFU mL⁻¹, correspond to a molar concentration of 1.66 × 10⁻¹⁷ M, almost negligible

in comparison with the initial concentration of methylene blue of 2.0×10^{-5} M. However, in terms of their biological risks for humans, disinfection technologies must reduce the microorganism concentration to virtually zero (below the experimental detection limit). The reason is that the destruction of molecules is generally irreversible, whereas regeneration mechanisms make feasible that some surviving bacteria grow and reproduce when irradiation is stopped in case that a complete disinfection has not been achieved (Rincón and Pulgarín, 2004b; Shang et al., 2009). Besides, bacteria might be in a non cultivable state due to the stress suffered by light but after a period of dark, bacteria may overcome the stress and return to their reproductive state (Dunlop et al., 2002). Moreover, organic and inorganic compounds coming from the lysis could serve as nutrients for the bacteria reactivation. Consequently, a 90% of conversion (1-log decrease) would be unacceptable for disinfection experiments, being necessary to achieve conversions as high as 99.9999% (6-logs decrease) to assure an effective disinfection. This “effective disinfection time” can obviously depend on the microorganism, water composition and operation conditions (Benabbou et al., 2007; Rincón and Pulgarín, 2005; Gomes et al., 2009).

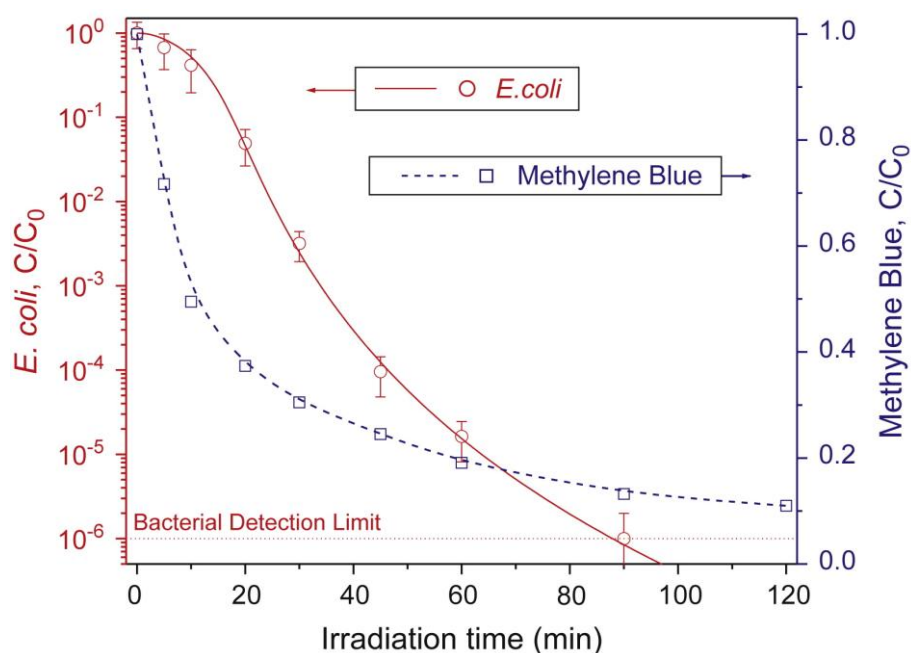


Figure 1. Experimental results of *Escherichia coli* inactivation and methylene blue oxidation (catalyst concentration: 0.1 g L^{-1} ; irradiation flow: $2.8 \times 10^{-6} \text{ Einstein s}^{-1}$). Solid line for the disinfection experiment corresponds to the fitting with the kinetic model represented by Eq. (1) and (2). Error bars calculated from eight independent bacteria counting.

Concerning the shape of the curves shown in Figure 1, it can be noticed that whereas the concentration of methylene blue decreases from the beginning (being the maximum reaction rate observed at the start of the reaction), the *E. coli* inactivation curve shows a more complex profile, also reported by other research groups (Benabbou et al., 2007; Rincón and Pulgarín, 2003, Dunlop et al., 2002). Whereas a minor modification in the structure of the dye leads to its decolorization (ideally a single hydroxyl radical attack), the inactivation of a microorganism requires a certain amount of cumulative damage (the number of hydroxyl radicals required for the inactivation of a single *E. coli* bacterium can be in the order of 10^9 (Marugán et al., 2008)). During the first minutes of irradiation, the reactive oxygen species (ROS) generated upon irradiation of the semiconductor particles start to attack the external membrane of the microorganism, but these attacks are not enough to cause the irreversible loss of cell wall function and to overcome the self-defense and auto-repair mechanisms. Consequently, this results in the apparent delay (or shoulder) in the profiles of viable cells concentration. When the level of damage induced in the cells is sufficiently high, the log-linear inactivation region is achieved, corresponding to a first order process dependent on the bacteria concentration. Finally, the deceleration at the end of the reaction is produced by the competition for the ROS between the viable cells and the organic compounds released to the medium upon the lysis of the cells, besides the competition for the photon absorption between these organic structures and the catalyst.

