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Synthetic and natural waters disinfection using natural solar radiation in a pilot plant with CPCs

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ABSTRACT

Solar disinfection of synthetic and natural waters from the Douro River, northern Portugal was studied in a pilot plant with compound parabolic collectors. Inactivation of *Enterococcus faecalis* was slower than *Escherichia coli* possibly due to the cell wall composition of the Gram-positive and Gram-negative bacteria, respectively. The high content of peptidoglycan, teichoic acids, polysaccharides, and peptidoglycolipids, in *E. faecalis* cell wall, when compared with *E. coli*, acts as a protective coating. Higher inactivation rate constants were obtained for higher initial bacteria concentrations; however a greater dose of UV energy was required. The flow rate effect in disinfection of synthetic waters was negligible. However, for natural waters with low bacteria contamination, the effect of the mechanical stress on the inactivation increased with the flow rate. Competition for the reactive oxidant radicals was observed in binary systems, containing similar concentrations of *E. coli* and *E. faecalis*.

No bacterial regrowth was observed for *E. faecalis* in synthetic waters. Oppositely, regrowth occurred for natural waters. This behaviour can be due to the natural water chemical composition, with the presence of various organic and inorganic species.

1. Introduction

Due to the lack of available on-site disinfection technologies, mainly in rural areas, the water supply is not widely treated, therefore the risk of transmission of diseases is high and has been largely responsible for several epidemics such as typhoid and cholera throughout the world [1]. The use of UV radiation from the solar spectrum can destroy many of the most "difficult" persistent microorganisms and organic pollutants, in a simple, cost effective, easy to use method, requiring minimal capital investment. The SODIS process is based on the use of PET bottles filled with contaminated water and exposed to sunlight for at least 6 h. This technology has been promoted in various developing countries for several years. Kenyan children under 5 years showed a 16% reduction of diarrhoeal illnesses among SODIS users compared to non-SODIS-users, over a 1-year observation period [2]. Hobbins et al. [3] reported that child diarrhoea was significantly less frequent in Bangladesh villages where a better adaptation of SODIS by the villagers was achieved. A study performed by Murinda and Kraemer [4] in Zimbabwe showed that although the majority of people had not heard of SODIS before, attitudes towards its introduction were very positive and the intention to implement SODIS in the future is high. Nevertheless, this method has several disadvantages, such as, low water production (a maximum of 2 L per bottle), long exposure time (typically a 2-day period), low disinfection rates and resistance of several microorganisms that persist after disinfection [5,6], which limits its application.

Solar photocatalysis has been studied by different authors for water disinfection [6–9]. The reaction takes place when UV radiation excites a semiconductor catalyst (usually TiO_2): hydroxyl radicals are generated, being able to inactivate microorganisms and oxidize contaminants, breaking up the molecules into carbon dioxide, water and diluted mineral acids.

Most information on the possibilities of using solar energy for disinfection is limited to results from lab-scale experiments. Additionally, information on natural waters degradation kinetics by solar photocatalysis is quite scarce. The present work is intended to be a step forward by using a pilot plant and natural waters.

Rincón and Pulgarin [10], are among the few authors, that studied solar photolytic and photocatalytic disinfection of synthetic and natural waters, at lab- and pilot-scale, using simulated and natural solar radiation, respectively. These authors observed negative effects caused by the presence of inorganic ions and NOM, on the disinfection efficiency with or without TiO_2, and also studied the durability of water disinfection through post-irradiation events.

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Navntoft et al. [11] performed field tests on a SOLWATER Reactor in Los Pereyra Tucumán, Argentina. This reactor prototype is composed by two tubes containing a supported heterogeneous photocatalyst and two tubes containing a supported photosensitizer, placed in a compound parabolic collectors (CPC) unit. Water samples containing high counts of coliforms and *Enterococcus faecalis*, variable levels of *Pseudomonas aeruginosa*, high organic matter content and various inorganic pollutants, were tested. Around 4 h operation on a sunny day, and 5–6 h on a cloudy day, was required to totally destroy fecal coliforms and *E. faecalis*. On the other hand, a small number of total coliforms remained and only partial destruction of *P. aeruginosa* was observed. Wist et al. [12] evaluated the photocatalytic disinfection water from the Cauca river (Cali, Colombia), using a lab-scale photoreactor with a UV lamp. Results showed drastic cultivable cell concentration in the post-irradiance events. When heterogeneous photocatalysis is applied for water disinfection, the catalyst, normally TiO_2, may be recovered by filtration or sedimentation, depending on colloidal stability, mobility and particles size [13]. In order to avoid this step, supported catalysts must be used. The objective of this work was to study the disinfection of synthetic and natural waters from the Douro River (North of Portugal), containing *E. coli* and *E. faecalis*, by solar photolysis and photocatalysis, in a pilot-scale plant using compound parabolic collectors.