In a previous work (Marugán et al., 2008) we reported the development of a kinetic model based on a serial-event reaction mechanism represented by the following equations:

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

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

where C_{undam} (CFU mL⁻¹) represents the undamaged bacteria population, C_{dam} (CFU mL⁻¹) is a lump of the bacteria in all the intermediate levels of damage, k (CFU mL⁻¹ s⁻¹) is the kinetic constant, K (mLⁿ CFU⁻ⁿ) is the pseudo-adsorption constant and n (dimensionless) the inhibition coefficient. This model successfully reproduces the inactivation profiles, as shown in Figure 1. Moreover, operational parameters such as catalyst concentration and irradiation flux are not expected to influence the value of parameters K and n . Consequently, the activity of the disinfection experiments will be analyzed in terms of the kinetic constant (k), whereas

methylene blue oxidation experiments will be compared through the values of the initial reaction rate (r_0).

3.2. Effect of TiO_2 concentration.

The effect of catalyst loading on the photocatalytic inactivation of *E. coli* and methylene blue oxidation using TiO_2 in suspension is illustrated in Figure 2, showing in both processes a very similar behavior. The activity increases linearly with the TiO_2 concentration until a certain value around 0.1 g L^{-1} , reaching a plateau for higher values, which means that the activity is not noticeably improved if TiO_2 concentration increases. This classical dependence between catalyst loading and photocatalytic activity has been already reported in the literature, both for disinfection (Benabbou et al., 2007; Coleman et al., 2005) and oxidation (Hermann, 1999; Marugán et al., 2007) processes. However, Benabbou et al. (2007) reported that bacterial inactivation requires less titania than the oxidation of organic compounds. According to this reference, the release of Fe^{2+} during the photocatalytic inactivation leads to the formation of the complex $\text{Fe}(\text{OH})^{2+}$, that may also absorb photons and generate OH radicals, favouring the inactivation process. The results presented in this work do not support this hypothesis. In both cases 0.1 g L^{-1} of TiO_2 can be considered as an optimum value for both processes, as higher values only lead to slightly better activities (van Grieken et al., 2009). The value of this optimum concentration strongly depends on the experimental setup (lamp emission and reactor geometry), as it is related to the amount of catalysts that leads to an almost complete absorption of the inlet radiation. Consequently, considering the absorption of photons as the limiting stage of the global kinetics, this optimum value should not depend on the target pollutant (or microorganism), unless it competes for photon absorption.

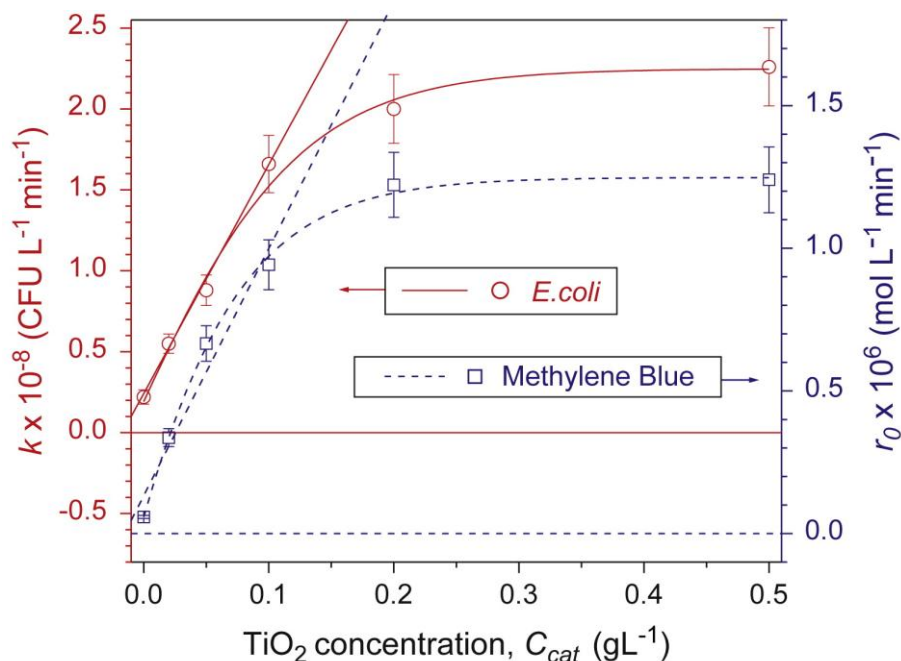


Figure 2. Kinetic constant for *E.coli* inactivation and initial reaction rate of methylene blue oxidation as a function of the TiO₂ concentration. (irradiation flow: 2.8×10^{-6} Einstein s⁻¹). Error bars estimated from duplicated experiments. Y-axes shifted to avoid overlapping.

3.3. Effect of Radiation Flux.

Figure 3 shows that the activity for both *E. coli* inactivation and methylene blue oxidation increase by increasing the intensity of the incident irradiation. These results are in agreement with other reports on photocatalytic disinfection in the literature (Chen et al., 2009; Benabbou et al., 2007; Rincón and Pulgarín, 2003). As the amount of photons increase, more electron-hole pairs will be formed, eventually leading to the formation of more OH radicals. On the other hand Cho et al. (2004) reported the existence of a linear correlation between inactivation of *E.coli* and $\cdot\text{OH}$ concentration. This linear dependence of the reaction rate with the photonic flux is only found at low intensities of irradiation, because at high intensities the concentration of charge carriers is so high that recombination (a second order process) is more favored, limiting the efficiency of the process (Vincze and Kemp, 1995; Herrmann, 1999). Thus, Figure 3 confirms that under the studied experimental range both photocatalytic processes show similar behavior, operating in the linear region corresponding to the optimal light utilization.

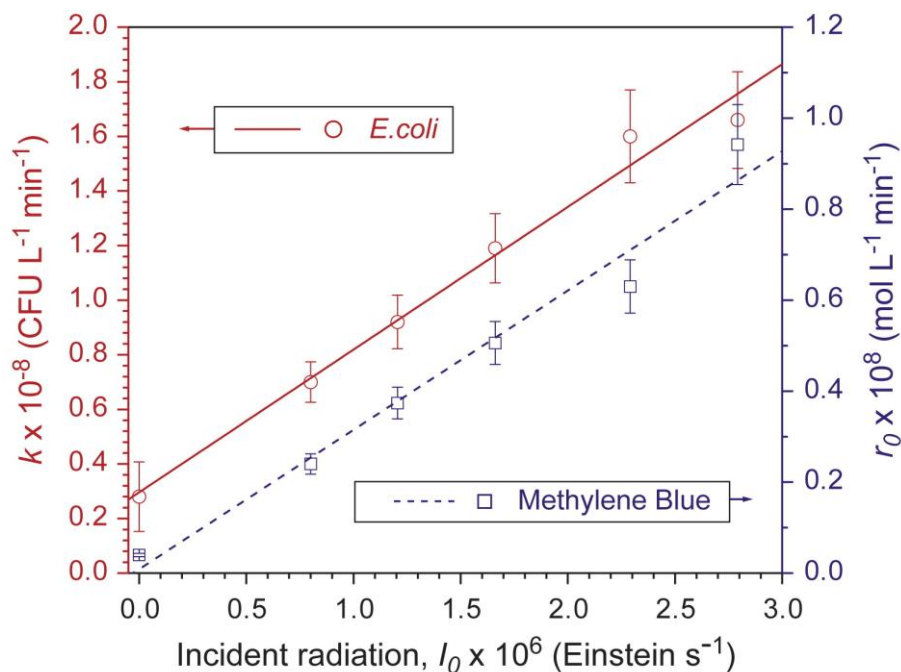


Figure 3. Kinetic constant for *E.coli* inactivation and initial reaction rate of methylene blue oxidation as a function of the incident radiation. (catalyst concentration: 0.1 g L^{-1}). Error bars estimated from duplicated experiments.

The inactivation profiles of the experiments (not shown) indicate that as incident radiation decreases, a longer initial delay is observed. This was expected, considering that the number of cumulative damage required to inactivate bacteria should remain the same, and consequently if the number of available photons decreases (and consequently the amount of OH radicals) more irradiation time is required to produce an irreversible damage. Therefore, it may not be a matter of decrease in efficiency of self-defense and regeneration mechanisms as suggested by Benabbou et al. (2007).

The results presented up to here suggest a correlation between inactivation and oxidation processes, as suggested by Chen et al. (2009). However, both catalyst concentration and radiation flux seems to be only involved in the physicochemical mechanism of OH radicals generation upon irradiation of the semiconductor particles, being this process independent of the kind of pollutant.

3.4. Effect of Water Composition.

The study of the influence of organic and inorganic matter on the efficiency of the photocatalytic processes is essential for real application of this technology in the treatment of

wastewater effluents and for the supply of drinking water from natural resources. Figure 4 depicts the effect of the water composition on the photolytic inactivation of *E. coli* in the absence of TiO_2 . Despite its much slower disinfection activity in comparison with photocatalytic runs with TiO_2 , experiment in pure water shows an almost total inactivation after 6 hours of irradiation. In these conditions bacteria are simultaneously exposed to two different stressing factors: osmotic pressure and radiation. It has been reported that self-defense mechanisms seem to be unable to protect the cells from the DNA damage produced by active species coming from the excitation of light over photosensitive molecules within the cell (Robertson et al., 2005), and when TiO_2 is added, more OH radicals are generated and consequently, the irreversible damage in the bacteria occur faster. Thus, whereas *E. coli* was almost completely inactivated by DNA damage caused by light after six hours of phototreatment, the effect of light on the photolytic degradation of organic compounds is less significant (Figure 4 inset), and independent on the water composition, in agreement with other results in the literature (Houas et al., 2001).