2. Experimental

2.1. Solar CPC photoreactor

The disinfection experiments were carried out under sunlight, using CPC constructed by Ao SOL, Energias Renováveis, Ltd. (Portugal) and supported by an aluminium structure developed by Ecosystem—Environmental Services, S.A. (Barcelona, Spain). The solar collector (concentration factor = 1) is constituted by one CPC unit (0.59 m^2) of four borosilicate tubes connected by plastic junctions tilted 41° local latitude. A 35-W photovoltaic cell provides electric energy, which is accumulated in a 2-V DC 35 Ah battery, for water recirculation between the recirculation tank and the CPCs using a centrifugal pump DANGER TEN-Swiftech. A more detailed description of the photoreactor was presented in previous work [14]. The intensity of solar UV radiation is measured by a global UV radiometer (ACADUS 85-PLS) mounted on the pilot plant at the same inclination, which provides data in terms of incident W_{UV}/m^2. Eq. (1) allows to obtain the amount of accumulated UV energy ($Q_{UV,n}$ kJ/L) received on any surface in the same position with regard to the sun, per unit of volume of water inside the reactor, in the time interval Δt:

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \overline{UV}_{G,n} \frac{A_r}{V_t}, \quad \Delta t_n = t_n - t_{n-1} \tag{1}$$

where t_n is the time corresponding to n-water sample, V_t total volume reactor, A_r illuminated collector surface area and $\overline{UV}_{G,n}$ is the average solar ultraviolet radiation measured during the period Δ_n.

2.2. Catalysts

The heterogeneous photocatalytic experiments were performed using TiO_2 (Degussa P25), 80% anatase and 20% rutile, surface area = 55 m^2/g, non-porous particles, average particles size = 30 nm. The experiments were carried out, to treat 15 L of contaminated water, using the catalyst in suspension, with a concentration of 50 mg/L, and also using TiO_2 coated on a paper matrix Type NW10 "Ahlstrom paper", at a dose of 11.8 g/m^2 [15]. The paper sheets (0.36 m^2) were fastened around the total perimeter of concentric PP support tubes placed inside the photoreactor tubes. The Ahlstrom paper was previously washed with distilled water.

2.3. Bacterial strain, growth media and quantification

E. coli DSM 1103 and *E. faecalis* DSM 20478 were inoculated into Nutrient Broth (NB) medium (Merck) and incubated at 37 °C by constant agitation, at 120 rpm, under aerobic conditions during 15–16 h. After this, the basal equilibrium of bacteria was reached, yielding concentrations of 10^9/mL (*E. coli*) and 10^8/mL (*E. faecalis*). The suspensions were centrifuged at 3000 rpm for 15 min and washed two times with saline solution (0.9% NaCl). Finally the bacteria pellet was resuspended and diluted in the 15 L tank to reach the initial concentrations of 10^5/mL (*E. coli*) and 10^4/mL (*E. faecalis*).

Filtration membrane methods (ISO 9308-1 and ISO 7899-2) were used for detection and enumeration of the bacteria, using Lauryl Sulfate Broth (Merck, Germany) for *E. coli* and enterococcus selective agar Slanetz and Bartley (Merck, Germany) for *E. faecalis*. All the material and solutions were sterilized before analysis.

2.4. Chemical analysis

The dissolved organic carbon (DOC) was determined by using a TOC analyzer (Shimadzu, model 5000A). UV–vis spectra between 200 and 700 nm were recorded in an UNICAM ΗΕΛΙΟS α spectrophotometer.

2.5. Water sources

Synthetic waters were prepared by mixing bacteria with distilled water. Natural water was taken from the Douro River, at WTP of Lever, Porto (Portugal). Table 1 shows some chemical and bacteriological characteristics of Douro River water.

2.6. CPC reactor disinfection procedure

The recirculation tank was filled with 15 L of synthetic or natural water. Bubbles inside the reactor were removed and the flow rate adjusted. In the beginning of the experiments the reactor was covered to obtain dark conditions. A first control sample was taken to ensure the absence of contamination in distilled water. The bacteria suspension was added (except for Douro River water) and perfectly mixed during 15 min. Then, the initial bacteria concentration was determined. For the photocatalytic slurry experiments the TiO_2 was added to the recirculation tank, after 15 min homogenization, and the suspension was mixed for more

Table 1
Some chemical and bacteriological characteristics of Douro River water.

Parameter	Average	Maximum	Minimum
pH	7.7	8.3	7.3
Conductivity (μS/cm)	235	302	88
Temperature (°C)	16.9	25.8	6.9
Colour (mg/L Pt–Co units)	11.6	27	5.3
Turbidity (NTU)	5.2	40	1.5
TOC (mg/L)	2.2	3.8	1.5
Chloride (mg/L)	15.7	19.4	12.1
Nitrate (mg/L)			
Phosphate (mg/L)	0.21	0.21	0.21
Sulphate (mg/L)	23.9	32.0	<10.0
Fluoride (mg/L)	0.10	<0.10	<0.10
Enterococcus (CFU/100 mL)	42	455	0
Escherichia coli (CFU/100 mL)	315	2818	14
Number of colonies at 37 °C (CFU/100 mL)	229	2243	12
Coliform bacteria (CFU/100 mL)	373	2818	18

15 min in the dark. A new sample was taken to evaluate the inactivation of the bacteria in the presence of TiO_2 in darkness. The solar disinfection experiments started after removing the cover and samples were taken at pre-defined times. Control tests were performed in dark conditions or in the presence of sunlight with or without catalyst.