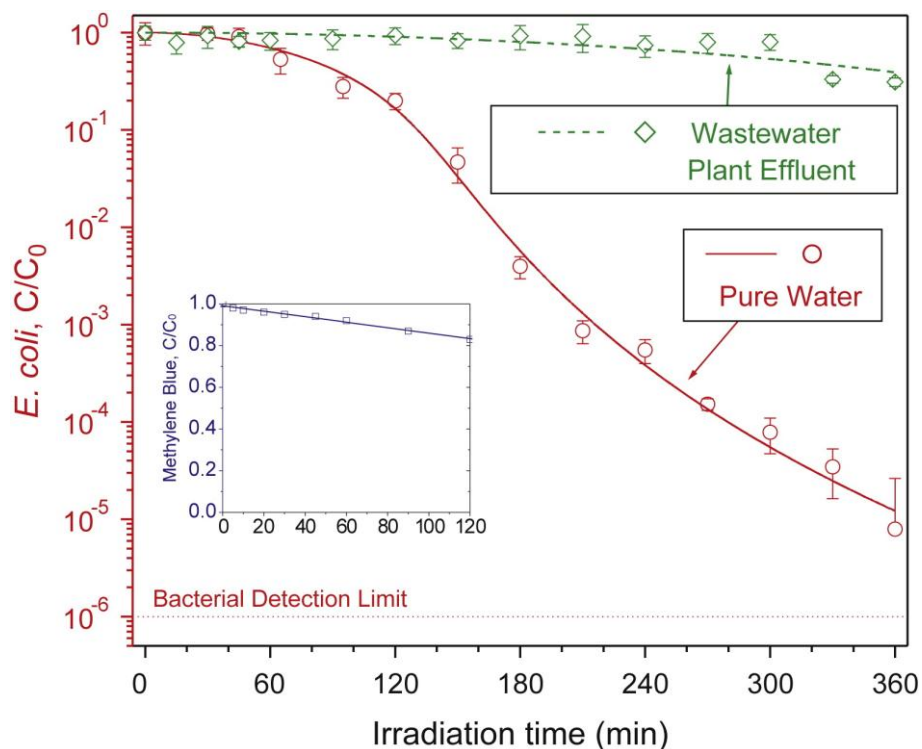


Figure 4. Influence of the water composition on the photolytic bacteria inactivation in the absence of catalysts. Inset: Photolytic degradation of methylene blue. Irradiation flow: 2.8×10^{-6} Einstein s^{-1} . Solid lines of disinfection experiments correspond to the fitting with the kinetic model represented by Eq. (1) and (2). Error bars calculated from eight independent bacteria counting.

In contrast with the previous discussion, Figure 4 also displays that the photolytic bacterial inactivation in a simulated wastewater plant effluent is negligible after six hours of irradiation, suggesting that the osmotic stress of bacteria in pure water strongly influences the inactivation. When osmotic stress is removed, bacteria remain viable despite the UV-A irradiation, in agreement with other reports (Cushnie et al., 2009). Additionally, it should be considered that anions and organic matter present in the water may serve as nutrients for the bacteria, helping to maintain their viability. Obviously, that does not apply to the photolytic degradation of organic compounds, which only depends on the radiation absorption of the molecules and is not influenced by the osmotic and nutrient effects of the substances present in the water.

Differences between the effect of the water composition on the photocatalytic inactivation of microorganisms and the degradation of organics are depicted in Figure 5, showing that generally speaking disinfection processes are more sensitive to the presence of inorganic and organic matter.

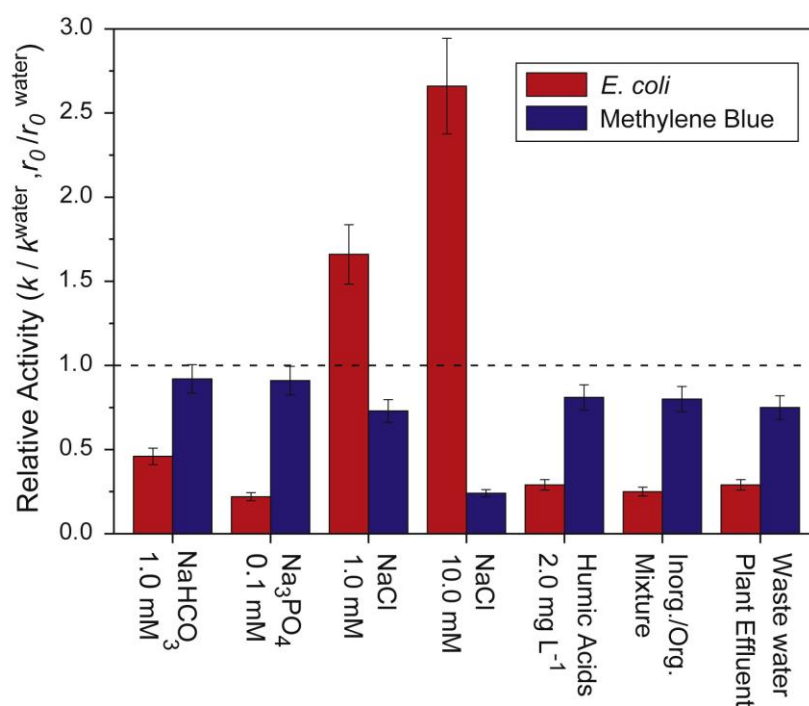


Figure 5. Influence of water composition on the photocatalytic efficiency for *Escherichia coli* inactivation and methylene blue oxidation. Results are expressed in relative terms to pure water experiments performed under equivalent conditions (catalyst concentration: 0.1 g L⁻¹; irradiation flow: 2.8 × 10⁻⁶ Einstein s⁻¹). Inorganic/Organic mixture: 1 mM NaHCO₃, 0.2 mM Na₃PO₄, 10 mM NaCl, 2 mg L⁻¹ humic acids. Error bars estimated from duplicated experiments.