3. Results and discussion

3.1. Disinfection of synthetic waters

Fig. 1(a) shows no inactivation of *E. faecalis* after 2 h in dark conditions in the CPC photoreactor, as obtained for *E. coli* in the same plant [14]. However, in the same conditions with 50 mg/L of TiO_2, a small decrease in the bacteria concentration can be observed in Fig. 1(a), due to possible cells interaction with the catalyst surface [6]. To an appropriate comparison with the results of the subsequent experiments a longer residence time (7 h) could be adopted but reported results in the literature [10,16] indicate that for *E. coli*, which shows a lower resistance to inactivation, no further decrease was detected after 2 h in dark conditions. The bacterial inactivation by sunlight is strongly enhanced by the presence of TiO_2 in suspension but photolysis seems to be better after 150 min of solar exposition (Fig. 1(a)). Fig. 2 shows the inactivation over the amount of accumulated UV energy per liter of water, and the number of cultivable bacteria in the presence of TiO_2 in suspension decreases to values <1 CFU/mL after 10 kJ/L, instead of 25 and 50 kJ/L (Fig. 2) for photolysis and supported TiO_2 photocatalysis, respectively. Similar results were obtained for *E. coli* inactivation and can be due to organic matter leaching from the paper matrix (Fig. 1(b)), which can protect bacteria against

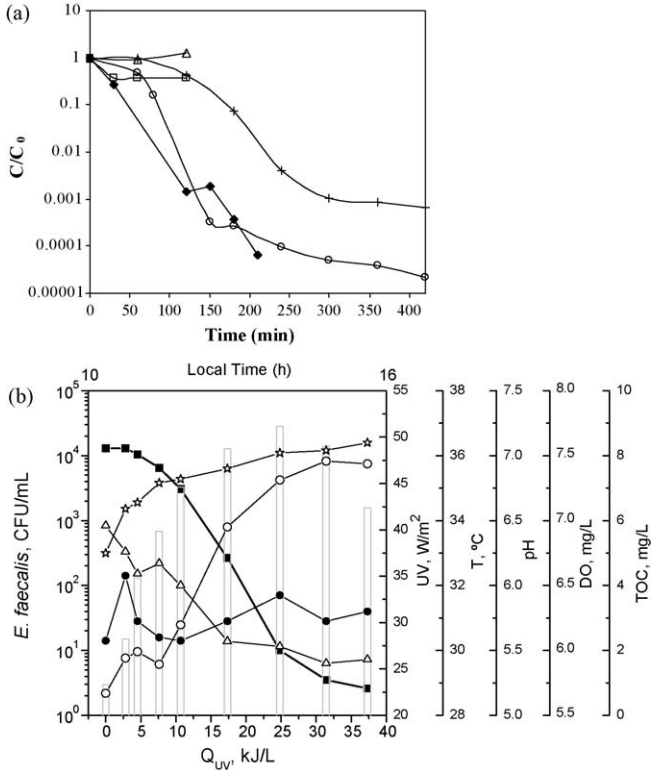

Fig. 1. (a) *E. faecalis* concentration over time during disinfection under different conditions. (△) control in the dark; (□) TiO_2 without sunlight; (○) sunlight; (◆) TiO_2 in suspension with sunlight; (+) supported TiO_2 with sunlight and (b) evolution of disinfection parameters over UV accumulated energy in the CPC reactor with immobilized TiO_2 at $Q = 10$ L/min: (■) *E. faecalis* concentration, (△) dissolved oxygen, (○) temperature, (▯) UV, (☆) pH and (●) TOC.

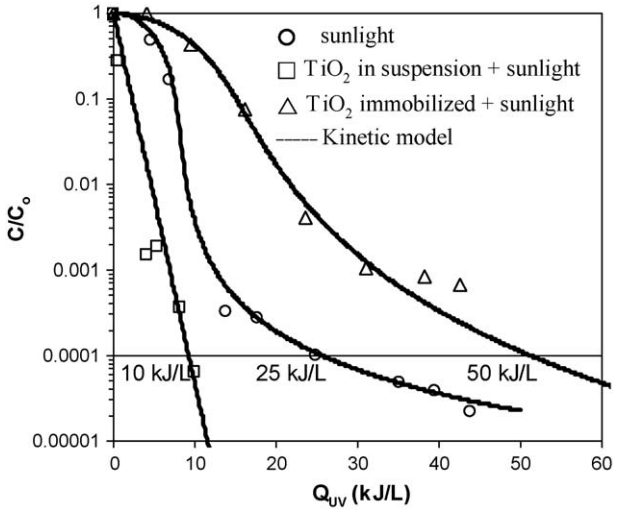

Fig. 2. *E. faecalis* inactivation kinetics: without TiO_2 or with suspended or immobilized TiO_2.