The presence of humic acids and bicarbonate ions do not substantially affect the efficiency of the methylene oxidation process, whereas leads to an important decrease of the *E.coli* inactivation kinetic constants. For phosphate ions this effect is even more pronounced since a much lower concentration leads to a drastic reduction of the disinfection rate, whereas the decolorization rate is only slightly affected. According to the literature, a detrimental role based on their radical scavenger behavior has been traditionally attributed to the presence of inorganic ions for both, photocatalytic disinfection of microorganisms (Rincón and Pulgarín, 2004a; Marugán et al., 2009; Coleman et al., 2005; Alrousan et al., 2009) and photocatalytic oxidation of organics (Sökmen and Özkan, 2002; Guillard et al., 2003; Guillard et al., 2005). Additionally, it has been proposed that the formation of an inorganic layer at the surface of TiO₂ hinders the adsorption of methylene blue and bacteria and that humic acids competes with the catalyst particles by the absorption of photons, reducing the radiation available to produce oxidizing species. Concerning the higher inhibition produced by phosphates, a stronger interaction of these anions with the catalyst surface is usually considered.

It is worth noting that all these explanations discussed above are based on the physicochemistry of the photocatalytic process, and consequently should lead to a similar influence in both types of reaction. Considering that the inhibitory effects are substantially higher for the photocatalytic disinfection experiments, additional phenomena must be taken into account. Li and Logan (2004) reported that an increase of ionic strength improves the bacteria adsorption, although anions such as bicarbonates and phosphates may lead to the formation of a negatively charged surface of the catalyst, increasing the bacterial TiO₂ repulsion since the cell wall is also negatively charged, decreasing adsorption and consequently also the inactivation rate. Gogniat et al. (2006) also determined that the presence of phosphates leads to a decrease of bacteria adsorption on the catalyst. Therefore, these results seems to emphasize the importance of the bacteria adsorption on the catalyst surface, since the ·OH attack occurs only where there is bacteria-TiO₂ contact. Therefore, the basic pH given by bicarbonates and phosphates may reduce the adsorption of bacteria on the catalyst and hinder the inactivation as suggested by Cohen-Yaniv et al. (2008). In contrast, it has been already reported that a basic pH favors the methylene blue adsorption on the catalyst, improving the photocatalytic oxidation and reducing the scavenging effect (Guillard et al., 2005).

Additionally, microbiological aspects must be also taken into account. The osmotic stress due to the lack of ions in deionized water leads to the leakage of calcium and

magnesium ions from the cell wall and consequently the loss of bacterial permeability. Therefore, the cells are more stable in buffered solutions, requiring a higher amount of cumulative damage to be inactivated, which results in longer reaction times (Guillard et al., 2008; Alrousan et al., 2009). Moreover, the strong detrimental effect of phosphates and humic acids in *E. coli* inactivation experiments suggests that these species could serve as nutrients, increasing the bacterial resistance to the photocatalytic treatment.

On the other hand, the decolorization rate of methylene blue solutions is negatively affected by the presence of chloride ions and the inhibition increases with the chloride concentration. In contrast, chloride enhances the *E. coli* inactivation efficiency, and this positive effect is higher as the concentration increases. Considering that the contrary effect has been also reported (Rincón and Pulgarín, 2004a, Dunlop et al., 2002), it is believed that chloride concentration seems to play an important role in the activity. For low chloride concentrations, a competition for ROS species and for active sites of the catalyst between the anion and *E. coli* could occur. In contrast, for higher concentrations, Gogniat et al., (2006) reported that chloride anions increase the adsorption of the bacteria on the catalyst compared to other ionic species. Besides, an excess of chloride would contribute to accelerate the inactivation since chlorine-based disinfectant species might be formed, coming from reaction between chloride anions and hydroxyl radicals. This fact allows us to explain the improvement of the photocatalytic inactivation rate, not observed when only UVA light is used (Cushnie et al., 2009). On the other hand, the oxidation potential of these species does not seem to be strong enough for the decolorization of the dye.

Finally, for the organic/inorganic mixture and the simulated wastewater plant effluent, the positive effects of chlorides and inhibitory effects of the rest of anions and organic matter seems to be counteracted in the global efficiency for bacterial inactivation. For methylene blue oxidation the inhibitory effects seem not to be additive, probably because the increase of the pH above the zero-charge point of titania produced by the presence of phosphates and bicarbonates in water, favoring the adsorption of the cationic methylene blue over the negatively charged titania surface.

In conclusion, it is clearly demonstrated that the effect of the compounds present in the water on the efficiency of photocatalytic oxidation processes can not be extrapolated to photocatalytic inactivation of microorganisms, as the microbiological aspects of the latter make disinfection processes much more sensitive to the water composition.

3.5. Reactor Configuration and Catalyst Modifications.

Figure 6 shows the influence of two different modifications of the catalyst (calcination and silver incorporation) and of two different immobilized reactor configurations on the efficiency of both types of photocatalytic reactions in terms of the relative activity with regard to Degussa P25 TiO₂ suspensions.