photocatalysis (for example by hydroxyl radicals scavenging) [14]. On the other hand, the inactivation rate decreases, since bacteria must diffuse through the porous support to reach the TiO_2 surface. Madani et al. [17] studied the photocatalytic degradation of diuron in aqueous solution in the presence of two catalysts, either as suspended powders or deposited on flexible industrial photo-resistant papers. Degussa P25 was as active in suspension as when deposited on paper KN47 and substantially less (20%) active when deposited on NW10, whereas Millennium PC-500 behaved oppositely. Fernandez et al. [7] showed that TiO_2 slurry is more efficient for bacteria inactivation than the supported photocatalyst KN47 (19.3 g TiO_2/m^2). However, these results are better than those obtained in the present work, using NW10. The lower concentration of TiO_2 per square meter of paper, the high amount of cellulose and organics leaching into the solution are the principal factors responsible for the low disinfection efficiency of the TiO_2 supported in the matrix NW10. Fernández et al. [7] using the KN47, did not detected organic matter leaching to solution.

A Langmuir–Hinshelwood-like-inactivation model (Eqs. (2) and (3)) based on the reaction scheme first proposed by Severin et al. [18], was able to fit photolysis and photocatalysis experimental data with supported TiO_2 of *E. coli* [19] and a first-order model described photocatalysis with TiO_2 slurry.

$$\frac{dC^*_{undam}}{dQ} = -k^* \frac{K^*(C^*_{undam})^n}{1 + K^*(C^*_{undam})^n + K^*(C^*_{dam})^n} \quad (2)$$

$$\frac{dC^*_{dam}}{dQ} = k^* \frac{K^*(C^*_{undam})^n - K^*(C^*_{dam})^n}{1 + K^*(C^*_{undam})^n + K^*(C^*_{dam})^n} \quad (3)$$

$$C^* = \frac{C}{C_0}, \quad C = C_{undam} + C_{dam}, \quad k^* = \frac{k}{C_0} \quad \text{and} \quad K^* = K \times C_0^n \quad (4)$$

where C_{undam} represents the undamaged population of bacteria, C_{dam} is a lump of bacteria in all intermediate levels of damage, C_0 is the initial bacteria concentration, k is the inactivation rate constant, K the pseudo-adsorption constant, which represents the interaction between the catalyst and the bacteria, responsible by the shoulder at the beginning of the reaction (however in the absence of catalyst, K can represent the interaction between the reactive oxidant species and bacteria) and n is the inhibition coefficient, that essentially means the reaction order with respect to the bacteria concentration.

Model predicted curves for the inactivation of *E. faecalis* are presented in Fig. 2. In this case photocatalysis by TiO_2 slurry was also well predicted by the Langmuir–Hinshelwood-like model. The inactivation rate, k^*, is approximately 12 and 18 times higher than for photolysis and immobilized TiO_2 photocatalysis, respectively.

E. faecalis exhibits higher inactivation resistance when compared with *E. coli*, principally at the initial reaction stage (up to 7 kJ/L). For example, to reach *E. coli*, <1 CFU/mL, 1, 4 and 16 kJ/L were necessary for TiO_2 slurry, sunlight-only and supported TiO_2, respectively [14]. The first-order inactivation rate constant for *E. coli* in photocatalysis with TiO_2 slurry is 2.6 higher than for *E. faecalis*. The same trend was observed for photolytic and supported photocatalytic systems [14]. The Gram stain broadly differentiates bacteria into Gram-positive (*E. faecalis)* and Gram-negative groups (*E. coli*). Gram-positive and Gram-negative organisms differ drastically in the organization of the structures outside the plasma membrane but below the capsule, in Gram-negative organisms these structures constitute the cell envelope, whereas in Gram-positive organisms they are called a cell wall. Most Gram-positive bacteria have a relatively thick, continuous cell wall, which is composed largely of peptidoglycan. In thick cell walls, other cell wall polymers are covalently attached to the peptidoglycan. In contrast, the peptidoglycan layer in Gram-negative bacteria is thin (about 5–10 nm thick); in *E. coli*, the peptidoglycan is probably only a monolayer thick. Outside the peptidoglycan layer in the Gram-negative envelope is an outer membrane structure (about 7.5–10 nm thick). Moreover, in Gram-negative bacteria such as *E. coli*, the outer and inner membranes adhere to each other at several hundred sites (Bayer patches); these sites can break up the continuity of the peptidoglycan layer [20–22].

The capsule of *E. faecalis* is very viscous due to high concentration of peptidoglycan, teichoic acids, polysaccharides, and peptidoglycolipids, acting as a protective coating to reaction of oxidant species.