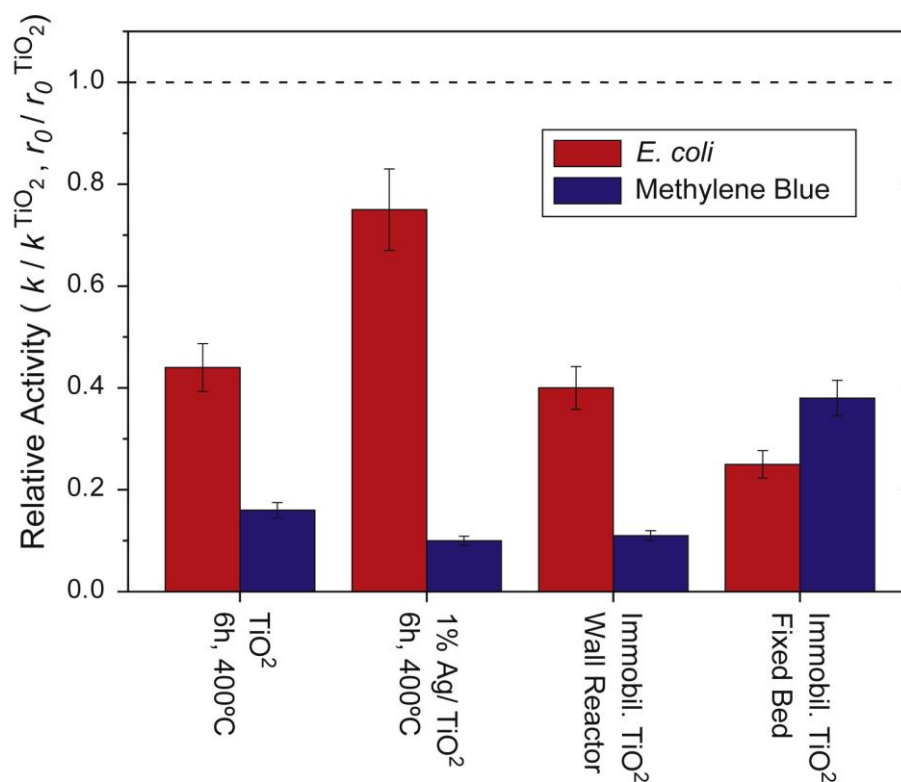


Figure 6. Influence of catalyst modifications and reactor configuration on the photocatalytic efficiency for *Escherichia coli* inactivation and methylene blue oxidation. Results are expressed in relative terms to suspensions of 0.1 g L⁻¹ of Degussa P25 TiO₂ under equivalent conditions (irradiation flow: 2.8 × 10⁻⁶ Einstein s⁻¹). Error bars estimated from duplicated experiments.

Thermal treatment of the catalyst at 400°C for 6h leads to an important decrease in the measured activities, being more significant for methylene blue oxidation. Considering that the decrease in the specific surface area is in the order of 20% (much lower than the decrease in the activity), it can be concluded that the dehydroxilation of the titania surface makes dye adsorption more difficult than the interaction with bacteria. On the other hand, incorporation of silver and further calcination to stabilize the material and avoid lixiviation further reduces the activity for the decolorization of methylene blue solutions. The expected increase in activity upon silver incorporation (Tran et al., 2006) seems to be counteracted by the decrease

in activity produced by the thermal treatment. In contrast, an increase in the efficiency of the disinfection reaction is observed in comparison with the calcined TiO₂, indicating that the improvement in the activity is more related to the bactericidal properties of silver nanoparticles rather than to the enhancement of the electron-hole separation and interfacial charge transfer usually attributed to silver-modified titania (Coleman et al. 2005). Finally, the immobilization of the catalyst onto the reactor wall and in a glass rings fixed-bed systems also shows opposite results when comparing the activity for both bacterial inactivation and dye oxidation processes, as reported previously (van Grieken et al., 2006). Whereas the activity for disinfection of the catalytic wall reactor is four times higher than that observed for oxidation of methylene blue, the activity shown by the fixed bed is higher for the decolourization reaction, indicating that the configuration of the catalytic surface inside the reactor is also crucial for the bacterial interaction with the catalyst.

Summarising, it has been demonstrated that changes in the activity for the oxidation of organic molecules coming from different reactor configurations and catalyst modifications can not be extrapolated to the activity of these systems in the photocatalytic inactivation of microorganisms.

4. Conclusions

Despite the much more complex mechanism of photocatalytic disinfection in comparison with the oxidation of chemical pollutants, the effect of operation parameters such as catalyst concentration and intensity of radiation is quite similar for both processes. The reason for these similarities seems to be related to the common photon absorption step and the physicochemical mechanism of OH radicals generation upon irradiation of the semiconductor particles, being this process independent of the kind of pollutant. Consequently, the evaluation of the radiation field during the photoreactor design and the optimization of both variables can be performed using a simple molecule as model pollutant, much easier to follow experimentally and to measure quantitatively.