Vidal et al. [23] showed also that the inactivation rate constant of *E. coli* was 1.3 times higher that for *E. faecalis*, using solar radiation. The inactivation of *Enterococcus* sp. was also tested in a lab-scale prototype using simulated solar radiation [24]. The authors observed that the photoinactivation was faster for *E. coli* than for *Enterococcus* sp.

3.1.1. Influence of the initial bacteria concentration

Fig. 3 illustrates the effect of the initial bacteria concentration on the inactivation. The inactivation curves are very similar,

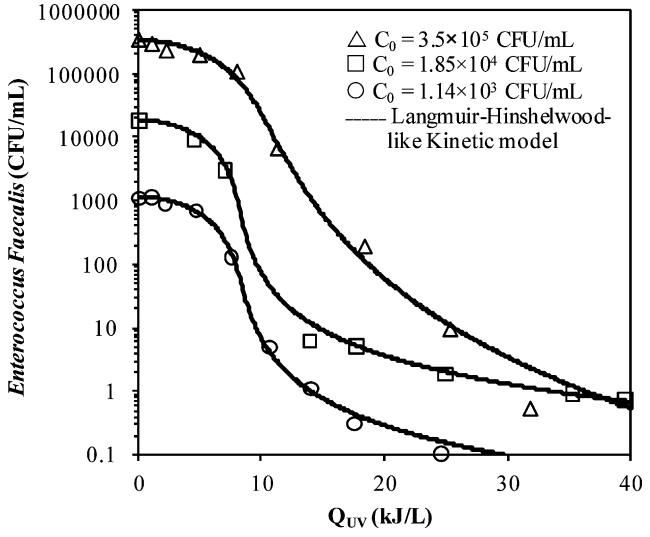

Fig. 3. Solar disinfection of *E. faecalis* at different initial concentrations and inactivation model fitting the experimental data.

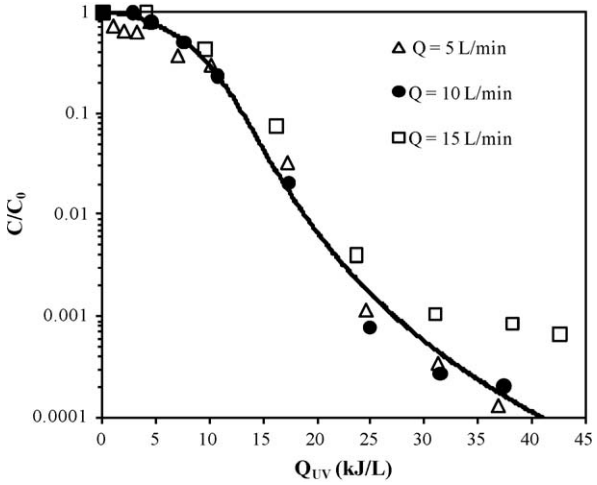

Fig. 4. *E. faecalis* concentration during solar supported TiO_2 photocatalytic experiments at different flow rates; (—) Langmuir–Hinshelwood kinetic model fitting the experimental data for the heterogeneous photocatalytic inactivation at Q = 10 L/min.

showing an initial shoulder up to ≈7 kJ/L, followed by a log-linear and a tail region. To reduce the initial concentration to values <1 CFU/mL the necessary energy is about 15 and 35 kJ/L, respectively for the lower and higher concentrations. Fig. 3 also shows that the Langmuir–Hinshelwood-like model is able to predicted the experimental data. The inactivation rate constant, k, increases with the initial concentration as was observed for the photolysis of *E. coli* [14], since the probability of interaction between the bacteria and the reactive oxidation species is higher. The inhibition coefficients (n) are >1, indicating a product inhibition phenomenon that seems to be lower for the highest concentrations.

3.1.2. Influence of the flow rate on the inactivation of E. faecalis

The flow rate effect on the inactivation of *E. faecalis* was studied in the supported TiO_2 system, since in this case, the diffusion of the microorganisms through the support matrix can be reaction limiting. Fig. 4 shows that inactivation is independent of flow rate suggesting that the interaction between the catalyst surface and bacteria is the limiting step. Table 2 shows that the K values, associated to the latency phase, are lower when using the supported catalyst, which can reinforce that the interaction between the bacteria and the oxidant species or interaction with TiO_2 surface is the limiting reaction step.

3.1.3. Inactivation of a mixture of E. coli and E. faecalis

Fig. 5 presents the inactivation results of a binary mixture of *E. coli* and *E. faecalis* in distilled water with initial concentrations of 1.2×10^5 and 2.0×10^4 CFU/mL, respectively, using supported TiO_2. These concentrations were chosen based on bacteriological results from previous studies we have performed on highly contaminated surface waters (Leça River). Approximately 10 and >40 kJ/L (≈60 kJ/L predicted by the Langmuir–Hinshelwood-like model) were necessary for a 3-log decrease in the initial concentration, respectively for *E. coli* and *E. faecalis*. For the same initial concentration and disinfection efficiency, only 8 and 25 kJ/L were required for the inactivation of only *E. coli* [14] or *E. faecalis* (Fig. 4(a)), respectively. The amount of UV energy necessary for *E. coli* inactivation in single or binary systems is very similar; however for *E. faecalis* inactivation the energy required is two times higher. This inhibition can be due, not only to the competition between the two bacteria for the oxidant radicals,

Table 2
Langmuir–Hinshelwood-like inactivation model parameters for synthetic waters disinfection contaminated with *E. faecalis*.

E. faecalis	Langmuir–Hinshelwood-like model							
	Q (L/min)	C_i (CFU/mL)	k^* (L kJ^{-1})	$k \times 10^4$ (mL^{-1} L kJ^{-1})	K^*	K (mL^n CFU^{-n})	n	S_2^R
Sunlight	15	3.50×10^5	0.255	8.9	10.0	2.5×10^{-6}	1.19	8.0×10^{-2}
	15	1.85×10^4	0.255	0.47	150.0	2.7×10^{-5}	1.58	0.234
	15	1.14×10^3	0.255	0.029	100.0	2.0×10^{-3}	1.54	2.0×10^{-2}
Sunlight + TiO_2	15	2.70×10^4	3.16	8.5	20.0	1.2×10^{-6}	1.63	1.5×10^{-6}
Sunlight + TiO_2 immobilized	5	3.15×10^4	0.434	1.4	1.2	1.8×10^{-5}	1.07	0.194
	10	1.30×10^4	0.210	0.27	6.4	6.1×10^{-5}	1.22	7.35×10^{-3}
	15	2.65×10^4	0.173	0.46	7.9	2.3×10^{-5}	1.25	2.0×10^{-2}
Sunlight + TiO_2 immobilized (binary system)	5[a]	2.00×10^4	0.097	0.20	10.0	2.8×10^{-5}	1.29	1.54×10^{-2}
	5[b]	1.20×10^5	0.52	6.2	149.2	3.5×10^{-7}	1.70	27.8

[a] *E. faecalis*.
[b] *E. coli*.

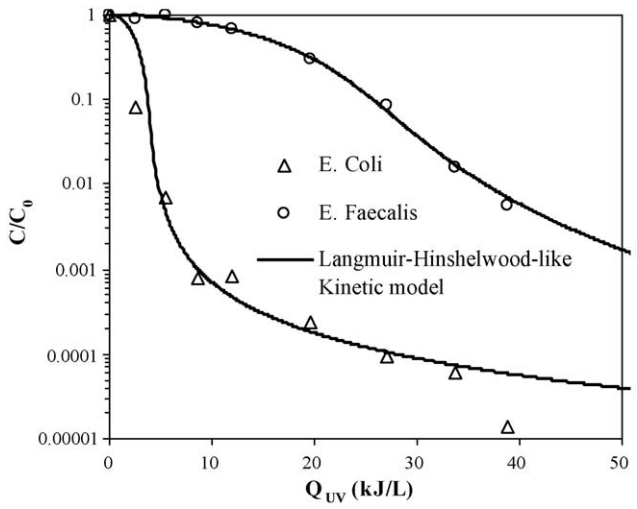

Fig. 5. Solar disinfection of a synthetic binary mixture of *E. coli* and *E. faecalis* and inactivation model fitting the experimental data.

but also by the *E. faecalis* lower initial concentration when compared with *E. coli*.

3.2. Disinfection of natural waters

Different disinfection experiments of natural water from the Douro River, collected near Lever WTP (Water Treatment Plant), were performed using sunlight-only or sunlight and the supported catalyst. Table 1 presents some chemical and bacteriological characteristics of Douro River. The disinfection of the river water was assessed by measuring the concentration of *E. coli* and *Enterococcus* sp., dissolved organic carbon and some physical parameters (pH, temperature, dissolved oxygen and conductivity). Two experiments were performed only under sunlight (Fig. 6(a) and (b)) and other three experiments were conducted using sunlight and the supported catalyst at different flow rates (5, 10 and 15 L/min). As previously verified using contaminated distilled water, photolysis is faster than supported TiO_2 photocatalysis, but the difference is small, since the initial bacteria concentration in the river water (Table 2) is very low when compared with the contaminated water used in this work (Table 1). An amount of 10 kJ/L of accumulated UV energy is enough to achieve complete inactivation of both bacteria. For low bacteria concentration, higher flow rates increase the disinfection kinetics, due to the stress caused by the fluid movement (Fig. 6(a) and (b)). A first-order inactivation model predicted the experimental data for the studied systems. Table 3 presents the inactivation rate constants.

The DOC remains approximately constant (data not showed), between 2 and 4 mg/L, with exception of the experiment at low flow rate. These results indicate that the degradation rate is similar to the release rate of DOC into the solution.