In contrast, the influence of the chemical composition of water is very different for both types of photocatalytic processes. The inhibition role of ions and organic matter in the photocatalytic oxidation of chemicals is usually attributed to the competition for adsorption sites and hydroxyl radicals scavenging. On the other hand, microbiological aspects concerning osmotic and nutrient effects as well as changes in the microorganism-TiO₂ interaction and the possible formation of chlorine-based species with high disinfection potential make disinfection processes much more sensitive to the water composition. Similarly, modifications

of the catalyst also influence in a different way the efficiency of both types of photocatalytic processes. Consequently, the results obtained in the evaluation of different types of water and catalyst configuration for the oxidation of organic molecules can not be extrapolated to the activity of these systems in the photocatalytic inactivation of microorganisms, being necessary the evaluation of the process in each specific application.

Acknowledgments

The authors thank the financial support of the Ministerio de Educación y Ciencia of Spain through the program Consolider-Ingenio 2010 (project CSD2006-00044 TRAGUA) and Comunidad de Madrid through the program REMTAVARES S0505/AMB/0395.

References

- Alrousan, D.M.A., Dunlop, P.S.M., McMurray, T.A., Byrne, J.A., 2009. Photocatalytic inactivation of *E. coli* in surface water using immobilised nanoparticle TiO₂ films. *Water Research* 43(1), 47-54.
- Benabbou, A.K., Derriche, Z., Felix, C., Lejeune, P., Guillard, C., 2007. Photocatalytic inactivation of *Escherichia coli*. Effect of concentration of TiO₂ and microorganism, nature and intensity of UV irradiation. *Applied Catalysis B: Environmental* 76(3-4), 257-263.
- Blanco-Gálvez, J., Fernández-Ibáñez, P., Malato-Rodríguez, S., 2007. Solar photocatalytic detoxification and disinfection of water: recent overview. *Journal of Solar Energy Engineering - Transactions of the ASME* 129(1), 4-15.
- Chen, F., Yang, X., Xu, F., Wu, Q., Zhang, Y., 2009. Correlation of photocatalytic bactericidal effect and organic matter degradation of TiO₂. Part I: Observation of phenomena. *Environmental Science & Technology* 43 (4), 1180-1184.
- Cho, M., Chung, H., Choi, W., Yoon, J., 2004. Linear correlation between inactivation of *E. coli* and OH radical concentration in TiO₂ photocatalytic disinfection. *Water Research* 38(4), 1069-1077.
- Cohen-Yaniv, V., Narkis, N., Armon, R., 2008. Photocatalytic inactivation of *Flavobacterium* and *E. coli* in water by a continuous stirred tank reactor (CSTR) fed with suspended/immobilised TiO₂ medium. *Water Science and Technology* 58(1), 247-252.
- Coleman, H.M., Marquis, C.P., Scott, J.A., Chin, S.S., Amal, R., 2005. Bactericidal effects of titanium dioxide-based photocatalysts. *Chemical Engineering Journal* 113(1), 55-63.

Cushnie, T.P., Robertson, P.K.J., Officer, S., Pollard, P.M., McCullagh, C., Robertson, J.M.C., 2009. Variables to be considered when assessing the photocatalytic destruction of bacterial pathogens. *Chemosphere* 74(10), 1374-1378.

Dunlop, P.S.M., Byrne, J.A., Manga, N., Eggins, B.R., 2002. The photocatalytic removal of bacterial pollutants from drinking water. *Journal of Photochemistry and Photobiology A: Chemistry* 148(1-3), 355-363.

Gogniat, G., Thyssen, M., Denis, M., Pulgarín, C., Dukan S., 2006. The bactericidal effect of TiO₂ photocatalysis involves adsorption onto catalyst and the loss of membrane integrity. *FEMS Microbiology Letters* 258(1), 18-24.

Gomes, A.I., Vilar, V.J.P., Boaventura, R.A.R., 2009. Synthetic and natural waters disinfection using natural solar radiation in a pilot plant with CPCs. *Catalysis Today* 144(1-2), 55-61.

Guillard, C., Lachheb, H., Houas, A., Ksibi, M., Elaloui, E., Herrmann, J.M., 2003. Influence of chemical structure of dyes, of pH and of inorganic salts on their photocatalytic degradation by TiO₂ comparison of the efficiency of powder and supported TiO₂. *Journal of Photochemistry and Photobiology A: Chemistry* 158(1) 27-36.

Guillard, C., Puzenat, E., Lachheb, H., Houas, A., Herrmann, J.M., 2005. Why inorganic salts decrease the TiO₂ photocatalytic efficiency. *International Journal of Photoenergy* 7(1), 1-9.

Guillard, C., Bui, T-H., Felix, C., Moules, V., Lina, B., Lejeune, P., 2008. Microbiological disinfection of water and air by photocatalysis. *Comptes Rendus Chimie* 11(1-2), 107-113.

Herrmann, J.M., 1999. Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. *Catalysis Today* 53(1), 115-129.

Houas, A., Hinda, L., Ksibi, M., Elaloui, E., Guillard, C., Herrmann, J.M., 2001. Photocatalytic degradation pathway of methylene blue in water. *Applied Catalysis B: Environmental* 31(2), 145-157.

Kositzi, M., Poullos, I., Malato, S., Cáceres, J., Campos, A., 2004. Solar photocatalytic treatment of synthetic municipal wastewater. *Water Research* 38(5), 1147-1154.