Fig. 6(c) depicts the evolution of pH, temperature, dissolved oxygen and conductivity for $Q = 10$ L/min. The UV radiation intensity increased up to approximately 55 W/m^2 and water temperature attained 36 °C. An initial rapid increase on the pH value was observed possibly due to the leaching of the supported catalyst. As expected, the dissolved oxygen pattern essentially follows the water temperature profile. The decrease in the

Table 3
First-order inactivation model parameters of natural waters disinfection contaminated with *Enterococcus* sp. and *E. coli*.

E. coli	Q (L/min)	C_i (CFU/100 mL)	First-order model	
			k (L kJ^{-1})	R^2
Sunlight	15	58.5	0.348	0.968
	15	41	0.332	0.984
Sunlight + TiO_2 immobilized	5	95	5.07×10^{-2}	0.946
	10	62	9.13×10^{-2}	0.957
	15	83	0.193	0.906
Enterococcus sp.	Q (L/min)	C_i (CFU/100 mL)	k (L kJ^{-1})	R^2
Sunlight	15	5.5	0.743	0.944
	15	6.5	0.549	0.813
Sunlight + TiO_2 immobilized	5	17.0	9.64×10^{-2}	0.941
	10	18.5	7.64×10^{-2}	0.926
	15	13.5	0.116	0.975

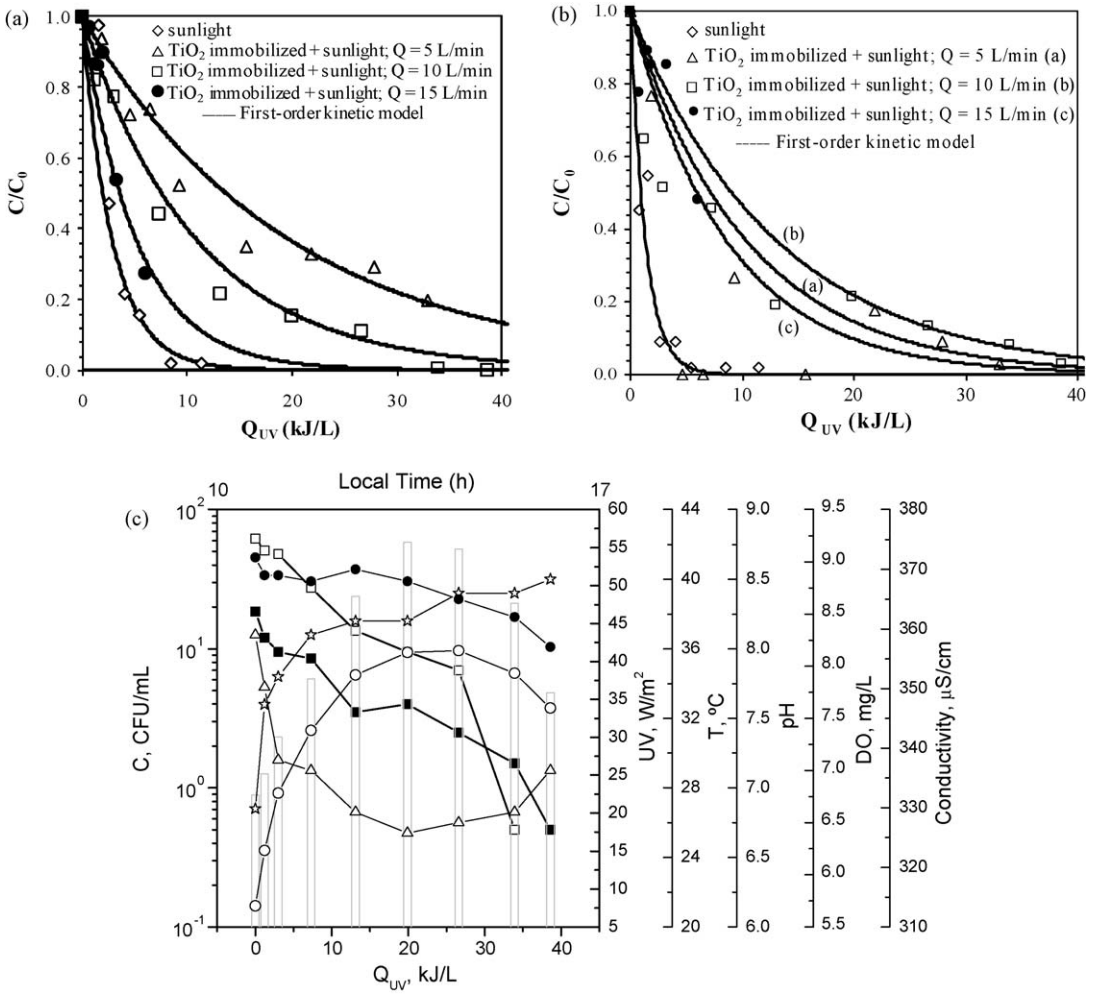

Fig. 6. Solar disinfection of water from the Douro River at different flow rates using the supported catalyst and sunlight-only (experimental data and predicted curves by a first-order kinetic model). (a) *E. coli*, (b) *E. faecalis* and (c) evolution of some parameters over UV accumulated energy using support catalyst at Q = 10 L/min. (■) *E. coli*, (□) *E. faecalis*, (△) dissolved oxygen, (○) temperature, (▯) UV, (☆) pH and (●) Conductivity.

conductivity during the experiment can be due to adsorption on the surface of the catalyst and bacteria. Rincón and Pulgarin [25] showed that the addition of some inorganic ions affects the bacteria sensitivity to sunlight in the presence and in the absence of TiO_2. These authors also observed that dissolved ion concentration decreased during the interaction of anion-bacteria, suggesting that the anions diffused into the bacteria.

Fig. 7 illustrates the durability of disinfection after 24 h in dark conditions. After total inactivation of *E. faecalis* using sunlight-only in synthetic water, no regrowth was observed (Fig. 7(a)).

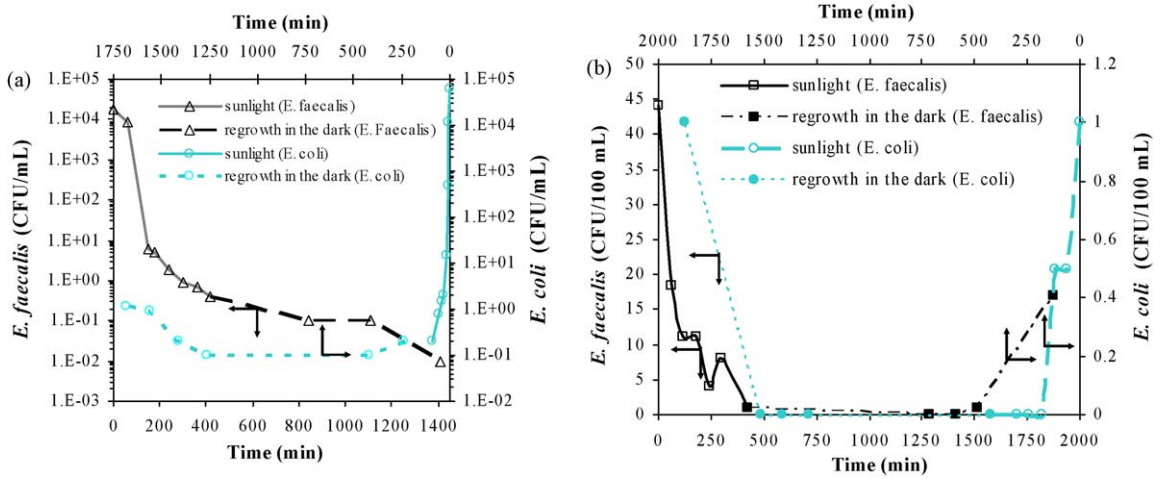

Fig. 7. Durability of solar inactivation of *E. coli* and *E. faecalis* in synthetic (a) and natural waters (b) (24 h in the dark).

However, using the natural water (Fig. 7(b)), the concentration of *E. coli* and *Enterococcus* sp. increased again during the dark period. This may be due to: (a) conversion of nonculturable cells into culturable ones and regrowth in the dark period and (b) bacteria regrow by using a new carbon source and nutrients present in natural waters [10].

4. Conclusions

E. faecalis inactivation can be achieved by photolysis, although using TiO_2 in slurry enhances the action of light on bacteria. The supported catalyst NW10 is not efficient for bacteria inactivation manly due to two factors: (i) the decrease in the interaction between the bacteria and the supported TiO_2, since bacteria must diffuse through the porous support, and (ii) the release of organic matter from the support, which can consequently be responsible by the absorption of UV light, radical scavenging and inhibition of the catalyst; in addition, it may also act as a nutrient supply for bacteria.

A non-empirical Langmuir–Hinshelwood-like inactivation model, considering a simplified reaction mechanism, was able to predict *E. faecalis* inactivation in synthetic waters. The inhibition coefficients allow to conclude that the bacteria inactivation reaction order is higher than 1. The inactivation rate constants increase with the initial bacteria concentration, as expected, since the probability of interaction between the bacteria and the reactive oxygen species (ROS) is higher. For the natural water tested, as the initial bacteria concentration was very low, a first-order inactivation model yielded better results.

Sunlight alone is sufficient to completely inactivate bacteria however, microorganisms can regrow up to the initial concentration after stopping illumination in natural waters. The required effective disinfection time for bacteria total killing has to be determined in order to assure no bacterial regrowth before water consumption. *E. faecalis* exhibits a lower inactivation rate when compared with *E. coli* possibly due to the high concentration of peptidoglycan, teichoic acids, polysaccharides, and peptidoglycolipids, in the cell composition, that act as a protective coating to reaction of oxidant species. The impact of the mechanical stress associated with high flow rates is only significant for low bacteria concentrations.

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