Li, B., Logan, B., 2004. Bacterial adhesion to glass and metal-oxide surfaces. *Colloids and Surfaces B: Biointerfaces* 36(2), 81-90.

- Malato, S., Fernández-Ibáñez, P., Maldonado, M.I., Blanco, J., Gernjak, W., 2009. Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends. *Catalysis Today* 147(1), 1-59.
- Marugán, J., van Grieken, R., Cassano, A.E., Alfano, O.M., 2007. Quantum efficiency of cyanide photooxidation with TiO₂/SiO₂ catalysts: Multivariate analysis by experimental design. *Catalysis Today* 129, 143-151.
- Marugán, J., van Grieken, R., Sordo, C., Cruz, C., 2008. Kinetics of the photocatalytic disinfection of Escherichia coli suspensions. *Applied Catalysis B: Environmental* 2008, 82(1-2), 27-36.
- McCullagh, C., Robertson, J.M.C., Bahnemann, D.W., Robertson, P.K.J., 2007. The application of TiO₂ photocatalysis for disinfection of water contaminated with pathogenic micro-organisms: a review. *Research on Chemical Intermediates* 33(3-5), 359-375.
- Richardson, S.D., 2003. Disinfection by-products and other emerging contaminants in drinking water. *TrAC - Trends in Analytical Chemistry* 22(10), 666-684.
- Rincón, A.G., Pulgarín, C., 2003. Photocatalytical inactivation of E. coli: effect of (continuous-intermittent) light intensity and of (suspended-fixed) TiO₂ concentration. *Applied Catalysis B: Environmental* 44(3), 263-284.
- Rincón, A.G., Pulgarín, C., 2004a. Effect of pH, inorganic ions, organic matter and H₂O₂ on E. coli K12 photocatalytic inactivation by TiO₂. Implications in solar water disinfection. *Applied Catalysis B: Environmental* 2004, 51(4), 283-302.
- Rincón, A.G., Pulgarín, C., 2004b. Bactericidal action of illuminated TiO₂ on pure Escherichia coli and natural bacterial consortia: post-irradiation events in the dark and assessment of the effective disinfection time. *Applied Catalysis B: Environmental* 49(2), 99-112.
- Rincón, A.G., Pulgarín, C., 2005. Use of coaxial photocatalytic reactor (CAPHORE) in the TiO₂ photo-assisted treatment of mixed E. coli and Bacillus sp. and bacterial community present in wastewater. *Catalysis Today* 101(3-4), 331-344.
- Rincón, A.G., Pulgarín, C., 2007a. Solar photolytic and photocatalytic disinfection of water at laboratory and field scale. Effect of the chemical composition of water and study of the postirradiation events. *Journal of Solar Energy Engineering - Transactions of the ASME* 129(1), 100-110.
- Rincón, A.G., Pulgarín, C., 2007b. Fe³⁺ and TiO₂ solar-light-assisted inactivation of E. coli at field scale. Implications in solar disinfection at low temperature of large quantities of water. *Catalysis Today* 2007, 122(1-2), 128-136.

Robertson, J.M.C., Robertson, P.K.J., Lawton, L., 2005. A comparison of the effectiveness of TiO₂ photocatalysis and UVA photolysis for the destruction of three pathogenic micro-organisms. *Journal of Photochemistry and Photobiology A: Chemistry* 175(1), 51-56.

Shang, C., Cheung, L.M., Ho, C-M., Zeng, M., 2009. Repression of photoreactivation and dark repair of coliform bacteria by TiO₂-modified UV-C disinfection. *Applied Catalysis B: Environmental* 89(3-4), 536-542.

Sichel, C., Tello, J., de Cara, M., Fernández-Ibáñez, P., 2007. Effect of UV solar intensity and dose on the photocatalytic disinfection of bacteria and fungi. *Catalysis Today* 129, 152-160.

Sökmen, M., Özkan, A., 2002. Decolourising textile wastewater with modified titania. The effects of inorganic anions on the photocatalysis. *Journal of Photochemistry and Photobiology A: Chemistry* 147(1), 77-81.

Tran, H., Scott, J., Chiang, K., Amal, R., 2006. Clarifying the role of silver deposits on titania for the photocatalytic mineralisation of organic compounds. *Journal of Photochemistry and Photobiology A: Chemistry* 183(1-2), 41-52.

Tschirch, J., Dillert, R., Bahnemann, D., Proft, B., Biedermann, A., Goer, B., 2008. Photodegradation of methylene blue in water, a standard method to determine the activity of photocatalytic coatings? *Research on Chemical Intermediates* 34(4), 381-392.

Van Grieken, R., Marugán, J., Sordo, C., Pablos, C., 2009. Comparison of the photocatalytic disinfection of *E. coli* suspensions in slurry, wall and fixed-bed reactors. *Catalysis Today* 144(1-2), 48-54.

Vincze, L., Kemp, T.J., 1995. Light flux and light flux density dependence photomineralization rate of 2,4-dichlorophenol and acid in the presence of TiO₂. *Journal of Photochemistry and Photobiology A: Chemistry* 87(3), 257-260.

World Health Organization, 2008. Guidelines for drinking-water quality, third edition incorporating the first and second addenda. WHO Library Cataloguing-in-Publication Data.